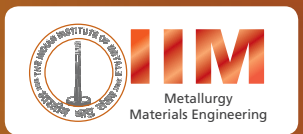
Indian Institute of Metals Series

Amiya Kumar Lahiri

Applied Metallurgy and Corrosion Control

A Handbook for the Petrochemical Industry



Springer

Indian Institute of Metals Series

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Amiya Kumar Lahiri

Applied Metallurgy and Corrosion Control

A Handbook for the Petrochemical Industry

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I dedicate this book to my
Beloved Parents
Late Shri Dakshina Ranjan Lahiri and Late
Smt. Tarubala Lahiri

Series Editors' Preface

The Indian Institute of Metals Series is an institutional partnership series focusing on metallurgy and materials sciences.

About the Indian Institute of Metals

The Indian Institute of Metals (IIM) is a premier professional body (since 1947) representing an eminent and dynamic group of metallurgists and materials scientists from R&D institutions, academia and industry mostly from India. It is a registered professional institute with the primary objective of promoting and advancing the study and practice of the science and technology of metals, alloys and novel materials. The institute is actively engaged in promoting academia—research and institute—industry interactions.

Genesis and History of the Series

The study of metallurgy and materials science is vital for developing advanced materials for diverse applications. In the last decade, the progress in this field has been rapid and extensive, giving us a new array of materials, with a wide range of applications, and a variety of possibilities for processing and characterizing the materials. In order to make this growing volume of knowledge available, an initiative to publish a series of books in Metallurgy and Materials Science was taken during the Diamond Jubilee year of the Indian Institute of Metals (IIM) in the year 2006. IIM entered into a partnership with Universities Press, Hyderabad and as part of the IIM Book series, 11 books were published, and a number of these have been co-published by CRC Press, USA. The books were authored by eminent professionals in academia, industry and R&D with outstanding background in their respective domains thus generating unique resources of validated expertise of

interest in metallurgy. The international character of the authors' and editors has enabled the books to command national and global readership. This book series includes different categories of publications: textbooks to satisfy the requirements of undergraduates and beginners in the field, monographs on select topics by experts in the field, and proceedings of select international conferences organized by IIM after mandatory peer review. An eminent panel of international and national experts constitutes the advisory body in overseeing the selection of topics, important areas to be covered, in the books and the selection of contributing authors.

Current Series Information

To increase the readership and to ensure wide dissemination among global readers, this new chapter of the Series has been initiated with Springer. The goal is to continue publishing high value content on metallurgy and materials science, focusing on current trends and applications. Readers interested in writing for the series may contact the undersigned series editor or the Springer publishing editor, Ms. Swati Meherishi.

About This Book

The current textbook "Applied Metallurgy and Corrosion Control—A Handbook for Petrochemical Industry" by Amiya Kumar Lahiri has 13 chapters of valuable information on metallurgy and corrosion aspects of various materials employed in petrochemical industries. After basic introduction about the book, the next highly relevant 12 chapters on the subject follow in an excellent sequence: Classification of Metallic Engineering Materials, Production and Working of Metals and Alloys, Structure of Metals and Alloys, Mechanical Properties and Strength of Metals and Alloys, Heat Treatment, Metallurgical Aspects of Welding, Material Degradation, Material Selection and Performance in Oil and Gas Industry, Material Selection and Performance in Refining Industry, Material Selection and Performance in Fertilizer Industry, Damage Assessment and Repair of Stationary Equipment, finally on Failure Analysis. The author has rich experience over four decades on the subject matter of the book while serving in industry, R&D and academic institutes. The expertise generated on materials selection, fabrication of components, application for various unit operations and finally maintenance and failure analysis has been lucidly brought out with firsthand knowledge and expertise in the subject. The author had the opportunity of working and interacting with plant engineers for the last forty years, as an engineer and consultant, and provides the knowledge in this regard which is hitherto not available in any open literature. It is a unique book in comparison to the existing books due to experiences and insights of the author. To

overcome unexpected failure of engineering components in petrochemical industry, personnel engaged in design, fabrication, operation, inspection and maintenance of plant components must use this book to have the basic understanding of material properties and the damaging effects that caused on them by the environment during operation.

This textbook is a treasure for the researchers, plant engineers and management personnel to update them with latest experience in the applied metallurgy and corrosion control of engineering components in petrochemical industry. The author and the editors of the series are of the conviction that this textbook will provide confidence to all those handling and working with components operating at high temperatures and highly aggressive corrosive conditions. We wish all readers better enrichment in knowledge and motivation to pursue challenging tasks ahead in their career by upgrading their knowledge in the domain. Also we await the feedback for improving the book when it goes to second edition.

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Preface

In process industry, materials have to handle corrosive and inflammable or lethal fluids at various temperatures and pressures. For example, in hydrogen plant the temperature to which the reformer tube is exposed is close to 1000 °C. On the other hand, in case of urea production the highly corrosive carbamate has to be handled upto a pressure of over 150 bar (2250 psi) and temperature ~180 °C. Similarly, in the production of sulphuric and nitric acid the equipment is to handle highly corrosive chemicals. In all these cases the degradation of material is primarily due to corrosion or oxidation. In the production and storage of LNG the conditions are, however, quite different. Here the problem is not corrosion but the susceptibility of materials to fail in a brittle manner at cryogenic temperatures. The equipment exposed to the different conditions need to remain operational without breakdowns for the longest possible time to maintain plant's profitability. To achieve this objective, proper selection of material, corrosion control and good engineering practices are to be incorporated in the design and construction of the plant. Once a plant is commissioned, it is expected to be operated within the designed parameters, which quite often is not possible because of a number of reasons like non-availability of required raw material, changes in the market demand and inadequate operational, inspection and maintenance practices adopted. In such cases, amongst others, upgradation of materials of construction may become necessary to maintain on-stream equipment availability and to avoid any failure which can cause explosion, fire or environmental damage.

In the operation of any continuous process the input feeds are subjected to reactions at different temperatures and pressures that have to pass through various equipment till the intended reactions are completed. Thus the feeds flow from inlet to outlet of the unit in a closed system. A continuous process unit consists of stationary equipment like vessels, towers, exchangers, heaters, piping and valves and rotating equipment like pumps and compressors. The materials used for the equipment are primarily metallic materials, the selection of which for the various components is the first and foremost step in the setting up of a chemical process unit. The first requirement of any material is that it should have requisite resistance to corrosion damage under the operating conditions to ensure the design life or

necessitate minimum replacements during the life time. Next, the selected materials should also have requisite mechanical properties and be amenable to forming and joining. Finally, even if the material of construction (MOC) is rightly selected, the performance of the plant may not be satisfactory if there are deficiencies in design, material specification, fabrication techniques, construction, operation and maintenance. All these aspects, including inspection and maintenance, are directly or indirectly related to the material and constitute what we can call *material engineering*.

Personnel engaged in design or operations of a plant must therefore have the basic understanding of material properties and the damaging effects of environment during operation. As a consultant having the opportunity of interacting with plant engineers for the last forty years, the author feels that the knowledge in this regard is generally limited which makes decision making difficult. To bridge this gap, a special training program was developed for the personnel engaged in design and operation of plant. During the last 17 years I have conducted number of training programs in India, Middle East, and Malaysia. The course contents of the program, along with the fruits of the author's long involvement in finding solutions to material problems during design and plant operation, have been incorporated in this book. The book covers different metallic materials and their properties, metal forming processes, welding and heat treatment, corrosion and corrosion protection, material selection and repair techniques of stationary equipment with respect to oil & gas, refinery and fertilizer industries.

Delhi, India Dr. Amiya Kumar Lahiri

Acknowledgements

My interest in conducting training program started with the request made by my ex-colleagues in Engineers India Ltd. and plant personnel in Indian Oil Corporation Ltd., Gujarat State Fertilizer Company Ltd. and Indian Petrochemical Corporation Ltd. with whom I constantly interacted during my service in Engineers India Ltd. I am greatly thankful to them. I would also like to acknowledge the encouragement I received in the National Metallurgical Laboratory, Jamshedpur, to undertake industrial problems related to material failure, in addition to my research activities, which formed the foundation of my subsequent association with the industry. I would also like to thank the participants in my training programs whose constant queries helped me in broadening the topics covered in this book. Finally this book would not have been written without the constant encouragement by Late Dr. Pranab Kumar Mukhopadhya, Director, Indian Oil Corporation, R&D Centre, which I gratefully acknowledge. The help of my affectionate Dr. U.K. Chatterjee, Former Professor of IIT Kharagpur, in correcting the manuscript is also duly acknowledged.

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Dr. Amiya Kumar Lahiri

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About the Author

Dr. Amiya Kumar Lahiri graduated with Ph.D. in Metallurgy from Banaras Hindu University, Varanasi, India and has more than 50 years' experience in corrosion. He was the Head of Corrosion Section of National Metallurgical Laboratory, Jamshedpur, and thereafter was the Head of the Materials and Maintenance Service Department of Engineers India Ltd. He also successfully completed two assignments as UNIDO consultant in Kuwait and Philippines, as expert in corrosion. After superannuation in 1989, he has been active in providing consultancy services in the areas of materials, corrosion control and plant inspection to refinery, fertilizer, petrochemical and oil and gas industries.

Since 1994, Dr. Lahiri has conducted over 75 training programs for oil and gas production, refining and fertilizer industries on applied metallurgy, failure analysis and corrosion control, 29 of them in the Middle East, and Malaysia. The present book is the compilation of the course material, revised and updated.

Dr. Lahiri had been a Fellow of the Institute of Metallurgist, London and Institution of Corrosion Science and Technology, U.K. and an Accredited Corrosion Specialist of National Association of Corrosion Engineer, USA. In recognition for his services Dr. Lahiri received the Best Metallurgist Award from IIM/Ministry of Iron & Steel, Government of India, in 1970 and Life Time Achievement Award from NACE Indian Chapter in 1999.

Chapter 1
Introduction

Abstract Profitability of modern high investment process industry depends on maintaining the operation of plant without unscheduled breakdowns, the primary responsibility of which depends on plant personnel. However, indirectly it largely depends on how the plant has been built with respect to material selection, engineering design and proper supervision during fabrication and construction activities. The plant personal has to ensure the reliability of these equipments by maintaining proper operating parameters and conducting periodic inspection and maintenance. This chapter introduces the basic considerations like (i) degradation under operating environment (ii) mechanical and physical properties (iii) type of equipment (iv) fabrication procedure and quality (v) plant inspection, maintenance, corrosion control and (vi) capital available which determine selection of material. Higher capital investment with better material would cost less in maintenance against high maintenance cost in a low investment plant. A step-by-step approach in final selection of material is also described. Finally six cases of catastrophic failures have been cited to emphasize the importance of strictly adhering to specified steps during all stages of a project implementation and operation.

Keywords Material selection · Plant engineering · Failure examples

1.1 Material Engineering

Profitability of any process plant is influenced by number of factors some of which are external and others internal. Important external factors like availability and cost of raw material, market demand, labour relation, etc., are basically management problem. Maintaining the operation of plant without unscheduled breakdown, on the other hand, is not generally affected by external factors because here the primary objective is to maintain the health of the equipment, a responsibility of plant personnel. Indirectly it also depends on the extent to which the *material engineering* aspects have been considered during design. Different aspects of *material engineering* are therefore to be understood by all concerned persons during the various

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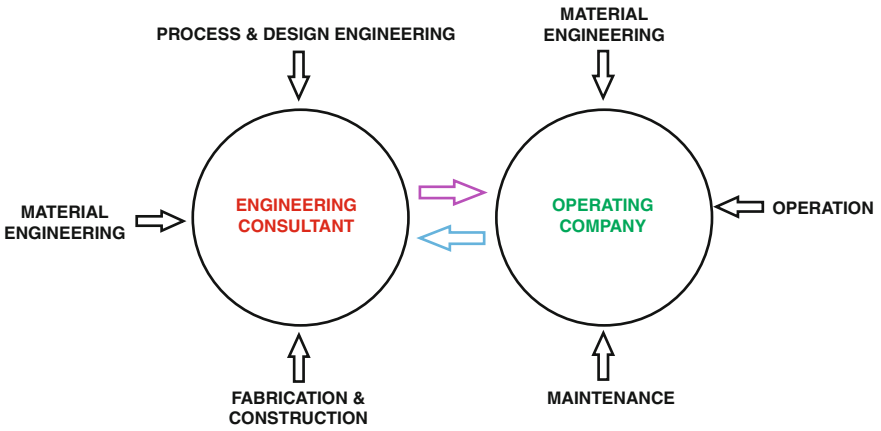


Fig. 1.1 Inputs of different engineering disciplines during project implementation and operation

steps involved from the concept to the completion and operation of any plant as illustrated in Fig. 1.1.

1.2 Considerations in Material Selection

1.2.1 Material Degradation

The first requirement is to set the design life of equipment, which is governed primarily by the extent of damage suffered by the environment. The important damage mechanisms are corrosion, oxidation, high temperature hydrogen attack and metallurgical degradation. Selection of material for resistance to different damage needs the following considerations:

(a) ***Operating conditions***—Nature of environment, operating temperature and pressure.
(b) ***Type of corrosive constituents***—(i) In presence of aqueous phase—acid, alkali, salts, H_2S, SO_2, etc. (ii) In absence of aqueous phase—H_2S, organic sulphur compounds, hydrogen, naphthenic acid, etc.
(c) ***Type of attack/damage***—(i) Corrosion—Uniform, pitting, stress corrosion cracking, dealloying, hydrogen damage, etc. (ii) Metallurgical degradation—Spheroidization, sigma formation, carburization and temper embrittlement.
(d) ***Modification of environment***—Corrosion control measures, e.g. neutralization, inhibitor addition, pH control, cathodic protection, cladding, coating, etc.
(e) ***Product purity***—Specified limits of impurities in product.

Based on the above considerations, the first step is to identify the minimum required material for a particular service. The final selection is to be made after considering additional requirements discussed next.

1.2.2 Mechanical and Physical Properties

Mechanical and physical properties which need to be considered are:

(a) ***Strength***—Higher the strength, lower is the thickness of material under a particular operating condition. This reduces the cost of material, cost of fabrication and in some cases the post-weld heat treatment (PWHT) requirement. On the other hand, too high a strength is not always preferred, because in certain environments cracking susceptibility increases with strength.
(b) ***Ductility/Fracture toughness***—The material should be sufficiently ductile for processing and fabrication, and tough to avoid any brittle failures. This property is dependent on alloy composition, heat treatment, metallurgical degradation, etc.
(c) ***Creep property***—In case of components operating at high temperatures in the creep regime, properties like creep strength and creep ductility become the dominant considerations. Higher the temperature and operating stresses, higher is the required creep resistance of material used.
(d) ***Thermal conductivity***—This property is important in case of heat transfer services like heater tubes and exchangers.
(e) ***Thermal expansion/contraction***—Where temperature changes are substantial or where two materials have substantially different coefficients of expansion, these properties are required to be considered in the design to avoid failures during service. Even for ambient temperatures, thermal expansion needs to be considered for long lengths of pipe.

1.2.3 Equipment Fabrication

In selecting any material of construction (MOC), the requirements related to design and fabrication also play an important role. The various factors are:

(a) Conformation to requirements of specification and codes being followed
(b) Good formability and adequate weldability of the material
(c) Post-weld heat treatment requirements
(d) Expertise available for shop and field welding

1.2.4 Type of Equipment

Type of equipment is considered for material selection primarily from the point of view of expected life, ease of replacement and safety considerations. Some important points are:

(a) ***Columns and vessels***—When used at temperatures below creep range these are designed for longer life (20–30 years), which is ensured by providing (i) higher corrosion allowance or (ii) use of clad steel or (iii) use of more corrosion resistant alloys. For operation under creep range design life is normally 100,000 h.
(b) ***Piping***—Pipes can be replaced with comparatively greater ease and, therefore, can be designed for an economic life using less corrosion resistant materials, considering service and risk.
(c) ***Exchanger tubes***—Depending on operational conditions exchanger tubes can be attacked from both tube and shell side. Wall thickness that can be used is also limited and, therefore, economic considerations, i.e. life-cycle cost comparison between higher metallurgy with longer life and less corrosion resistant material having shorter life need to be made before final selection.
(d) ***Heater tubes***—Conditions of operation here are more severe and the choice in many cases is for better material.
(e) ***Pumps***—These are subjected to erosion/corrosion damage and, therefore, depending on service, use of corrosion resistant material may be preferred.
(f) ***Criticality***—For critical equipment, generally better material is selected or a standby is provided. The decision is based on the cost.

1.2.5 Material Maintenance

Maintenance plays a vital role to get optimum performance from any equipment. With best of material selection, plant life will be affected if maintenance and operation are inadequate. On the other hand, with good maintenance and operation practices, an economic life can be obtained even if a less corrosion resistance material is used. Maintenance involves a multidisciplinary approach and a good maintenance practice requires the following important inputs:

(a) Mechanical inspection
(b) Preventive and predictive maintenance
(c) Regular turnaround
(d) Input of plant experience
(e) Input of expertise in various related fields
(f) Keeping abreast with the latest developments
(g) Failure and success analysis.

Earlier, plants were designed considering maintenance shutdown once every year which was reflected in the popularly used word in industry as *annual shutdown*. This approach has changed, and the present trend is to increase the period of continuous run to 2 or more years (depending on type of industry) in between shutdowns. This approach requires that no breakdown should occur during this period due to material failure. The emphasis has, therefore, shifted to specifying better material and improved corrosion control measures, better inspection and maintenance practices and close control on plant operation. As the length of run varies from industry to industry which is mainly decided by the plant management, this aspect is not always taken into consideration by the designer. In such cases, material upgradation becomes a part of plant maintenance activities.

1.2.6 Design Philosophy

In material selection, the first step is to decide on materials having the minimum desired properties required on the basis of operating conditions, corrosion resistance, design life, criticality and product quality requirements. Once this is done, the other factors discussed earlier are considered along with economics (capital cost, interest on capital, labour cost, cost of corrosion control measures, cost of replacements, cost of inspection and maintenance, etc.) for the final material selection. Basically, three approaches to design are possible, namely:

(a) Minimum investment design, i.e. maximum maintenance or short life design.
(b) Minimum maintenance design, i.e. minimum maintenance or overdesign.
(c) Economic design, i.e. optimum cost and maintenance design.

Generally, economic design is used. In situations like offshore oil and gas production, not only the investment is high but also the cost of maintenance is many fold compared to an identical plant on shore because of constraints of space and logistics involved. The other approach is to consider life-cycle cost for optimization of final selection, especially where the reliability is of great importance.

1.3 Steps in Selection of Material

Presently, a number of metallic and non-metallic materials having wide ranging properties are available to choose from. Similar is the case with corrosion protective measures. Lists of both are growing every day. In many such cases, one has to depend only on claims of manufacturers for the performance of their products with none or limited feedback on their actual performance. The selection of material is, therefore, not an easy task. On the other hand, new processes are being

commercialized, where the severity of the operating conditions is high. Environmental requirements are also becoming stringent. Under these conditions, in the author's opinion, the best approach is to take the following points into consideration:

(a) For new projects where the number of equipment and investments are large, the materials with proven experience should be preferred within the basic requirements enumerated earlier. Use of unproven or material/treatment with limited experience should be avoided. Fortunately, nowadays mass of published data are available, and the plant management has become less secretive whereby transfer of experience has become possible. These information and past experience of the engineers in the plant/design organization should be properly reviewed before selection.
(b) For a running plant, the approach can be different. Though due weightage is to be given to proven materials or protective systems, one has got the option to try new or not widely used or even costlier alternatives for special situations/problems experienced during the operation of plant. If proven experience is available, change can be directly made. If not, information should be collected and laboratory or preferably field trial conducted before the final selection for replacement or modification. The decision should also take into consideration the time required, cost involved and safety hazards.
(c) It is advisable to get feedback from users about the performance of any new material and not to depend fully on manufacturers' claim.

1.3.1 Steps in Material Selection

The step-by-step approach to material selection by concerned persons/groups for design of the plant will be as follows:

(i) Study the process flow diagram and identify temperature, pressure and composition of the streams. Here attention should be given even to the impurities or small amounts of constituents which might have not been considered by the process designer.
(ii) For selection of material in an operating plant, review the operation, inspection and maintenance history, conduct failure analysis and try to identify the causes of failure. Once the cause is established, the selection of material or corrosion control measure or design change becomes easier.
(iii) Identify the various alternatives available, including design and operational modifications. Grade these according to effectiveness and make the selection based on analysis of various factors, because the best is not always practical or economical. If necessary and if time permits, carry out simulated laboratory and field tests.

(iv) In many instances, plant throughput is increased or product pattern changed for which detailed study to set new process parameters is made, based on which de-bottlenecking is carried out. Increase throughput and changed operating parameters can in many cases adversely affect material performance leading to early failures. It is important that during such reviews, the impact on material performance should also be carried out and necessary action taken.

Once the selection of material and corrosion control measures are finalized, the next steps are:

(a) Preparation of Material Selection Diagram (MSD) as per NACE SP 0407 "Format, Content, and Guidelines for Developing a Materials Selection Diagram",
(b) Preparation of detailed specifications conforming to applicable specifications which include methods of manufacture, heat treatment, mechanical properties and code requirements,
(c) Identification of special requirements from the point of view of material performance, e.g. (i) PWHT, (ii) hardness limitations, (iii) minimum thickness of coating or cladding, (iv) welding parameters, (v) type of inhibitors to be used, (vi) location of inhibitor injection points, (vii) any special design features, (viii) operational changes, (ix) corrosion allowance, etc.
(d) Specifying inspection and supervision requirements during procurement, fabrication and repair,
(e) Confirming that all the stipulated requirements have been met during project implementation,
(f) 100% verification of materials other than carbon steel (PMI Testing) with the suitable methods as described in API RP 578, "Material Verification Program for New and Existing Alloy Piping Systems",
(g) Involvement of materials and corrosion engineers in the plant for corrosion monitoring, inspection, material procurement, failure analysis and constant interaction with engineering and process groups.

1.3.2 Design and Operational Considerations

Material selection alone does not ensure that the equipment will perform well in service. Design also plays an important role. Some of the design rules to minimize chances of material damage are:

(i) In service where stress corrosion cracking is a possibility (a) specify stress relief after fabrication where permitted. (b) Avoid crevices or vapour space where corrosive chemicals can get concentrated. (c) Do not use material, in cold worked condition, (d) use fabrication process which would minimize additional stresses, e.g. proper welding process, minimum mismatching of

parts to be joined (specially for piping), free thermal movement, (e) ensure full bore flow. Keep in view the limitations, if any, for a particular material, e.g. PWHT of stainless steel.

(ii) Vessels and tanks should be designed with provision for full drainage. The drainage point should be at the lowest point and the drain pipe flushed with the bottom.

(iii) All parts should be approachable for inspection and maintenance.

(iv) Avoid as far as possible the use of dissimilar metals having a large potential difference.

(v) Where impingement/erosion-corrosion is likely to occur, (a) provide corrosion resistance or replaceable impingement plate in tanks and columns, (b) use ferrules in heat exchanger tubing inlet, (c) use long radius bends, 3 or 4D bends in place of normal 1.5D for root pass of welds use TIG welding to have a good full penetration weld.

(vi) Provide injection facilities to reduce corrosivity of medium by neutralization, or inhibition, e.g. for boiler condensate, overhead corrosion and acidic water.

(vii) For lined vessels, both metallic and non-metallic, ensure that before lining (a) the surface is without protrusions, weld splatters and burrs, (b) the edges are rounded and not sharp.

(viii) For equipment and piping subjected to thermal stresses (a) allow for free movement, (b) eliminate sharp corners and edges, (c) provide expansion bellows, (d) provide expansion loops to pipes, (e) provide angle and spring supports.

(ix) Operate the plant within design parameters and use recommended start up and shutdown procedures. If parameters, such as, temperature, pressure and throughput are required to be changed, ensure to get the effect of these changes checked on corrosion and mechanical behaviour of various equipment and make necessary modifications, where necessary.

1.4 Some Failure Examples

Examples of some major failures which have occurred as a result of different deficiencies in material selection, design and operation of plant have been outlined.

1.4.1 A Case of Correct MOC But Wrong Specification and Repair Procedure

Rupture followed by explosion in amine absorber in gas sweetening plant of a refinery resulted in loss of 17 lives and more than 100 million $ loss. The bottom

two courses of 2.6 m diameter × 16.8 m high absorber developed extensive blistering and second ring was replaced in situ with a new plate. No preheat and PWHT was carried out. MOC of the absorber was carbon steel conforming to A 516 Gr. 60. After about 10 years run a 150 mm long circumferential crack appeared along the weld joining replaced second and first course which rapidly developed to a length of 600 m. Before action could be taken large quantities of gas escaped and exploded blowing up the top 15 m of the absorber (Fig. 1.2) [1]. Investigation showed presence of high hardness of 40–48 HRc in some areas of fusion line. The cause of failure was found to be initiation of crack at localized high hardness zones followed by its propagation by hydrogen induced cracking (HIC), a possibility which was overlooked and not included in the specification of the plate.

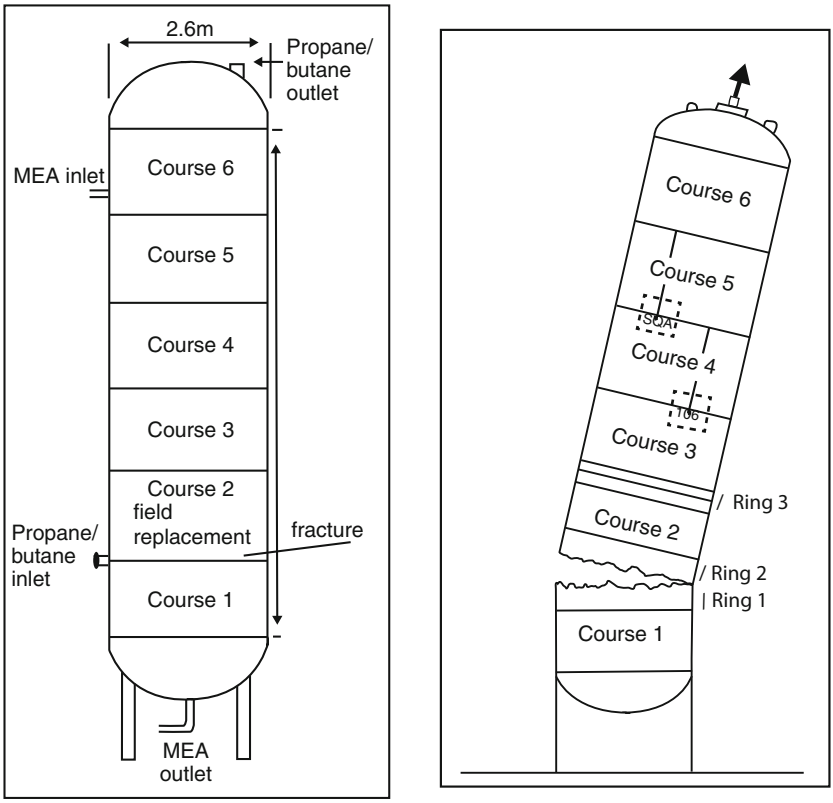


Fig. 1.2 Rupture of column in bottom section where a course was replaced

1.4.2 Selection of Control Valve of Wrong Design

In the production of hydrogen by steam/hydrocarbon process, the carbon dioxide from reformed gas is removed by treating in amine or carbonate/bicarbonate solutions. The corrosivity of CO_2 rich solution is controlled by adding vanadium pentoxide as inhibitor which forms protective layer of Fe_3O_4. The film is removed at high velocities resulting in accelerated corrosion. Control of velocity is of utmost importance in smooth running of plant. Because of process requirement, a control valve had to be replaced. The design of new valve was different which caused the flow to be nearer the pipe wall. Higher velocity resulted in erosion corrosion downstream of valve, resulting in rupture of bend (Fig. 1.3). Stream of hot CO_2 rich solution broke the glass of control room and flashed inside resulting in 12 fatalities due to asphyxia.

1.4.3 Catastrophic Failure Due to Inadequate Piping Stress Analysis

Highly explosive cyclohexane and cyclohexanon are intermediate chemicals used in the production of caprolactam. In the Flixborough plant in UK the reaction was carried out in six reactors placed in series. Reactors were of clad stainless steel lined carbon steel. The shell of reactor 'V' developed a crack and had to be by passed for continuous operation of the plant. This was done by rerouting of pipe to join the reactor 'IV' to 'VI' (Fig. 1.4). On the basis of piping stress analysis carried out in-house, a bellow of suitable specification was provided in the new line and the plant put on stream. Soon after commissioning, the pipe ruptured at junction of the pipe and bellow. A vapour cloud of cyclohexane and cyclohexanon was formed which exploded with force equivalent to 15 tonnes of TNT devastating the unit and the whole plant and badly affecting neighbourhood areas as shown in Fig. 1.5 [2, 3]. The incidence also resulted in number of fatalities.

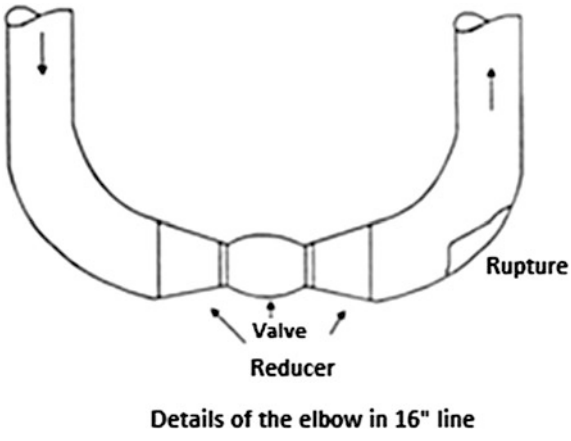


Fig. 1.3 Rupture downstream of valve

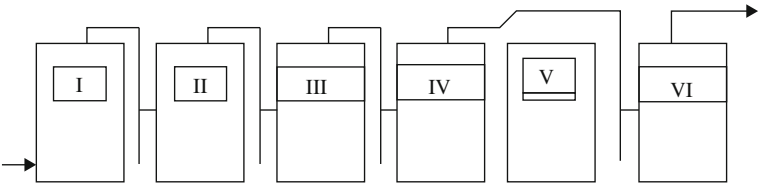


Fig. 1.4 Sketch showing six reactors in series

Detailed investigation identified the following to be the main reasons for the incidence:

- Poor piping stress analysis resulted in high stresses which resulted in failure. The correct procedure would have been to take the assistance of a professional consultant.
- Cracking of shell which necessitated by passing of the reactor was found to be related to the shell being sprayed temporarily with water because of flange leak, a normal practice. Here, however, river water in place of process water was used for spraying which later was found to contain high level of nitrate that led to nitrate stress corrosion cracking of carbon steel.
- Some secondary explosions were found to be due to cracking of stainless steel by molten zinc (Liquid metal embrittlement). Based on the observation, use of insulation wrapped in galvanized steel wire net has since been discontinued for insulating stainless steel equipment and piping.

1.4.4 Capsize of Semi-submersible Offshore Platform Because of Poor Workmanship

The oil drilling platform Alexander Kielland in the Norwegian sector of the North Sea was commissioned in 1978. A drain along with a hydrophone was fitted, 260 mm apart, in the D6 bracing (Fig. 1.6). Considering the importance of strength of D6 bracing the drain was provided taking into consideration all aspects of a good design. In case of hydrophone (325 mm diameter), however, a hole was gas cut and without proper dressing of the edges of the hole, it was double fillet welded with a throat of 6 mm. Examination of fractured surface showed the nature of fracture to be fatigue where the fatigue cracks propagated from two initiation sites of the fillet weld of the hydrophone in the direction circumferential to the D6 bracing. The bad workmanship/supervision left behind welding defects which aided by alternating stresses due to wave action in turbulent sea resulted in crack to extend to such an extent that the D6 bracing followed by other bracings snapped and column D got detached. This resulted in toppling of the platform (Fig. 1.7) [4].



Fig. 1.5 Overview of the plant complex and the unit after the disaster [2, 3]

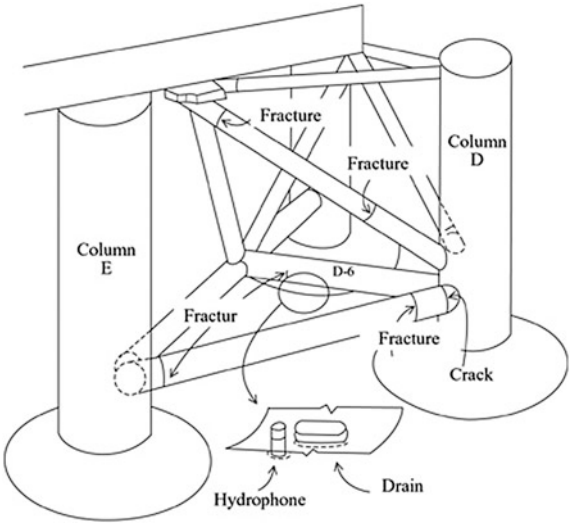


Fig. 1.6 Locations in bracings of platform where fracture occured [4]

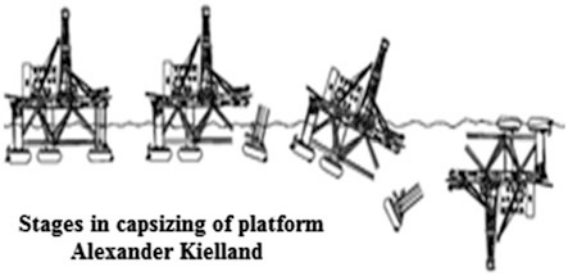


Fig. 1.7 Schematic representation of different stages in capsizing of platform [4]

It was a stormy evening with wind velocities of 16–20 m/s when the tragedy struck on 27 March, 1980. 123 workers out of 212 present were killed in the accident.

1.4.5 *Rupture of Pipe in Crude Distillation Unit Due to Wrong Specification*

Rupture in a 1250 mm (50″) long section of light gas oil (LGO) draw offline in the crude distillation unit at Chevron Refinery in Richmond, California on August 6 2012 caused formation of vapour cloud followed by fire. A plot plan/isometric of the crude unit shows the leak location relative to the column C-1100. The MOC of 200 mm diameter 8.18 mm thick (8″ Schedule 40) pipe section was carbon steel and was operated at 343 °C (650 °F). The rupture occurred as a result of thinning in a small length of 1300 mm (52″) due to sulphidation attack shown in Fig. 1.8. No substantial thinning in rest of the portion during regular measurements at different corrosion monitoring locations (CML) on the line and the bends were recorded. As

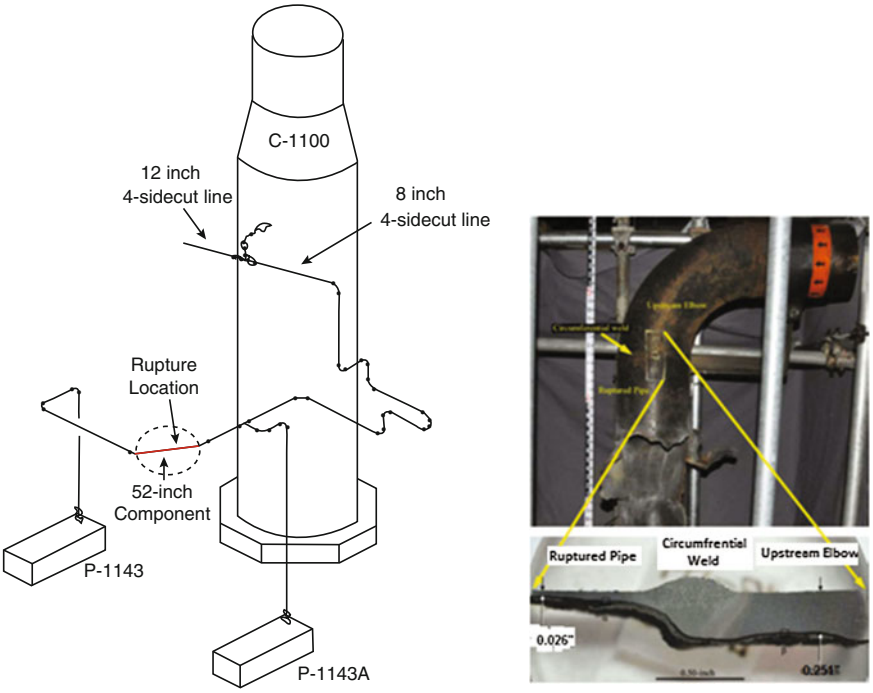


Fig. 1.8 Rupture of section of pipe having low silicon content in steel [5]

no CML was located in the short length of ruptured section, the thinning during service went unnoticed.

Investigation carried out by U.S. Chemical Safety and Hazard Investigation Board, brought to light the reason for the failure. The main difference between the affected portion and rest of the pipe was the silicon content, the former having 0.01 wt% against 0.16 wt% in case of the latter. The importance of silicon content in steel against sulphidation was known only since 1974 and refiners are specifying this requirement only since 1980s. Normally, A 53 or A 106 piping is used of which the former does not specify silicon content against minimum 0.1% in case of the latter. Thus piping used where sulphidation is possible should conform to A 106.

Subsequent to fire the MOC of whole LGO draw offline was upgraded to 9Cr-1Mo.

1.4.6 Failure of Thick Low Alloy Steel Vessel Due to Inadequate PWHT

An ammonia reactor, measuring 18.2 m (59 ft, $8^{9}/_{16}$ in.) in overall length and outside diameter of 2.0 m (6 ft, $6^{3}/_{4}$ in.), was fabricated from 150 mm ($5^{7}/_{8}$ in.) thick, normalized and tempered low alloy steel. The welds were locally given post-weld heat treatment (PWHT) and seams were examined during all stages by gamma radiography, automatic and manual ultrasonic testing and magnetic particle inspection. Hydro testing of the vessel was then started. After the pressure reached 90% of design pressure, the vessel ruptured and extensive damage occurred when four large pieces were blown from the vessel [6].

Investigation showed presence of a flat facet (9 mm), partly on heat-affected zone (HAZ) of the circumferential weld on fractured surface. A small crack in this area was visible which might have been missed during non-destructive examination because of its small size. The hardness in the susceptible area was of the order of 426–460 HV against the hardness of 251–265 HV elsewhere. The presence of hard spots shows that during local stress relief, the vessel in some portion had not reached specified temperature through full wall. The fine crack triggered brittle fracture under the influence of hydrostatic test.

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Chapter 2
Classification of Metallic Engineering Materials

Abstract Materials are classified under the three categories of (i) metals (ii) non-metals and composites. Of these, metals and its alloys broadly meet all requirements to be considered as the most suitable engineering material. Amongst metals, the largest use in the petrochemical industry is of ferrous metals and alloys like carbon and low alloy steels and stainless steels. Once selected, it is necessary to finalize the material specification as per requirement and adhere to the same for all procurements during construction and maintenance. Though limited to some specific services, non-ferrous metals and alloys are also used in petrochemical industry. In the first part of the chapter, a brief description and composition of the commonly used grades of carbon and alloy steels are given, followed by those of the conventional and high performance austenitic, ferritic and duplex stainless steels. Compositions of some important non-ferrous alloys have also been included. In the second part, the importance of standardization and material specification has been discussed which sets the requirements with regard to chemical analysis, mechanical properties heat treatment, dimensional tolerance, etc., that a product should satisfy. In a way, specification is considered as a contract between users and manufacturers.

Keywords Engineering materials · Carbon and alloy steels · Stainless steels · Non-ferrous alloys · Material specification

2.1 Introduction

In the early state of civilization, the only known constructional materials were mud, wood and stone which were used for construction of dwellings, containers and hunting weapons. This was followed by use of bronze and finally iron and these are known in archaeological terms as stone, bronze and iron ages. It is difficult to visualize the past scenario when today different metals and alloys are available and new developments are taking place in the production of materials having specific properties. If the non-metallics are also taken into consideration, there appears to be

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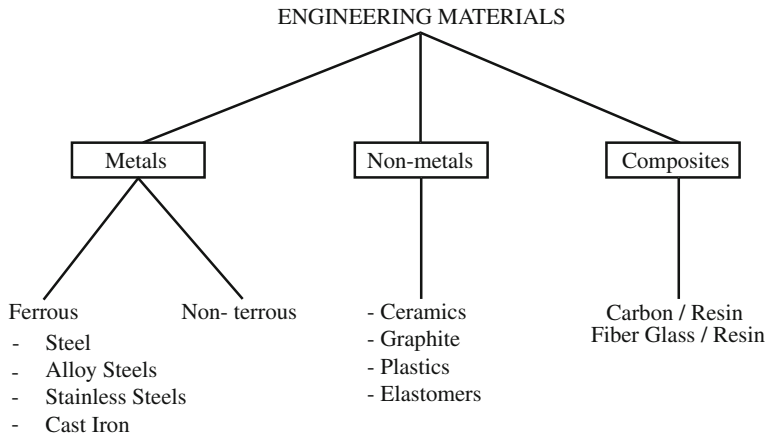


Fig. 2.1 Classification of engineering materials

no end to the range of materials which are available and will be available in the coming years.

Figure 2.1 gives some of the important and commonly used groups of materials, which can be broadly defined into metallic, non-metallic and the composites. Among these, metals and alloys form the bulk of engineering materials. In the present book, the emphasis is on metallic materials and their uses in petrochemical and chemical process industries. As of 2016 out of 118 confirmed elements the periodic table shows presence of 94 naturally occurring elements (rest of 24 occurs only when synthesized in the laboratory) and a large number of them fall under the category of metals. However, only a few of the metals are of practical value as far as their usability as engineering material is concerned. This is because any metallic engineering material should meet certain specific properties, viz. strength, ductility, workability, comparative ease of production and availability. If we consider the metallic materials, it is found that:

* There are two basic groups, ferrous and non-ferrous, and
* Most of the engineering materials are alloys and only a few are used as pure metals.

It is interesting to note that though Iron Age followed Bronze Age, finally it is the ferrous base alloys which occupy the leading position as the 'most used' engineering material. The reasons for this are:

* Abundance of iron ore in the earth crust,
* Comparatively easier and cheaper methods of production of iron and its alloys,
* Some special inherent features of iron which can be utilized by suitable alloying and heat treatment to obtain a wide range of strength combined

with toughness; from soft low strength Armco iron to ultra-high strength steels,
* Producing materials by suitable alloying, having requisite mechanical properties, suitable for use at as low as −270 °C or as high as 1150 °C.
* Vast improvement in corrosion and oxidation resistance properties that can be attained by alloying.

Unlike ferrous materials, which have iron as the base metal, non-ferrous material includes all other metals. The important practical materials which fall under this group are copper, nickel, aluminium, titanium, zinc, tin and lead and their alloys. Metal like chromium, manganese, tungsten, antimony, bismuth, boron, etc., are used only as alloying elements. On the other hand, metals like zirconium, tantalum, silver, gold, etc., and their alloys are too expensive and are used for very specific applications.

2.2 Ferrous Materials

2.2.1 Cast Irons

Cast irons (CI) are Fe-alloys, with carbon varying from 2.5 to 4.5%. Depending on the composition and cooling rate from the molten state the carbon in CI is present as either Fe_3C (cementite) or free carbon (graphite) or both. The various types of cast irons have basic variations in the form and morphology of carbon distribution. The strength and brittleness of cast irons depend on the form in which the carbon is present and increase with increase in the amount of Fe_3C.

The graphite in normal cast iron (grey cast iron) is distributed in flake form in a ferritic or pearlitic matrix. The poor workability or brittleness of graphitic cast iron is due to the presence of graphite in flake form. However, by suitable treatment (during melting and alternately by suitable heat treatment), the shape of graphite can be modified into nodular form. Nodular and malleable cast iron fall under this category. The nature of graphite in two irons in shown in Fig. 2.2a [1] and b [2]. These have improved ductility and are less prone to failure under shock loading as compared to grey cast iron. The white cast irons, on the other hand, are hard and highly brittle and are used only where wear resistance is required.

Cast irons cannot be worked and easily welded and therefore used only in cast form, which does not involve any mechanical working. Some of the important components made of cast irons are: pumps, valves, pipes, gears, cover boxes, pump base plates, etc. Being brittle in nature, use of CI in hydrocarbon service is generally avoided.

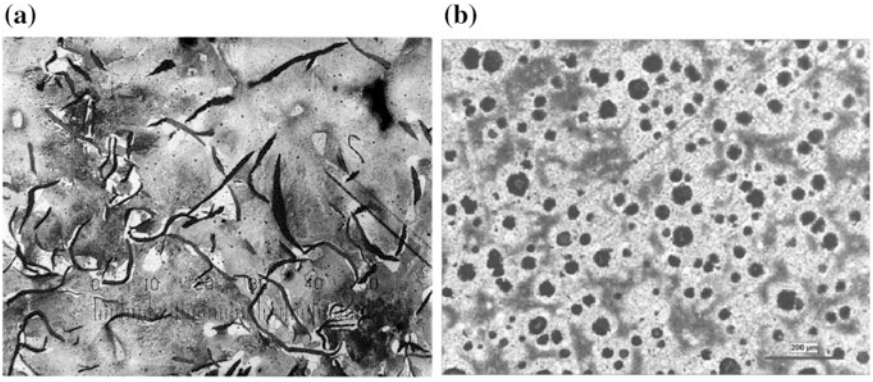


Fig. 2.2 **a** Graphite flakes seen in unetched *grey* cast iron [1]. **b** Nodular graphite observed in etched SG iron [2] X 100

2.2.1.1 Alloy Cast Irons

Cast irons, like other metals, can be alloyed with nickel, silicon, chromium, molybdenum, etc., either singly or in combination, to impart resistance to corrosion in various media and to impart high wear resistance. Ni-hard, austenitic cast irons (Ni-resist), high silicon iron are some of the commonly used alloyed cast irons. Ni-resist also possesses better mechanical properties, especially when graphite is in the nodular form.

2.2.2 Plain Carbon Steels

Plain carbon steels constitute the largest tonnage of ferrous material in use and cover alloys of iron and carbon, with small amounts of Mn, Si, S, P either added deliberately or present as impurities. As impurities, P and S are most deleterious and special care is needed to keep their contents at low levels. Sulphur (and also selenium) is, however, sometimes deliberately added to improve machinability of iron and its alloys. For structural, plates for pressure vessels, sheets, rods and pipes, the carbon content varies from 0.1 to 0.35%. For higher strength and wear resistance and for components requiring heat treatment, higher carbon, normally up to 1.0%, are used for specific end uses, e.g. files, saws, cutting tools, rails, shafts etc. For deep drawing purposes, for making components like cans and car bodies the low carbon steel (<0.1%C) is specified.

Carbon is the most important element to impart strength. Higher the carbon content higher is the strength. However, higher carbon adversely affects toughness and weldability. Thus to retain the strength and also good weldability, carbon steels containing lower carbon (0.2–0.30%) are used for pressure vessels. The carbon

Table 2.1 Typical composition of some plain carbon steels

AISI/SAE	%C	%Mn	%P max	%S max	UNS No.
1010	0.08–0.13	0.30–0.60	0.04	0.05	G10100
1015	0.13–0.18	0.30–0.60	0.04	0.05	G10150
1020	0.18–0.23	0.30–0.60	0.04	0.05	G10200
1025	0.22–0.28	0.30–0.60	0.04	0.05	G10250
1030	0.28–0.34	0.60–0.90	0.04	0.05	G10300
1040	0.37–0.44	0.60–0.90	0.04	0.05	G10400
1055	0.50–0.60	0.60–0.90	0.04	0.05	G10550
1080	0.75–0.88	0.60–0.90	0.04	0.05	G12250
1522	0.18–0.24	1.30–1.60	0.04	0.05	G15220

steels generally have adequate impact strength at low temperatures (−29 °C), but for still lower temperature fine-grained impact tested steels are used up to a temperature of −48 °C. For high temperature use (above creep limit), creep rupture strength and resistance to oxidation are the two important criteria. Almost all codes allow use of carbon steel up to 480 °C, though in earlier times it is used to be prescribed for temperatures as high as 520 °C (ASME Section VIII Div. 1 gives design stress of carbon steel up to 527 °C). The present-day accepted practice is to limit its use to a maximum temperature of 450 °C. Composition of some commonly used carbon steel containing different carbon is given in Table 2.1 [3].

2.2.3 Low and Medium Alloy Steels

Innumerable grades of steels containing comparatively small amounts of alloying elements, e.g. chromium, molybdenum, nickel, vanadium, boron, etc., in different combinations are in commercial use. The total alloying content in these steels may vary from 0.5 to 9.0%. The alloying elements are added to increase strength; to lower UTS/YS ratio; improve ductility, fracture toughness, heat treatment and carburizing properties; corrosion resistance in specific environments; high temperature creep strength and resistance to oxidation. Excluding carbon, the alloys of iron containing <5% and 5 to <10% alloying elements are broadly classified as low and medium alloy steels, respectively. The carbon and low and medium alloy steels are available both in wrought and cast forms and designated by numbering systems in different national and international specifications like SAE, AISI, DIN, BS, EN, etc. To have an idea of the range of different alloys available, composition of some of the low and medium alloy steels (AISI/SAE designation) are given in Table 2.2 [4]. The trend during the last 20 years has been to produce steels with high degree of cleanliness and low UTS/YS ratio, by micro-alloying and giving greater attention

Table 2.2 Typical composition of some alloy steels

AISI/SAE	%C	%Mn	%Ni	%Cr	%Mo	%V	UNS No.	Type
1330	0.28–0.33	1.60–1.90	–	–	–	–	G13300	Mn steel
1340	0.38–0.43	1.60–1.70	–	–	–	–	G13400	
2317	0.15–0.20	0.40–0.60	3.25–3.75	–	–	–	G23150	3% Ni steel
2330	0.38–0.43	0.70–0.90	3.25–3.75	–	–	–	G23300	
3115	0.13–0.18	0.40–0.60	1.10–1.40	0.55–0.75	–	–	G31150	Ni–Cr steel
3140	0.38–0.43	0.70–0.90	1.10–1.40	0.65–0.95	–	–	G31400	
4023	0.20–0.25	0.75–0.90	–	–	0.20–0.30	–	G40230	Mo steel
4037	0.35–0.4	0.70–0.90	–	–	0.20–0.30	–	G44190	
4130	0.28–0.33	0.75–1.00	–	0.80–1.00	0.15–0.25	–	G41300	Cr–Mo steel
4140	0.38–0.43	0.75–1.00	–	0.80–1.10	0.15–0.25	–	G41400	
4340	0.38–0.43	0.60–0.80	1.65–2.00	0.70–0.90	0.20–0.30	–	G43400	Ni–Cr–Mo steel
5120	0.17–0.22	0.70–0.90	–	0.70–0.90	–	–	G51200	Cr steel
5140	0.38–0.43	0.70–0.90	–	0.70–0.90	–	–	G51400	

N.B Significance of the digits: The first two digits represent the major alloying elements (Types) and the last two digits the carbon content

to production and working techniques like quenched and tempered and thermo mechanical treatment. Line pipe steels (API 5LX) having YS up to 584 Mpa (85 ksi) are presently in use. In the recent years, line pipe material of X 120 grade has been developed specially for transport of gas [5].

2.2.4 High Alloy Steels

High alloy steels are mainly those which contain high amounts (>10%) of alloying elements. Stainless steels constitute the major material of construction among the high alloy steels in petrochemical industry.

2.2.4.1 Wrought Austenitic, Ferritic and Martensitic Stainless Steels

Stainless steels are alloys with a minimum of 10.5%Cr. In addition, these can also have nickel, and comparatively smaller amounts of molybdenum, titanium, niobium and nitrogen. It is chromium which imparts the resistance to corrosion by forming a thin ($\sim$2 nm) passive layer of chromium oxide on the surface [2]. Many metals and alloys form a thin oxide film when exposed to air, but these are not stable and get easily destroyed when exposed to corrosive environments. However, for the film to impart protection it should form easily, be stable and most importantly re-form quickly once damaged. These requirements are fulfilled by chromium when added to iron as an alloying element. A number of commercial alloys are available, having high resistance to corrosion and oxidation and improved creep rupture properties. Some alloys, in addition, also possess much higher strength. Stainless steels are classified mainly into three categories based on their crystal structure, i.e. Fe–Cr martensitic, Fe–Cr ferritic (4XX series) and Fe–Cr–Ni austenitic (3XX series). While the first two are magnetic, the latter is non-magnetic. It is important to remember that numbers 4XX and 3XX refer to stainless steels shaped by working, such as rolling, forging, etc. Both these categories of alloys were developed in early twentieth century. The credit for discovery of the corrosion resistance stainless steel goes to P. Monnartz in Germany in 1911 when the first detailed data on the corrosion of stainless steel as a function of composition were published. In 1912, Eduard Maurer at Germany's Krupp Iron Works patented the first austenitic stainless steel. In 1913, Harry Brearly of Sheffield, England, discovered and patented the first martensitic stainless steel. For these achievements, Maurer and Brearly are given the distinction as co-discoverers of the industrial usefulness of stainless steel [6].

Stainless steels can be broadly divided into four groups

- Straight chromium ferritic/martensitic stainless steels
- Austenitic Stainless Steels:
  - Chromium–nickel
  - Chromium–nickel–molybdenum
  - High performance
  - Heat resistant
- Duplex Stainless Steel
- PH steels

Of these most commonly used stainless steels in process industry are of austenitic chromium–nickel–molybdenum grades. Austenitic steels are more ductile and can be formed and welded with comparatively greater ease than the ferritic grades. They have good creep rupture strength and oxidation resistance up to 1100 °C. They are also suitable for cryogenic use up to almost 0° absolute (−270 °C). Many of the austenitic stainless steels are also available in low carbon (with suffix L) or stabilized grades (e.g. 321 and 347). Alloys meant for high temperature service wrought alloys are given a suffix of H, e.g. 304H, 347H, 316H, 321H etc., which specifies minimum carbon content of 0.04%, the amount of other elements remaining the same. Fe–Cr or Fe–Cr–Ni alloys are also used in cast form for number of services. Austenitic stainless steels of cheaper varieties are also available, where nickel has been partly or fully replaced by manganese + nitrogen to get a stable austenite phase (2XX series). This is possible because like nickel both manganese and nitrogen is austenite stabilizer. These alloys have better strength, but lower resistance to corrosion compared to Fe–Cr–Ni alloys and not very much in use as engineering material. Table 2.3 gives the nominal composition of various grades of 300 and 400 series of stainless steels [7].

Ferritic stainless steels are mainly Fe–Cr alloys with chromium content of 10.5% and above. As mentioned earlier, these are available in hardenable (martensitic) or non-hardenable (ferritic) grades. The former, with suitable heat treatment can develop high strength and hardness. The hardenable grades contain 12–15% chromium with carbon above 0.1%. Alloys containing still higher chromium are non-hardenable. In higher chromium containing alloys sometimes titanium is added in small amounts (1.5%) to improve corrosion resistance.

Ferritic stainless steels have very good resistance to high temperature oxidation but their use is limited because of their susceptibility to 475 °C embrittlement. Thus, the use of ferritic stainless steels is limited to ∼300 °C.

Table 2.3 Some typical wrought austenitic and ferritic stainless steels

Designation	Type	%C max	%Cr	%Ni	% Others
AISI (UNS NO)					
304 (S30400)	Austenitic	0.08	18–20	8–12	
304L (S30403)	Austenitic	0.03	18–20	8–12	
321 (S32100)	Austenitic	0.08	17–19	9–12	Ti, 5X(C + N); 0.7 max
347 (S34700)	Austenitic	0.08	17–19	9–12	Nb, 10XC; 1.0 max
304H (S30409)	Austenitic	0.10	17–19	9–12	C-0.04 min
316 (S31600)	Austenitic	0.08	16–18	10–14	2–3 Mo
316L (S31603)	Austenitic	0.03	16–18	10–14	2–3 Mo
317 (S31700)	Austenitic	0.08	18–20	11–15	3–4 Mo
317L (S31703)	Austenitic	0.03	18–20	11–15	3–4 Mo
309 (S30900)	Austenitic	0.08	22–24	12–15	
310 (S31000)	Austenitic	0.08	24–26	19–22	
304LN (S30451)		0.03	18–20	8–12	N 0.10–0.16
316LN (S31653)		0.03	16–18	10–14	N 0.10–0.16
201(S20100)	Austenitic	0.15	16–18	3.5–5.5	Mn 5.5–7.5; N 0.25
405 (S40500)	Martensitic	0.08	11.5–14.5	–	
410S	Martensitic	0.08	11.5–13.5	–	
410 (S41008)	Martensitic	0.15	11.5–13.5		
430 (S43000)	Ferritic	0.12	16–18		
444 (S44400)	Ferritic	0.025	17.5–19.5		Mo 1.75–2.5; (Ti + Nb) [0.2 + 4(C + N)] to 0.80 max

2.2.4.2 Cast Stainless Steels

Many stainless steel components, like other metals and alloys, are available in both wrought and cast forms, such as, pumps, valves, bends, reformer tubes, etc. On the other hand, some of the alloys are available only in cast form because they cannot be worked into various shapes. However, wrought and cast alloys are designated separately even in case of those having similar composition. Cast stainless steels are usually specified on the basis of composition by using the alloy designation system established by the Alloy Casting Institute (ACI). The ACI designations of corrosion resistant castings have been adopted by ASTM International and are preferred for cast alloys over the American Iron and Steel Institute (AISI) designation for similar

Table 2.4 Some typical cast stainless steels

Designation	Type	%C max	%Cr	%Ni	% Others
[a]*ACI/UNS No.*					
CA-15 (J91150)	Ferritic	0.15	11.5–14	1 max	
CC-50 (J92615)	Ferritic	0.50	26–30	4 max	
CF-8 (J92600)	Austenitic	0.08	18–21	8–11	
CF-8M (J92999)	Austenitic	0.08	18–21	9–12	2–3 Mo
CF-8C (J92710)	Austenitic	0.08	18–21	9–12	Nb (8xC)
CH-20 (J93402)	Austenitic	0.20	22–26	12–15	
[b]*ACI/UNS No.*					
HC (J92605)	Ferritic	0.50	26–30	1 max	2.0 Si
HH (J93503)	Austenitic	0.2–0.5	24–28	11–14	2.0 Si
HI (J94003)	Austenitic	0.2–0.5	26–30	14–18	2.0 Si
HK (J92224)	Austenitic	0.2–0.6	24–28	18–22	2.0 Si
HT (J94605)	Austenitic	0.35–0.75	13–17	33–37	2.5 Si
HX	Austenitic	0.35–0.37	15–19	64–68	2.5 Si
HPJ95705	Austenitic	0.25–0.5	24–27	33–37	2.0 Si; Nb, Ti, W

[a]Cast corrosion resistant alloys
[b]Cast heat resistant alloys

wrought steels. Table 2.4 gives some of the typical cast stainless steels used for corrosive and high temperature services [8].

The alloys are identified by the letters and numbers assigned. The terms C and H indicate use of alloy for corrosive and heat resistant service, respectively. The second term indicates nominal Cr–Ni type as per ASTM E527 [9]. Increasing nickel content of the alloy is indicated by adding A–Z to the ACI designation. Number following this letter denotes carbon content of the alloy. In case of any additional element in the alloy, the same is indicated by adding a letter to the designation. For example Alloy CF8M would mean "cast corrosion resistant alloy containing 19Cr–9Ni (location F in the ASTM E527) containing max 0.08C with addition of Mo". Cast alloys are classified as corrosion resistant when used in corrosive and vapour environment below 650 °C and heat resistant above this temperature. Cast stainless steel is considered to have corrosion rates equivalent to wrought grade but this may also be lower because of cast structure's inhomogeneity or micro segregation [10].

2.2.4.3 Duplex Stainless Steel (DSS)

First developed and introduced in mid 1970s duplex stainless steels (DSS) ideally consist of a mixture of about equal proportion of ferrite and austenite. The mixed phase (Fig. 2.3) [11] is obtained by using a balanced composition of chromium, nickel, molybdenum and nitrogen, with nickel reduced in the range of 5–7%, depending on the chromium content. To compensate the reduction in nickel small

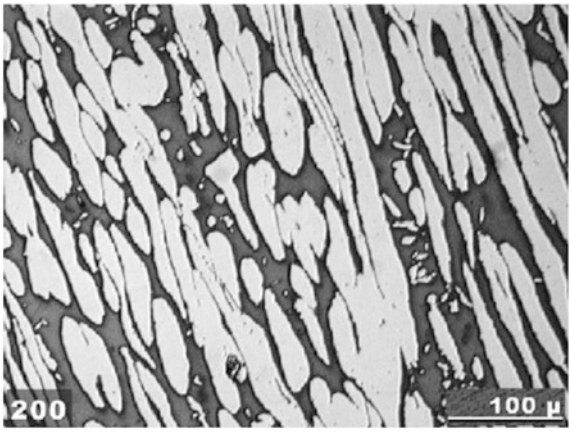


Fig. 2.3 Duplex stainless steel micro structure of austenite and ferrite [11]

amounts of nitrogen is added, which as stated earlier is an austenite stabilizer. In practice, it is not possible to get equal proportion of austenite and ferrite and variations in the same primarily affect corrosion rate (decreasing austenite) and impact energy (increasing ferrite). Optimal results are obtained in ferrite range between 35 and 60%. Though first produced in 1930s [12], use of DSS was limited. The first-generation DSS provided good performance in non-welded conditions in some service but had limited use in as-welded condition. Presence of excessive ferrite in weld and HAZ drastically affected toughness and corrosion resistance of welds. It was only in early 1970s that a new grade (18Cr grade), with good properties was added to the first-generation DSS which was accepted by the industry for its resistance to chloride SCC and used primarily for coolers and condensers where the service involved water or processing medium containing high level of chloride. Subsequently, a number of DSS alloys have been produced based on 22Cr, 23Cr and 25Cr grades [12–14] with different amounts of nickel, molybdenum and nitrogen; the 25Cr grade being called Super DSS. In addition to good corrosion resistance, these have much higher strength than the 300 series of alloys. Charles [15] has published an excellent review on the development and importance of DSS.

Considerable work is still going on in the development and studies on DSS. During the last few years DSS having high PRE of minimum 48, called Hyper DSS [16], has been developed for use under highly corrosive conditions. Of all the alloying elements in stainless steels, nickel is not only costliest but its price also fluctuates considerably. Therefore cheaper varieties of DSS, where nickel has been replaced with manganese and nitrogen, called lean DSS [17] have been developed. It is claimed to be suitable for use in place of 304L and 316L for many services. These alloys also have the advantage of higher strength and resistance to chloride stress corrosion cracking.

DSS is not as easy to weld as austenitic stainless steels but has better weldability than ferritic and martensitic stainless steels. Initial problems experienced in welding

Table 2.5 Nominal composition of major grades of duplex stainless steels (wt%)

Steel Name/UNS No.	C	Si	Mn	Cr	Ni	Mo	Cu	N
LDX 2101[a] S32101	0.03	0.6	5.0	21.5	1.5	0.3	0.3	0.22
LDX 2404™ S82441	0.02	–	3.0	24.0	3.6	1.6	–	0.27
2304[b] S32304	0.02	0.4	1.5	23.0	4.8	0.3	0.3	0.10
2205[c] S32205	0.02	0.4	1.5	22.0	5.7	3.1	0.2	0.17
2507[d] S32750	0.02	0.2	0.7	25.0	7.0	4.0	0.3	0.27
2707[e] S32707	0.03	–	–	27.0	6.5	5.0		0.4

[a]Recent development—low Ni, high Mn Lean DSS
[b]Recent development—low Ni, high Mn Conventional DSS
[c]Present-day Lean DSS
[d]Present-day DSS (conventional)
[e]Present-day DSS (Super DSS)
[f]Recent development, Hyper DSS

DSS have now been overcome. Table 2.5 gives composition of some of the typical DSS compiled from data of reputed manufacturers [13, 14, 16, 17].

Another important group of stainless steels falls under the category of precipitation hardening (PH) stainless steels used primarily where wear resistance is an important requirement.

2.2.4.4 High Performance Ferritic and Austenitic Stainless Steels

Number of highly alloyed materials have been developed and are under development to meet the requirements of highly corrosive services in oil and gas, chemical, petrochemical and other industries. Under some of the conditions encountered in these services conventional stainless steels and nickel alloys fail to give satisfactory service. These alloys fall under the category of super austenitic, super ferritic, super duplex and nickel base alloys; last two having been discussed separately. While super austenitic stainless steels are used for fabrication of different equipment, ferritic stainless steels have been developed to be used primarily as heat exchanger tubing in seawater service where resistance to pitting and chloride stress corrosion cracking is an important requirement. Moreover, these have the advantage of lower cost compared to high nickel containing super austenitic stainless steels. Table 2.6 gives the composition of some of the high performance stainless steels [18].

2.2.4.5 Comparison of Different Stainless Steels

It will be apparent from the above discussion that number of alloys have been developed falling in the category of stainless steels. Table 2.7 summarizes the comparative properties of the various grades of stainless steels. These varying physical, mechanical and corrosion resistant properties enable their use under varying conditions which will be discussed in detail at appropriate sections in the book.

Table 2.6 Composition of wrought high performance ferritic and austenitic stainless steels showing major alloying elements

Name	UNS No.	C	N	Cr	Ni	Mo	Others	PRE No.
Super austenitic								
904L	N08904	0.02	–	19.0–23.0	23.0–28.0	4.0–5.0	Cu 1.0–2.0	32
Alloy 28	N08028	0.02	–	26.0–28.0	29.5–32.5	3.0–4.0	Cu 0.6–1.4	36
254 SMO	S31254	0.02	0.18–0.22	19.5–20.5	17.5–18.5	6.0–6.5	–	42
Al-6XN	N08367	0.03	0.18–0.25	20.0–22.0	23.5–25.5	6.0–7.0	0.76	43
654 SMO	S32654	0.02	0.45–0.55	24.0–28.0	21.0–23.0	7.0–8.0	Mn 2.0–4.0	54
Super ferritic								
E-BRITE 26-1	S44627	0.01	0.015	25.0–27.0	0.5	0.75–1.5	Nb	27
SEA-CURE	S44660	0.03	0.040	25.0–28.0	1.0–3.5	3.0–4.0	Ti; Nb	35
AL-29-42	S44800	0.01	0.020	28.0–30.0	2.0–2.5	3.5–4.2		40

Table 2.7 Comparison of properties of different types of stainless steels

Characteristics	Austenitic	Ferritic	Duplex
Basic composition	Cr. 18–25, Ni 8–40	Cr 10–27	Cr. 18–25; Ni 5–27
Phases	Austenite	Ferrite	50 Austenite + 50 Ferrite
Magnetic properties	Non-magnetic	Strongly magnetic	Magnetic
R.T. strength	Fair	Good	Very good
H.T. strength	Very good	Poor (>300 °C)	Poor (>300 °C)
Cryogenic property	Very good	Poor	Poor
Weldability	Very good	Poor	Fair
Corrosion/Oxidation	Very good	Fair/Good (>300 °C)	Good (>300 °C)

2.3 Non-ferrous Materials

2.3.1 Aluminium and Aluminium Alloys

Of the non-ferrous metals, tonnage-wise aluminium occupies the highest position. It is soft, has low strength and comparatively low melting point (about 660 °C). In spite of this, its lightness (about 1/3rd of that of iron), good resistance to corrosion, good electrical conductivity and comparatively lower cost make these as attractive alternative in many structural, decorative, electrical and corrosion resistance service. Aluminium and its alloys are extensively used in aerospace industry. An important property of aluminium is its ability to develop considerable strength by suitable alloying and in some cases by subsequent heat treatment, known as *age hardening*. The aluminium and its alloys on cold working retain good ductility with increase in strength and therefore, are available in various degrees of cold working, known as *tempers* that are mentioned in alloys specifications.

2.3.2 Copper and Copper Alloys

Copper is the second most important non-ferrous metal after aluminium. Its largest use is as electric conductor but is also extensively used in producing various alloys having good resistance to corrosion, especially in fresh and sea water service. Copper and its alloys are highly ductile and can be easily cast and worked to produce various components. The largest use of copper alloys in process industries is in tubing and piping. Where resistance to some specific corrosive media is required, the preferred method of using copper and its alloys is to use as lining over steel base for fabrication of pressure vessels, tanks, etc.

The most important copper alloys are brasses (Cu–Zn, Cu–Zn–Sn; Cu–Zn–Al), bronzes (Cu–Al, Cu–P, Cu–Zn–Si), cupronickels (Cu–Ni), etc. Some of the

Table 2.8 Composition of some copper alloys used in process industries

UNS No.	Copper	Aluminium	Nickel	Zinc	Iron	Others
C28000	59.0–63.0	–	–	Balance		
C44300	72.0	–	–	Balance		Sn 0.9–1.2; As 0.04
C44400	70.0–73.0	–	–	Balance		Sn 0.9–1.2; Sb 0.02–0.10
C44500	70.0–73.0	–	–	Balance		Sn 0.9–1.2; P 0.02–0.10
C60800	Balance	5.0–6.5	–			0.02–0.35
C68700	76.0–79.0	1.8–2.5	–	Balance		0.02–0.10
C70400	Balance	–	4.8–6.2	1.0 max	1.3–1.7	
C70600	Balance	–	9.0–11.0	1.0 max	1.0–1.8	
C71000	Balance	–	19.0–23.0	1.0 max	0.5–1.0	
C71500	Balance	–	29.0–33.0	1.0 max	0.40–1.0	
C71600	Balance		31.0		1.7–2.3	

important uses of copper alloys used in process industries are heat exchanger tubing, piping and fittings for handling sea water, fasteners and other hardware, etc. Table 2.8 lists some important copper alloys [19].

2.3.3 Nickel and Nickel Alloys

Compared to aluminium and copper, nickel is costlier but in spite of this it is extensively used both as pure nickel or mainly its alloy both for corrosion and high temperature services. Some of the important nickel base alloys are Monel® (Ni–Cu), Inconels® (Ni–Cr–Fe), Hastelloys® (Ni–Cr–Mo,). Use of nickel and its alloys is specially made where resistance to specific highly corrosive environment is needed as in strong caustic or hydrofluoric acid service. Table 2.9 lists some important nickel alloys [20].

2.3.4 Lead and Lead Alloys

Lead and its alloys as engineering material have limited but important uses. Lead alloys are used for soldering (Pb–Sn, Pb–Sn–Sb) and bearings (Pb–Sn–Sb, Cu–Pb, Cu–Sn–Pb). Pure lead and Pb–Sb (hard lead) sheets and pipes are used in specific corrosive environment, e.g. dilute sulphuric acid service. Lead has low melting point (327 °C) and low strength. Its creep resistance is poor and creep failure occurs at normal temperature under self-load. By alloying, its strength, both normal and

Table 2.9 Nominal composition of typical nickel alloys

UNS No.	Nickel	Copper	Iron	Aluminium	Chromium	Molybdenum	Others
Monel (N04400)	66.5	31.5	1.0				1.0Mn
Monel K 500 (N05500)	64.0	30.0		2.8			0.60Ti
Incoloy 600 (N06600)	75.0		8.0		15.5		0.15C
Alloy 825 (N08825)	42.0		29.5		21.5	3.0	1.3Cu; 1.0Ti
Alloy G2 (N06985)	44.0		19.5		22.0	7.0	1.5W; 2.0Cu
Hastelloy C276 (N10276)	Balance	57.0	5.5		15.0	16.0	3.8W
Hastelloy C22 (N06022)	Balance		3.0		22.0	13.0	3.0W

creep, can be increased, e.g. Pb–Sb (hard lead) has better stability as lining. Because of its low strength it is more commonly used as a lining (sheet or homogenous).

2.3.5 *Titanium and Titanium Alloys*

In process industry unalloyed titanium (also known as commercially pure or *CP* titanium) is commonly used. Titanium is selected for its excellent corrosion resistance properties in large varieties of environments, especially in applications where high strength is not required. However, because of high cost its use is limited to exchanger tubes using sea water as coolant and for some specific corrosive chemicals. CP grade titanium is available in four ASTM grades, i.e. 1, 2, 3 and 4 where strength of the material increases progressively from 240 MPa (35 ksi) to 640 MPa (93 ksi). The chemical composition and strength for the four CP grades are given in Table 2.10 [21]. It will be evident from the table that, the variations in mechanical properties are dependent on interstitial solid solution (oxygen, hydrogen, nitrogen) and impurity (iron) levels.

Titanium is light compared to iron (about 50%) and therefore it has the advantages of having lower weight to strength ratio. Ti6 Al–4V alloy is widely used titanium alloy where strength and toughness are required.

Table 2.10 Variations in composition (by wt%) and strength of unalloyed titanium

ASTM B265/UNS	Fe max	O max	N max	C max	H max	Elongation %	Y.S. MPa	UTS MPa
Gr. 1/R50250	0.2	0.18	0.3	0.1	0.015	24.0	170–310	240
Gr. 2/R50400	0.3	0.25	0.3	0.1	0.015	20.0	275–450	345–480
Gr. 3/R50550	0.25	0.3	0.5	0.1	0.015	18.0	360–480	480–700
Gr. 4/R50700	0.5	0.4	0.5	0.1	0.015	15.0	500–530	600–680

2.3.6 *Other Non-ferrous Metals*

The other non-ferrous metals have either no utility in process industries (zinc, silver, tin, etc.) or have limited use under special conditions (tantalum, zirconium, magnesium, cobalt, etc.). Others like silicon, antimony, barium, etc., are used in small quantities as minor or micro-alloying elements. For example, magnesium is used for handling hydrofluoric acid, zirconium for its resistance to carbamate solution, tantalum for its resistance to many highly corrosive solutions.

2.4 Unified Numbering System

Originally alloys were classified independently by producers and users of metals and alloys and societies and trade associations concerned for identification. Ferrous materials in USA were classified by AISI, SAE, and Foundry Societies, etc. With increasing number of alloys being developed, numerous uncoordinated designation systems created a lot of confusion. To overcome this, the Unified Numbering System (UNS) was developed in 1977 [22] jointly by Society of Automotive Engineering (SAE) and ASTM to unify the different systems in vogue over the years. In this system, the metals and alloys are divided into 18 series with designations starting with a letter followed by five numbers. The letter identifies the family of material such as, S for stainless steels, C for copper alloys G for carbon and alloy steels. The following five numbers represent as far as possible the commonly designated user friendly numbers. For example, stainless steel type 316 would be designated as S31600 and carbon steel containing 0.2%C as G10200. Thus, it also provides the uniformity necessary for efficient indexing, record keeping, data storage and retrieval and cross referencing. Some of the important items of UNS system are listed in Table 2.11.

Two important aspects of UNS are that (1) arbitrary assignment of UNS numbers derived unofficially from former members is avoided and proper trade association contacted and (2) a UNS number is not a specification in itself but is only for identifying metals and alloys specified elsewhere. A UNS number therefore should not be considered as a specification as it does not set any requirements but identifies groups of metals and alloys whose controlling limits have been established in specifications published elsewhere. The UNS numbers identify metals and alloys that are generally in regular production and use. According to ASTM E 527, UNS number will not ordinarily be issued for a material that has just been conceived or that is still in only experimental trial.

Table 2.11 Unified alloying number system (UNS)

Ferrous metals and alloys			
D00001–D99999	Specified mechanical properties steels		
F00001–F99999	Cast irons and cast steels		
G0000–G99999	AISI and SAE carbon and alloy steels		
H00001–H99999	AISI H steels		
K00001–K99999	Miscellaneous steels and ferrous alloys		
S00001–S99999	Heat and corrosion resistance stainless steels		
T00001–T99999	Tool steels		
Non-ferrous metals and alloys			
A00001–A99999	Aluminium and aluminium alloys		
L00001–L99999	Low melting metals and alloys		
M00001–M99999	Miscellaneous non-ferrous metals and alloys		
N00001–N99999	Nickel and nickel alloys		
P00001–P99999	Precious metals and alloys		
T00001–T99999	Reactive and refractory metals and alloys		
Examples			
Alloy description	Former designation	System No.	UNS designation No.
Al–1.2Mn	AA	3003	A93006
Copper electrolytic (Tough Pitch)	CDA	110	C11000
Carbon steel (0.2%C)	AISI	1020	G10200
Stainless steel (18Cr–8Ni)	AISI	304	S30400

2.5 Material Specification

2.5.1 Material Standard

It is a document that contains a technical specification or other precise criteria designed to be used consistently as a rule, guideline or definition and thus increase reliability and the effectiveness of many goods and services. Standards are created by bringing together the experience and expertise of all interested parties such as the producers, sellers, buyers, users and regulators of a particular material, product, process or service. Standards are designed for voluntary use and do not impose any regulations. However, laws and regulations may refer to certain standards and make compliance with them mandatory.

2.5.2 Purpose of Specification

In the previous sections, the classification of metallic materials on the basis of composition, e.g. C-steel, C–0.5Mo, 2.25Cr–1.0Mo, 18Cr–8Ni, 90Cu–10Ni,

70Ni–30Cu, etc. has been briefly presented. Composition forms the first step in the selection of material under certain conditions. However, during design or procurement simply mentioning the general composition does not suffice because metals and alloys of the same composition may be required to have different shapes to fulfil some specific purpose, which in turn can depend on purpose, requiring different

1. Manufacturing processes
2. Working and shaping of metals
3. Heat treatment
4. Mechanical properties
5. Workability, ductility and toughness
6. Weldability

To facilitate and ensure the right material having required properties, there is need to have some definite guidelines which can be used by both the users and manufacturers. The need for this has resulted in the development of material standards. Almost all countries have National Standards and follow the same or internationally well-recognized standards for metallic materials and codes like ASTM, ASME and API, of USA. Other important standards such as BS of U.K., DIN of Germany, JIS of Japan and GOST of Russia. International Standard Organization (ISO) and European standards (EN) are also slowly getting accepted. Presently all EU nations have adopted the EN Standard.

For familiarity with original designations and trade names these, instead of UNS numbers, have been mostly used in this book. Readers can get the equivalent UNS number by referring to relevant ASTM/ASME standards.

2.5.3 Preparation of Standards

Preparation for standards involves various steps, such as (a) repeatability of composition and property data submitted by the manufacturer (b) existence of any standards of similar material in other accepted standards (c) and extensive trial and its feedback from fabricators, designers and actual users. Standards do not include products having company trade names but only requirements of a particular material, which any manufacturer is free to produce and market under the relevant specifications. All data submitted/collected are reviewed by a panel of experts and, if the result is found to be satisfactory, the standard is prepared and issued. Some of the organizations bring out an interim specification and make it a permanent one only after the performance is found to be satisfactory. If not, the standard is either withdrawn or modified.

When a new alloy is developed, the manufacturers are required to submit room, low or high temperature properties, depending on the proposed service, welding procedure and weldability, feedback on field performance and other necessary

details. Once the committee is convinced that the material will meet the requirements of safe pressurized components, then only it is accepted. ASME first publishes these as Code Cases and then subsequently issued as standard. It may be mentioned that such standards exist not only for metals and alloys but also for all products, including various testing and analytical procedures.

2.5.3.1 Broad Coverage Under Specifications

Standards are prepared with a view to specifying minimum requirements for the material to be certified as usable. It is natural that the specification cannot include special requirements under all types of uses. For example, all pressure vessel quality carbon steels can be used up to sub-zero temperatures of −29 °C as per ASME. For use at still lower temperatures, additional requirement of impact test is included only in those specifications of carbon steels, where the design/operating temperatures are in the sub-zero range of −29 to −46 °C. In addition, there are some service-related specific requirements, which are not covered in specifications. For example, many ferrous and non-ferrous metals and alloys used in sour service (in oil and gas production/refineries) fail if the composition, strength and or hardness are not controlled within required limits. In such cases, it is the responsibility of the users to specify these, where necessary, as an additional requirement.

For metallic material of interest to the process industry, separate specifications cover the different forms in which the material of the same group, such as, low and medium alloy Cr–Mo steel, stainless steels, etc., are produced. These are

- Plates
- Tubes/Pipes
- Forgings
- Casting, etc.

In addition, some specifications are also made for specific services. For example, there are separate specifications for superheater tubes, high temperature castings, steel plates for use at medium and low temperatures, and so on. It may be mentioned that, unless specially required, the standards give only room temperature mechanical properties, which form the basis for both production and acceptance of a material.

Some of the important contents of material specifications are:

Shaping Process

The metals and alloys come in various forms like plates, pipe, tube, wire, valve, etc. The methods used are rolling, extrusion, drawing, forgoing, casting, etc. While composition may be the same, properties may vary depending on the process need. Thus for each of these processes there are different specifications.

Manufacturing Process

The material properties will also vary with the presence of small amounts of additional elements, which may be deliberately added or present as impurities. The

various grades of carbon and low alloy ferritic steel can be produced in rimmed, semi-killed and killed conditions which form part of a specification. Each of these have advantages and disadvantage and the user has to decide under what condition the material will meet his requirements.

Chemical Composition

Any metal or alloy does not have a fixed composition because it is never possible to ensure the same for all the heats (molten metal/alloy) during manufacturing. In other words, there will always be some range within which different elements can vary without affecting the basic characteristic of the alloy. In addition, there is likely to be other elements, either added or present as impurities. For example, in any iron base alloys there is presence of manganese and silicon, which are to be added during production. On the other hand, sulphur and phosphorous are always present as impurities. Thus it is necessary that the composition remains within limits to be designated as a particular metal or alloy. Normally the maximum content of each element is specified, except in some cases where the range is mentioned.

Mechanical Properties

Mechanical properties like, strength, elongations, toughness, etc., are very important parameters to judge the suitability of an alloy for a particular service. Again the mechanical properties will depend on heat treatment to which the material is subjected. So the specification also states the heat treatments to be used. For example, the properties of carbon steel will vary with heat treatments like annealing or normalizing and tempering. Thus heat treatment becomes an important step for both manufacturer and users. For example, the user can ask for the product to be provided in normalized and tempered condition to have optimum properties. On the other hand, the manufacturer can attain the desired properties by adjusting the composition (mainly carbon and manganese) and heat treatment.

Specification gives the minimum mechanical properties like UTS, Y.S (0.2% Proof stress), % elongation, and reduction in area (% RA). The minimum value is given because while manufacturing one can never attain repeatedly the some preset fixed properties. So within a reasonable range, changes in mechanical properties, as in case of chemical analysis, are permitted. If the user asks for say carbon steel plates of Gr. 60 (min UTS of 410 MPa (60 ksi)), the manufacturer guarantees that it would meet the minimum requirement of all properties specified. However, the actual properties of plates supplied may be more and vary from plate to plate but in no case it will be less than the minimum specified values.

Quality

The quality of the finished material is also important. Presence of inclusions or lamination will have an adverse effect on performance. In case of cladding, only limited amount of disbonded area can be permitted to avoid in-service failure. Similarly, dimensional variations of any product or component should be within limits. For example, tolerance limits in plate thickness and size, inner diameter and outer diameter of tubes/pipes, flanges, rods, etc., are to be set. All these

requirements are covered under specification. Thus in the use of material, it is always essential to procure the material based on recognized specifications along with any requirements specially required for a particular service.

2.5.4 Dual Certification

Presently available in market are stainless steel products which have dual or multiple certifications, often involving both standard and low carbon variants of the grade being certified together. Dual or multiple certifications means the issue of two separate inspection certificate for the same inspected/tested or delivered batch of steel. Since 1980s, it has become a practice and acceptable by stainless steel supplier to provide dual certificate for the same batch of steel. According to the British Steel Association, [23, 24] to reduce inventory the suppliers certify together if the chemical composition and mechanical properties match the grades, such as, 304/304L or 316/316L or 304/304H. Full compliance with all the requirements of the first (primary) standard is assured and for the others only the cast chemical composition and room temperature mechanical properties of the products are certified, Dual certification can be used for other materials also provided they meet all the requirements of the identified material specification and grade [25]. For example, steel plates of SA-516 come in five grades, that is, 55, 60, 65 and 70 with composition and mechanical properties (tensile and yield stress) as given in Table 2.12.

If we examine the table above, we find that a material with maximum carbon of 0.18%, manganese content of 0.9%, having a tensile strength of 476 MPa (70 ksi) and a yield strength of 239 MPa (35 ksi) will satisfy for all four grades of SA-516. In that case, it can be dual stamped for all four grades provided it also meets other requirements stipulated in the specification. The designer can therefore consider its use for any of the four grades.

Once the material is selected and the specification decided, the equipment is to be designed and fabricated using applicable Codes. Codes are systematically arranged comprehensive collection of laws or procedure to attain desired objective of safety. However, unlike specifications, Codes have got statutory status binding on parties concerned.

Table 2.12 Chemical and mechanical properties of A-516 plate with respect to different grades

Requirement	Gr. 55	Gr. 60	Gr. 65	Gr. 70
Carbon max— $\leq$ ½ in.	0.18%	0.21%	0.24%	0.27%
Manganese— $\leq$ ½ in.	0.60–0.90%	0.60–0.90%	0.85–1.20%	0.85–1.20%
Tensile strength—ksi	55–75	60–80	65–85	70–90
Yield strength, min—ksi	30	32	35	38

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Chapter 3
Production and Working of Metals and Alloys

Abstract Metals are produced from ores that exist in nature mostly as oxides or sulphides. Steel has the largest use of any metal and is extracted from iron ore. Initially liquid iron extracted from ore in blast furnace contains substantial amounts of C, Si, Mn, S and P which is further purified by blowing with oxygen to reduce the C, Mn, S and P content within specified levels and cast into ingots or used for producing semi-finished shapes directly from molten steel by continuous casting. Advanced processes are also used to meet the demand of clean steel containing low sulphur, phosphorus, inclusion and dissolved gases. Steel thus produced is converted into blooms, slabs and billets and these semi-finished shapes are further worked to get the desired products. The chapter includes broad outline of production of steel from iron ore and various forming techniques used like rolling, forging, extrusion along with the production of seamless and welded tubular products. Also included is the process of cladding higher strength cheaper carbon or low alloy steels with a comparatively thinner layer of corrosion-resistant alloy using the techniques like sheet lining, hot rolling, weld cladding and explosion cladding. There are some equipments like pump, valves, etc., of intricate shape alloys, which are not amenable to deformation, are produced by casting. Activities like cutting and bending required for fabrication of different equipment have been described.

Keywords Steel making · Rolling · Forging · Pipe making · Cladding · Casting

3.1 Metal Production

Metals exist in nature as simple or complex oxides (iron, aluminium, manganese, chromium, titanium) or sulphides (copper, zinc, lead, nickel). Further, many of the ores contain a number of useful metals and it is difficult to extract them directly. In such cases, more than one route is to be used for winning different metals.

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Low metal containing ores are first upgraded in metal content by using ore beneficiation processes. Jigging, gravity separation, froth floatation and various other techniques are used depending on the metal and nature of the ore. The main objective is to separate unwanted mineral components from the useful ones using mainly differences in their physical properties, e.g. specific gravity, magnetic properties, surface tension, etc. For this purpose, ores are crushed and subjected to grinding. Where necessary, the crushing and grinding are followed by size grading (by using screens and sieves) depending on the end requirement. Even where beneficiation is not involved, the ore mined in big size lumps are to be crushed to smaller size for further processing. The prepared ores are used for extraction of metals. Primarily, there are two routes for production of metals from ores, i.e. pyro-metallurgical and electrometallurgical. In some cases, combination of the two is used. In pyro-metallurgical process, the oxides are reduced to produce the metal (iron). In case of sulphide ores, the sulphur is oxidized to produce the metal or their oxides. The oxides, the turn, are leached in suitable solvents and the metal produced by electrolysis of aqueous solution as in case of zinc, tin, copper, etc. Metals like aluminium, magnesium, sodium, etc., which get easily oxidized and hydrolysed, are produced by electrolysis of oxides dissolved in fused salts.

3.1.1 Metal Purification

Ores in addition to compound of metal to be extracted contain other minerals from earth crust (mostly simple or complex compounds of silicon, aluminium, manganese, etc.). In commercial processes most of the metal produced, especially those by pyro-metallurgical processes, contain lot of impurities which also get partly reduced into respective metals. For example, the first stage in the production of iron is pig iron, which in addition to about 3–5% carbon (used as reducing agent) contains a good amount of silicon, manganese, sulphur and phosphorus, the compounds of which also get reduced along with iron. These impurities therefore are to be removed to produce steel. Similarly copper produced by pyro-metallurgical process is to be further purified by electrolysis to remove unwanted elements and recover metal like silver which is present in small quantities. On the other hand, aluminium produced by fused electrolysis contains small amounts of impurities like Mn, Mg, Si, Fe, etc. While for many engineering applications, these small amounts are not considered deleterious, for special applications further purification is carried out.

Being the most important engineering material, the production of iron and steel has been discussed in detail.

3.2 Iron and Steel Making

3.2.1 Pig Iron

Large demand for steel as a major engineering metal could be met only after the blast furnace process for the production of pig iron was introduced.

The blast furnace is a tall circular structure having a conical shape and consists essentially of hearth, bosh and stack (Fig. 3.1) [1]. The prepared ore along with coke and limestone, in measured proportion, is charged continuously from the top while hot air is blown through tuyeres from the bottom. The air burns the coke and the hot gas consisting of CO, CO_2 and N travel upwards, heating the solid charge moving downwards. As the charge gets heated, the iron oxide in the ore gets reduced by carbon and carbon monoxide and finally the iron melts when it reaches the bottom section where the temperature is highest.

The reduction takes place by the following reactions:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2 \tag{3.2.1}$$

$$2Fe_2O_3 + 3C = 4Fe + 3CO_2 \tag{3.2.2}$$

The SiO_2, MnO, P_2O_5 and sulphur compounds, present in iron ore, coal and limestone also get partly reduced to respective metals or elements. The remaining oxides in this zone along with sulphur (from coke) are bound by lime (CaO) to

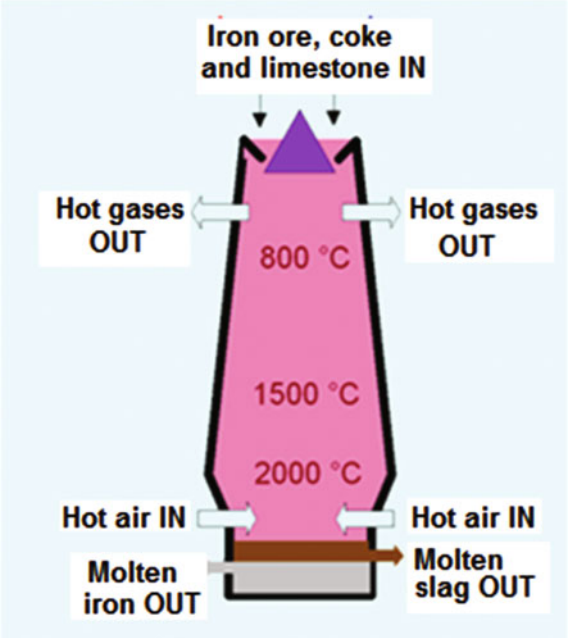


Fig. 3.1 Schematic cross section of a blast furnace [1]

produce a molten mixture of oxides, known as *slag*. At high temperature, the molten iron dissolves carbon (from coke) and other elements get reduced in the blast furnace. Thus the iron produced in the blast furnace is not pure iron but contains high amounts of carbon (3.5–4.5%), silicon (0.5–1.2%), manganese (0.4–1.0%), phosphorous (0.15% max) and sulphur (0.04% max) and this is known as *pig iron*. Pig iron is used to produce either cast iron or steel.

3.2.2 Conventional Steel Making

Production of steel from the point of view of chemical reaction is oxidation which is opposite to production of pig iron which is basically a reducing reaction. The process consists of controlled oxidation of excess silicon, carbon, manganese and phosphorous in pig iron to near the level desired in steel. Here also, the oxidized impurities are bound by CaO to form a low melting low density slag which floats over the molten steel. The production techniques for steel have evolved over time, starting with puddle iron to present-day processes. Old steel specifications mention acid and basic Bessemer processes and open hearth process. Recent specifications commonly mention only two, basic oxygen process (BOP) and electric arc process.

3.2.2.1 Basic Oxygen Process (BOP)

BOP is a pneumatic process of making steel which was originally known as L.D. process, referring to Lanzand Donawitz in Austria where the first plant was set up in 1957 [2]. Basic construction of a BOP converter is shown in Fig. 3.2. The charge for BOP generally consists of 70–80% molten metal from blast furnace and balance scrap. These are charged into a vertical vessel, known as the basic oxygen furnace (BOF), and blown with 99.5% pure oxygen at very high velocities to oxidize the carbon, silicon, manganese and phosphorus present in pig iron. In the process some iron is also oxidized. Because of using high purity oxygen, direct contact with molten metal takes place, which in turn increases the reaction rates and temperature rise is fast and therefore the reactions are completed in very short time compared to earlier processes. Calcium oxide is added to maintain the required basicity and fluidity of slag. The final composition of steel produced is controlled by the time of blowing. From the appearance of burning flame, the operators get an indication of the molten steel. The time for steel making by these processes may vary from 20 to 30 min for a charge of 50–350 tonnes. In modified BOP, inert gas like argon is also blown through bottom mounted tuyeres to improve mixing in the metal bath. The molten steel at 1600–1650 °C is tapped and further processed to fine-tune the composition before casting.

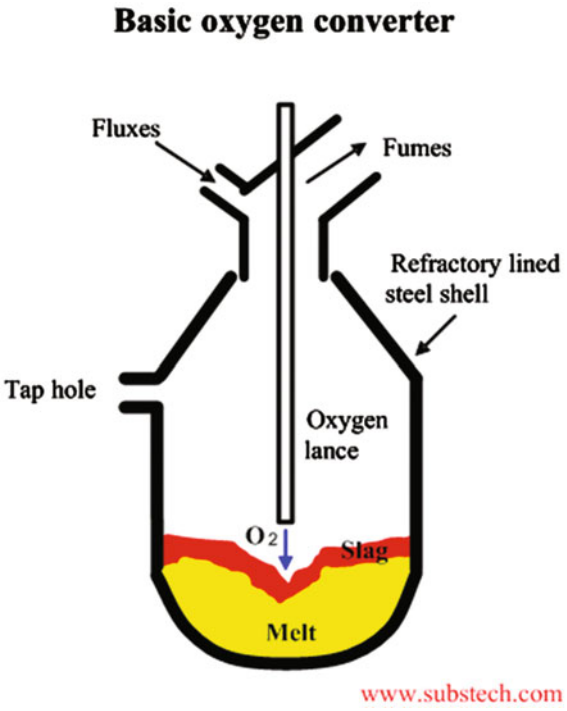


Fig. 3.2 Schematic view of basic oxygen converter

3.2.2.2 Electric Arc Furnace Steel Making

For steel making/melting, electrical energy is also used. Two methods used are arc and induction melting. Arc furnace generates heat by striking an arc between the metal and graphite electrodes. In case of induction heating, on the other hand, high-frequency AC is used. Production of steel in electric arc furnace is commonly used where production capacity is low, special alloy steels are to be made and where the raw material is primarily scrap. Directly reduced sponge iron is also further processed in electric furnace. Thus, for foundries, mini steel plants, alloy steels, stainless steels and high quality steel producing units electric melting are extensively used. This method is also preferred in production of non-ferrous alloys.

In electric arc furnace, the heating is done by the striking arc on metal through three graphite electrodes inserted into the furnace through the top roof. First, scrap is melted and then molten pig iron is added along with CaO. Purification is achieved by blowing (lancing) air or air + oxygen. The molten steel is tapped after the required composition is attained. Induction furnace is used primarily for melting the different constituents of an alloy together without any purification step.

3.2.2.3 Deoxidation and Ladle Treatment of Steel

In all steel making processes, the final composition is adjusted after the molten steel is poured into the ladle from the furnace. The most important step is to reduce the oxygen content of steel, which at the time of tapping may contain 400–800 ppm of oxygen. The amount of oxygen primarily depends on the final carbon content of the bath and increases with decrease in carbon content. The importance of deoxidation lies in the fact that the carbon oxygen reaction, producing CO gas, continues even when the hot metal is cast into ingots. Depending on the amount of reaction occurring in the ingot, the product is classified broadly as *rimmed, semiskilled and killed*. The major difference between these various types of steels is in the amount of gas trapped and distribution of resulting blow holes in the solidified ingots, the rimmed steel having the maximum concentration of blow holes and killed steel the least (Fig. 3.3). Killed steel has also a more homogeneous structure and has lesser amounts of inclusions. Pressure vessel steel is either of semi-killed or killed grades. The degree of suppression of gas evolution is controlled by adding deoxidizers to molten steel during casting. Manganese is added as a deoxidizer but its action is mild. Silicon, titanium and aluminium are stronger deoxidizers and their effectiveness at atmospheric pressure (Fig. 3.4) increases in the order stated above. This figure also shows that the reactions are pressure dependent and if the pressure is lowered to say 0.1 atmosphere, oxygen would preferably react with carbon than silicon. On the other hand at 0.01 ATM, carbon becomes stronger deoxidizer than titanium or aluminium. This property forms the basis of vacuum deoxidation. It may be mentioned that deoxidizers used in practice are manganese, silicon and aluminium. The killed steel is generally produced by using Mn/Si/Al as deoxidant, semi-killed by Mn/Si and rimmed by Mn or Mn/Si. Al_2O_3 formed as a result remains as hard particles in solidified steel, and therefore minimum amount of aluminium is added at the end after major amount of oxygen is removed with silicon and manganese.

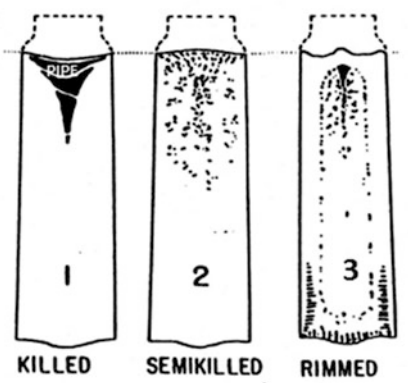


Fig. 3.3 Cross section of ingots showing distribution of blow holes in rimmed, semi-killed and killed steel

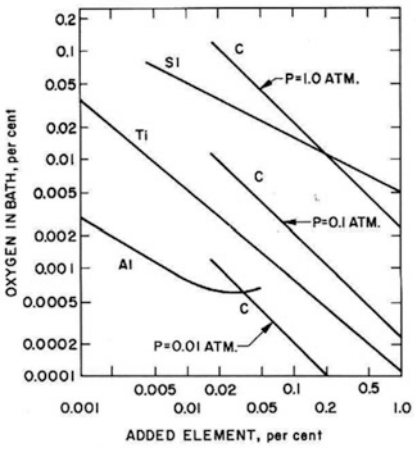


Fig. 3.4 Equilibrium relationships between total oxygen and deoxidizing elements

Molten metal occupies higher volume than solid and, therefore on solidification, there is shrinkage in the ingot. While in rimmed and to a great extent in semi-killed steel, this decrease in volume is compensated by blow holes, the same is not the case with fully killed steel. Thus is killed steel, the top section which cools last, a depression occurs which is known as *pipe*. The surface of pipe is exposed to air and therefore gets oxidized and the two surfaces cannot be bonded during rolling (hot or cold). In killed ingots, therefore, this pipe section is removed prior to further working. Thus the tonnage of finished metal produced from killed steel is 20–25% less than the amount cast thus lowering the productivity.

3.2.3 Modern Steel Making by Ladle Treatment

There is greater emphasis today on producing quality steel with low sulphur and phosphorous, low inclusion level and eliminating dissolved gases like hydrogen, nitrogen and oxygen. For better control on these parameters, various processes have been developed, which are carried out after the steel is poured into the ladle. Argon oxygen decarburization (AOD), vacuum treatment, etc., are some of the processes commercially used. These processes also form part of the present day production of stainless steels.

3.2.3.1 Desulfurization

Sulphur is one of the most undesirable impurities in steel. In normal steel making processes, sulphur content is specified to be in the range of 0.03–0.04%. Sulphur is present as MnS or (FeMn)S, mostly as stringers. In addition, non-metallic inclusions steels present make the steel ‘dirty’. These are likely to adversely affect

mechanical properties and introduce defects which can lead to failure when used in hydrogen and sour service, centrifugal and reciprocal compressor shafts, etc. Use of clean steel with improved tensile ductility, Charpy impact and fracture toughness, etc., has a large role to play in many of the modern industries, where service is critical. In this connection low sulphur, shape control calcium treated steels play an important role. Use of calcium treatment started in early 1970s after it was recognized that calcium has limited solubility in steel [3]. The basic approach in making these steels is mixing of Al killed liquid steel with calcium by feeding a cored wire filled with $CaSi_2$ into the molten metal at the bottom of ladle as boiling point of calcium is below that of steel. Simultaneously, argon purging is carried out for proper mixing and removal of any residual gases in the molten metal. By ladle desulphurization, it is possible to reduce the sulphur level below 0.005% (targeted to as low as 0.001%) and control the shape (spheroidal), size and distribution of sulphide and other inclusions. Low sulphur clean steel is commonly used for plates for pressure vessels, off shore platform, plates and skelp for line pipes, large diameter shafts, etc. Such a treatment forms integral part of modern clean steel technology and all reputed steel makers are fully equipped for this.

3.2.3.2 Ladle Decarburization

In production of stainless steel, carbon content is to be reduced to a very low level, i.e. below 0.08%. While this is possible by using stainless steel scrap (which already has low carbon), it is not so with the more economical route of using charge chrome. Use of conventional process results in considerable loss of chromium in the slag but this is avoided by using argon oxygen decarburization process. Here, argon and oxygen in the ratio of 1:3 (in initial stags) and 1:1 (in finishing stage) are blown through molten alloy to which fluxes are added. Sulphur, oxygen and nitrogen are also reduced to low level. Argon purging is also used quite extensively with the main objective to homogenize the melt temperature and composition. It assists in floatation of deoxidation products and facilitates alloying element dissolution.

3.2.3.3 Ladle Degassing

Ladle degassing is done by using two basic techniques, i.e. inert gas flushing and vacuum degassing. There are various techniques available for vacuum degassing and by this process oxygen (via CO formation), hydrogen and nitrogen are removed from steel.

3.2.4 Summary

Once the steel is produced from pig iron, subsequent treatments are carried out in the ladle and the treatment followed depends on objectives to be achieved. A large

percentage of commonly used steel in engineering and process industries is still manufactured by conventional methods but with greater degree of control to get better quality products, compared to that practiced two or three decades back. The major objective of the advanced techniques is to produce cleaner, more homogeneous steel with low sulphur, desired inclusion morphology and better through thickness mechanical properties, especially where thicknesses are high and operating conditions are severe.

3.3 Ingot Casting and Forming

3.3.1 Conventional Casting

Once the desired molten product (both ferrous and non-ferrous) is produced, the same is poured from the ladles in moulds to produce blooms, slabs or billets depending on size of the melt and desired finished products. Ingot mould has a tapering shape (with the smaller cross section at top), with the inner walls being plain, corrugated or fluted. For killed steel, inverted moulds with hot top are also used. The moulds are filled either by top or bottom pouring, the latter for ingots of smaller cross section. The slabs, on the other hand, have a rectangular cross section and used for flat products of thinner cross sections.

The liquid in the mould solidifies from sides towards the centre and from bottom to top. The top is the last to solidify. The structure of the solidified metal varies along the cross section. The metal immediately in contact with the mould wall has more or less uniform randomly oriented grain structure, but subsequently because of slow cooling large columnar (elongated) grains consisting of dendrites is formed, which is inhomogeneous and has comparatively poor workability. Many impurities get segregated in the central areas, which are last to solidify. For the production of various shapes, the cast ingots are to be reheated first to break the cast structure and then rolled to semi-finished shapes. The shape and size of semi-finished products depend on the shaping of final products like plate, rod, skelp, structural, forging, etc., it will be used for. The working on the ingots and semi-finished shapes is carried out at high temperatures in number of stages which requires repeated heating in between different stages. Because of number of heating steps involved, the cost of production goes up.

3.3.2 Continuous Casting

To reduce the cost of production, continuous casting techniques were developed so that semi-finished shapes could be directly produced form molten metal. In short, the process consists of directly pouring the molten metal at top end of water cooled

mould and the solidified metal continuously withdrawn from the bottom through drive rolls. Cast sections are straightened and then cut to the desired length by torches or shears. The arrangement is shown in Fig. 3.5. As the cooling is rapid and the thickness is comparatively less, more uniform structure is produced with less harmful dendrite structure. If induction stirring located around the mould is used, the harmful segregation is further reduced.

The advantages of continuous casting over ingot casting are (i) increase yield due to reduction in scrap generation, and losses associated with pouring operation and oxidation during repeated ingot heating (ii) better quality or products having greater uniformity in composition, less centre segregation along the cross section and superior surface finish (iii) energy saving by reduction in number of reheating, power consumption in rolling mills, etc. (iv) reduced capital and operation costs and (v) reduction in pollution.

3.4 Shaping of Metal and Alloys

There are two methods of forming that is casting and working. In casting we get the finish product directly, in case of working the material has to pass through various stages for the same.

3.4.1 Casting

In case of casting, the molten metal is poured directly into a sand mould of the final shape of the casting. On cooling, the mould is broken and the casting is cleaned and given heat treatment, where required. The only job to be done is machining of flanges, valve seat, etc., required for a particular item. As the material solidifies directly from liquid and no working is involved, all castings have cast dendritic structure compared to worked material which shows uniform structure (Fig. 3.6). This structural characteristic is one of the reasons for inferior mechanical properties compared to worked item of the same composition.

3.4.1.1 Advantages and Disadvantages of Casting

Casting has the following advantages:

- Produces the final component from molten metal in one step.
- Precision and complicated shapes can be more easily produced by casting.
- High production rate can be obtained in low melting point metals and alloys, e.g. aluminium and zinc using pressure die casting.

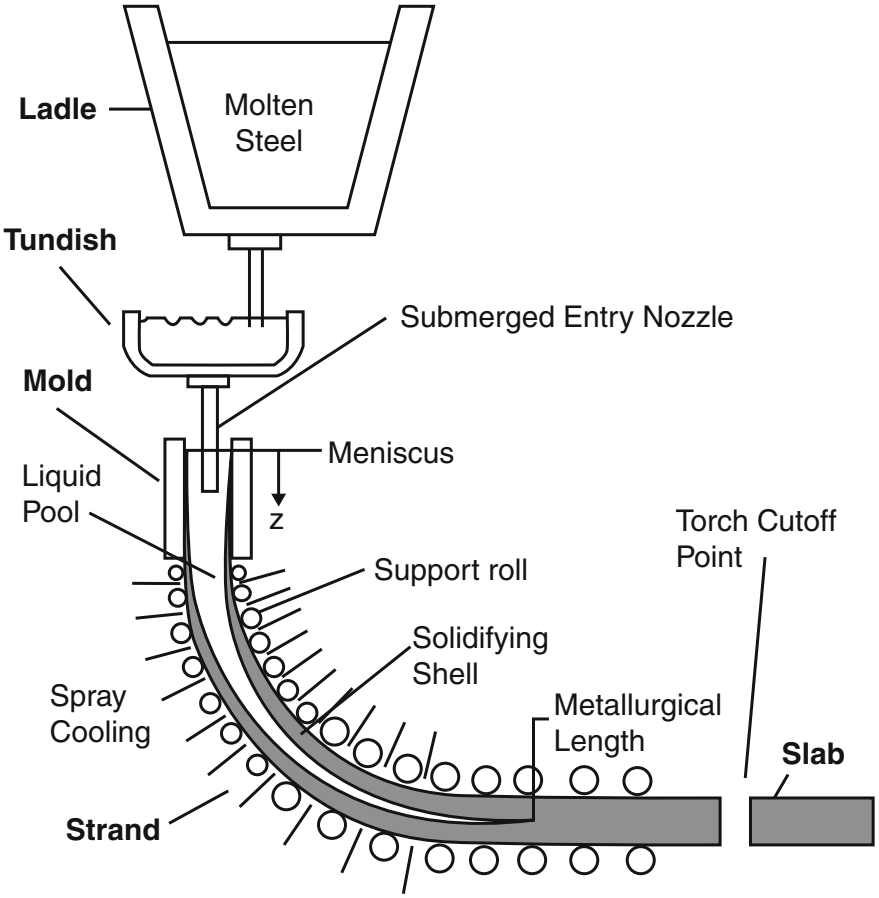


Fig. 3.5 Schematic sketch of continuous casting of steel

- Nonworkable alloys, e.g. cast iron can be produced only by casting (except powder metallurgy).
- Cast structures have generally higher creep strength compared to the wrought alloy of similar composition.

Disadvantages of the casting are:

- Cannot normally be produced in thinner sections.
- Workability/ductility are lower.
- There are size limitations.
- Required close control during production to avoid internal defects like blow holes shrinkage cavities, etc.
- Normally production rates are low.

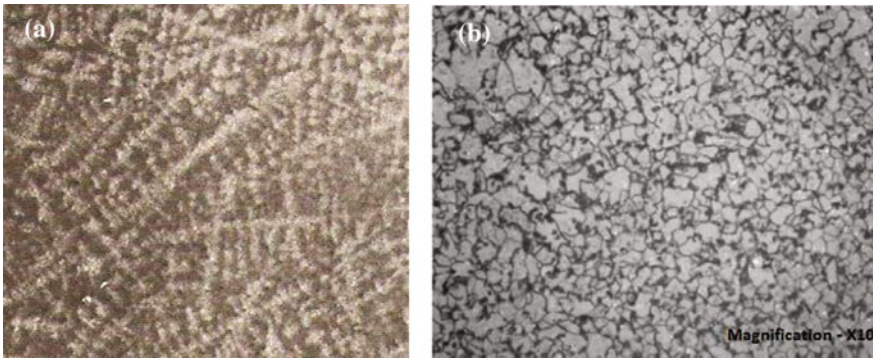


Fig. 3.6 **a** Cast steel with dendritic structure. **b** A106 grade pipe showing ferrite and pearlite grains

– Liable to segregation with respect to alloying elements, resulting in loss in properties, especially resistance to corrosion.

3.4.1.2 Centrifugal Casting

There are various casting processes, e.g. ordinary sand moulding, shell moulding, die casting (gravity and pressure) and spun casting (horizontal or vertical). Centrifugal casting is used to produce hollow cylindrical products like pipe, bearings, bushing, nozzles, etc. Hydrogen reformer and gas/naphtha cracker tubes, etc. are produced by centrifugal casting.

In this process, molten metal is poured into a rotating mould of the diameter of the desired product. The moulds made of either steel or cast iron, are normally placed horizontally. The process (Fig. 3.7) can be described to broadly consist of the following steps:

- Mould Preparation—Walls are coated with refractory ceramic coating to avoid sticking of the component with the mould.
- Pouring—The step consists of rotating (300–3000 rpm) and pouring the metal directly into the mould. As the mould fills the material under the influence of centrifugal force moves towards the wall of the mould.
- Cooling—The mould continues to spin after the requisite amount of material has been poured and the material cooling takes place from the mould wall inwards.
- Removal of Casting—After cooling the rotation is stopped and casting removed.
- Finishing—Casting is then machined on inner surface to remove inclusions which float upward and segregate at the outer surface and also any solidification shrinkage.

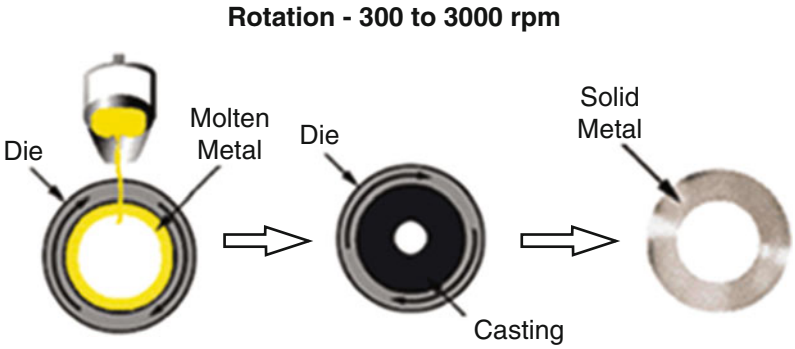


Fig. 3.7 Centrifugal casting process

3.4.2 Shaping by Mechanical Working

The cast ingots, billets, slabs, etc., form the starting material for the production of plates, rods, pipes, sheets, angles, beams, etc., by mechanical working. The working of the metal, which involves deformation, is performed either at high or room temperatures (actually above or below recrystallization temperature) and the two processes are termed as *hot working* and *cold working*, respectively. The route chosen amongst others depends on the workability of the metal and the desired surface finish.

3.4.2.1 Workability

Softer material requires less pressure (so, less power) than a harder one for the same degree of deformation. Similarly, a coarse-grained and inhomogeneous material has higher susceptibility to cracking while working than a homogeneous and fine-grained material. It is easier to work on a metal at high temperature as it can take higher deformation and the deformed grains easily revert back to the normal homogenous structure through recrystallization making further deformation easier. The working temperature here should be above the recrystallization temperature of the particular material. In case of cold working, on the other hand, the deformed grains do not recrystallize, resulting in increase in hardness, making further deformation increasingly more and more difficult. This phenomenon is termed as *work hardening*. A stage reaches where any further deformation results in cracking. If a material has low susceptibility to work hardening then a greater degree of cold working can be performed on it. Metals and alloys like gold and silver are very soft and have very low work hardening characteristics and, therefore, can be cold worked to a high degree to get thin foils and wires. Ferrous materials like carbon steel, alloy steels and stainless steels, on the other hand, have low ductility, are liable to rapid work hardening and, therefore, require primarily hot working. Further in case of carbon and alloy steels, the hot working temperature is to be

maintained in austenite range. Cold working, if necessary is done only to a small extent in the final stages. Low carbon steel used for car bodies, cans and roofing, is much softer and, therefore, can be subjected to cold working to a greater extent for the production of thin gauge sheets.

Finally, there are metals and alloys having working properties, in between these two groups. In addition to hot working, these can be cold worked to a large extent, with intermediate annealing to restore ductility. Such materials are copper and its alloys, aluminium and its alloys and others.

3.4.2.2 Surface Finish

The final finish required is also an important consideration. Cold working gives a smooth and bright surface finish than hot working. Where surface finish is a requirement, hot rolled products are given final finish by cold working.

3.4.3 Types of Forming Processes

The main forming/working processes used for the finished products are:

Rolling: Carried out in two-high, three-high and four-high mills for plate, sheet, tube, rod, structural sections, etc.
Extrusion: Hot and cold pressing through dies for rods and sections and piercing for tubes.
Forging: Carried out with presses, hammers, dies, etc. for gears, shafts, bends and fittings.
Drawing: Carried out on drawn benches, drawing machine for tube, rod, wire.

3.4.3.1 Rolling

Rolling is primarily a squeezing process, where flat rolls are used for plates and sheets and grooved rolls for rods and sections. The equipment consists of two, three or four rolls, placed one over the other and moving in opposite directions. Of the two rolls through which the plate passes, one is the driving roll and other the idle roll. In four-high mills, the top and bottom-most rolls are backup rolls resulting in higher reduction with greater tolerance. Ferrous materials are normally hot rolled. As only limited amount of reduction in thickness is possible during each pass, the total number of passes required is many. Initial rolling temperature of about 1100–1150 °C therefore drops down, requiring several reheating. During hot rolling, continuous deformation and recrystallization of grains take place as shown in Fig. 3.8. The metal elongates in rolling direction only, except for slight side spreads. Plates and sheets are therefore rolled in two directions at right angles during the initial stages to minimize

the degree of variations in properties along longitudinal and transverse directions. In spite of this, differences remain especially in impact strength. Impact test data of transverse samples therefore have greater weightage. For production of sections and rods, the rolls are not flat but have required variations in contour for different stages of rolling. By proper control of range of temperature of rolling, finished steels having fine or coarse grains can be produced.

Hot rolled products have thick oxide scale and the surface is not smooth which normally do not have any effect on their use for most of the purposes. However, in some cases good surface finish and uniformity in thickness are required. Cold rolling is sometimes done in the final stages of production to get a reasonably good finish. With increasing demand for good quality thin steel sheet, production of cold rolled products has increased many folds. Nowadays high speed cold rolling mills are used to meet high production rate and good tolerance in thickness and surface finish. These sheets are used primarily for roofing, panels, automobile bodies, etc. Normal hot rolling cannot be used to produce thin sheets. Earlier, pack rolling was extensively used for production of thin gauge sheets. This consisted of putting a number of sheets one over another to have sufficient thickness and roll the whole pack as a single piece. To avoid the sheets sticking/hot welded to each other, phosphorous content of these steels were kept high. Phosphorous oxide layer prevented sticking of the sheets to each other.

Controlled rolling can be used to achieve higher strength (both UTS and YS) in steels containing lower carbon content. These are special working process falling under the general category of *thermomechanical controlled process* (TMCP). The process consists of producing refined grains by a series of high temperature rolling in the alpha + gamma stability range combined with a heat treatment cycle. In case of steels containing micro-alloying elements, additional advantage is taken of formation of dispersed phases. The objective is also to get higher strength with low carbon content having improved weldability plus good toughness. These steels

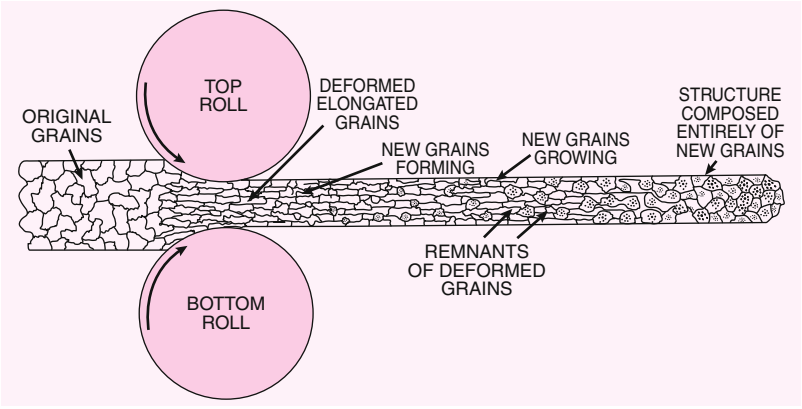


Fig. 3.8 Change in grain structure during hot rolling

cannot, however, be hot formed later to avoid structural changes which adversely affect the strength and toughness. High alloy steels are also amenable to TMCP, the most known alloy being *maraging steel*.

3.4.3.2 Extrusion

Extrusion is the process by which long straight metal parts of different cross sections can be produced. Extrusion is done by squeezing metal in a closed cavity through a tool, known as *die*, using either a mechanical or hydraulic press of very high capacity and can be likened to the squeezing of tooth paste from a tube. The shape of the extruded article is similar to the cross section of opening of the die. Both solid and hollow sections can be produced. For hollow items, the metal flows at the outlet of die over a mandrel having the cross section of the hollow part.

The billet is the starting stock for the extrusion operation. The billets may be a solid or hollow, commonly cylindrical, and charged lengthwise into the extrusion press container. The actual extrusion process begins when the ram starts applying pressure to the billet within the container. A typical sketch of extrusion press is shown in Fig. 3.9. Depending on ductility the extrusion is done hot or cold.

Cold Extrusion

Cold extrusion is the process done at room temperature or at slightly elevated temperatures (actually below or above the recrystallization temperature). This process is extensively used for most of the softer materials like, lead, tin, magnesium, aluminium and copper alloys. This can also be used in special cases for higher strength materials, subject to designing robust enough tooling that can withstand the stresses created by extrusion and availability of heavy extrusion press. The advantages of cold extrusion are:

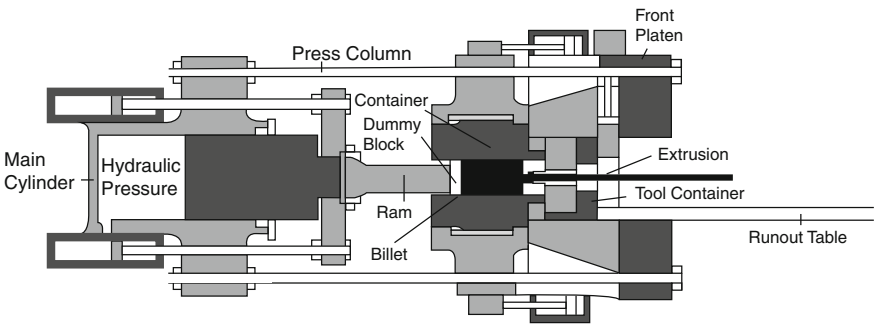


Fig. 3.9 Different parts of an extrusion press

- No oxidation takes place.
- Good mechanical properties are obtained due to severe cold working as long as the temperatures created are below the recrystallization temperature.
- Where necessary, further heat treatment can be carried out to get optimum property.
- Good surface finish is obtained if proper lubricants are used.

Extrusion often minimizes the need for secondary machining, but extruded components are not of the same dimensional accuracy or surface finish as machined parts. However, this process can produce a wide variety of cross section that is hard to produce cost-effectively using other methods.

Hot Extrusion

Hot extrusion, above the recrystallization temperature, is done normally for high strength materials. High temperatures and pressures have detrimental effect on die life, as well as other components, and therefore good lubrication is necessary. Oil and graphite work at lower temperatures, whereas at higher temperatures glass powder is used. Hot extrusion is used for copper alloys, steels, etc. Extrusion produces compressive and shear forces in the stock. No tensile stress is produced, which makes high deformation possible without tearing the metal. The cavity in which the raw material is contained is lined with a wear resistant material to withstand the high radial loads that are created when the material is pushed through the die.

3.4.3.3 Forging

Forging is one of the most important methods for shaping of metals and alloys. In forging, the deformation to a determined shape is accomplished by application of compressive stress, with the help of press or hammer. There are different methods for forging and some of the important ones are briefly described. Forging refines the grain structure and improves physical properties of the metal and because of restricted flow, also introduces grain flow pattern in the component. With proper design, the grain flow can be oriented in the direction of principal stresses encountered in actual use. Because of directionality, the physical properties (such as strength, ductility and toughness) are much better in a forging than in rolled metal, which has randomly oriented crystals. Further, forgings are consistent from piece to piece, without any of the porosity, voids, inclusions and other defects. Thus, finishing operations such as machining do not expose voids, because there are not any. Some of the important methods are described here.

Closed Die Forging

Close die forging, also known as impression die forging, consists of deforming the metal between two dies that contain a precut profile of the desired part. For this process commonly hammering is used. Carbon and alloy steels, tool steels, stainless steels aluminium and copper alloys and certain titanium alloys, can be produced in an almost limitless variety of 3-D shapes. The weight of forging can vary from a few grammes to 30 tonnes. Forging is done using hydraulic presses, mechanical presses and hammers, with capacities up to 25 tonnes. Steps involved in the process are shown in Fig. 3.10a. Two or more dies containing impressions of the part shape are brought together by pressing until its enlarged size touches the sidewall of die. Then, a small amount of material begins to flow outside the die impression forming flash that is gradually thinned. The forging is normally done hot to ensure good flow of metal inside die. Figure 3.10b shows a forged high performance gear.

Open-Die Forging

In open-die forging, unlike close die forging, the metal is not confined laterally by impression dies during forging as the operation is done between flat-faced dies to get the desired shape to get the desired shape. In a number of cylindrical components, a semicircular die is used in place of flat-faced bottom die. Broad range of shapes like round, square rectangular and hexagonal, etc., can be produced by this method. As regards the size range, open-die forgings are limited only by the size of the starting stock, namely, the largest ingot that can be cast. Practically all forgeable ferrous and non-ferrous alloys can be open-die forged, including some exotic materials like age-hardening super alloys and corrosion-resistant refractory alloys. The method is illustrated in Fig. 3.11. The forging method can be tailored to attain the proper amount of total deformation and optimum grain flow structure, thereby maximizing property enhancement and ultimate performance for a particular application.

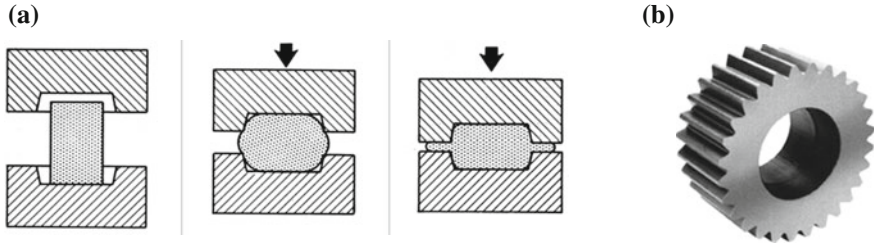


Fig. 3.10 **a** Various steps involved in closed die forging [11]. **b** Open-die forged gear

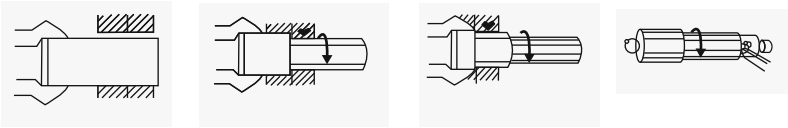


Fig. 3.11 Open-die forging illustrating steps starting from initial stock to final forged machined shaft

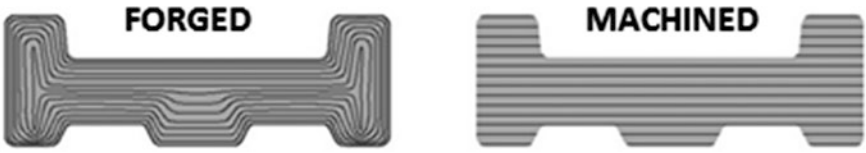


Fig. 3.12 Grain structure of forged and machined parts

During any deformation process there is flow of metal. In case of rolling, the flow is predominantly in direction of rolling. Forging changes size and shape and not the volume and therefore in case of forging the flow of material is confined within a restricted volume, determined by the shape of die. As a result, the flow pattern of grains in case of forging has a fibrous structure and is quite different than in case of rolled product. The difference in flow pattern of forged and rolled product will be quite different as shown in Fig. 3.12. Forged components therefore show better mechanical properties, toughness and impact properties. If we compare the above two with say a cast component, which is not subjected to any working to develop a flow pattern, the preference for service will be in the increasing order of cast, machined and forged component.

Cold Forging

Though most forging is done at high temperatures, cold forging is also performed where the temperature of metals being forged may range from room temperature to several hundred degrees (warm working). The products include various shaft-like components, cup-shaped geometrics, hollow parts with stems and shafts, etc. Materials which have been successfully cold forged are carbon and low alloy steels, stainless steels, selected aluminium alloy, brass and bronze.

Seamless Rolled Ring Forging

Development of ring forging has considerably helped in mass scale production of circular items of different sizes. As regards process industry is concerned, ring-forged thick-walled cylinders have been of particular help in the fabrication of

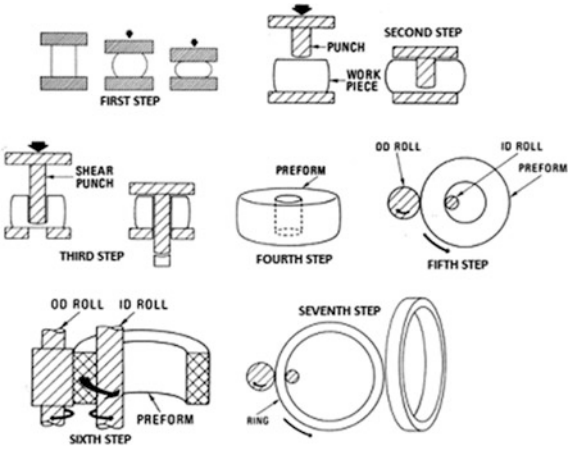


Fig. 3.13 Seven steps involve in ring forging

mono wall high pressure, high temperature reactors and vessels, production of which from thick plates would have required heavy machineries. This has helped in the increasing use of mono wall over layered vessels. The other advantage of ring forged cylinder is decrease in cost of welding as only circumferential welds are required to be made. Seamless rolled ring forging is typically performed by punching a hole in a thick, round piece of metal (creating a donut shape), and then rolling and squeezing (or in some cases, pounding) the donut into a ring. Various steps involved in the production are shown in Fig. 3.13.

Rings forged by the seamless ring rolling process can weigh from less than ½ kg up to 18 tonnes, while the outer diameter (OD) ranges from just a few mm up to 10 m. Heights of rolled rings range from a few mm up to more than 3 m. Depending on the equipment utilized, wall thickness/height ratios of rings typically range from 1:16 up to 16:1, although greater proportions have been achieved with special processing. Because of forging action, the final product has minimum voids and gas pockets, uniform grain size and flow characteristics. These specific characteristics translate into ring forgings having good impact strength and fatigue resistance. Rolled rings can be produced in thousands of different shapes with contours on both the inside and/or outside diameters. A key advantage to contoured rings is a significant reduction in machining operations. High tangential strength and ductility make forged rings well suited for torque and pressure-resistant components, such as gears, engine bearing for aircraft, wheel bearings, couplings, rotor spacers, sealed discs and cases, flanges pressure vessels and valve bodies. Materials that have been successfully ring forged include not only carbon and alloy steels, but also non-ferrous alloys of aluminium, copper, titanium and nickel-based alloys.

3.4.3.4 Manufacture of Pipes and Tubes

In petroleum and petrochemical industry, pipes and tubes are used in large tonnage. Therefore, their manufacturing methods are discussed in brief. The steel pipes are either seamless or longitudinally welded. The latter can be further divided into electric resistance welding (ERW) (present-day practice is to use high frequency instead of resistance heating, HFIW) although *spirally welded* pipe is being increasingly used. Welded pipe is a tubular product made out of flat plates, known as *skelp* that are formed, bent and prepared for welding. The welding can be done by two methods namely, fusion welding and electric resistance welding (ERW).

Fusion Welded Pipe

Longitudinal Weld: The welding, depending on diameter, is done using single or double vee of plate or skelp. For large diameters, double-submerged arc welded (DSAW) pipe is preferred whose longitudinal butt joint is welded in at least two passes, one of which is on the inside of the pipe. For diameters above 36 in. (900 mm) double seam welded pipe is specified. This has two longitudinal seams 180° apart, formed by the submerged arc welded (SAW) process. Finished pipes are normally 40 ft (12 m) and occasionally 60 ft (18 m) in length, depending on the capacity of the pipe mill and the ease of transport of the pipe.

Spiral Welded Pipe

As an alternative process, spiral weld construction allows large diameter pipe to be produced from narrower plates or skelp. Unlike other methods, there is no restriction on width for different diameter pipe as the same width can be used for large or small diameter pipes by changing the angle of twisting of plate followed by welding. A typical spirally welded pipe is shown in Fig. 3.14. This is possible because smaller pipes require greater angles than larger pipes manufactured from the same width coil. The defects that occur in spiral welded pipe are mainly those associated with the SAW weld and are similar in nature to those for longitudinally welded SAW pipe. An additional problem with the early spiral welded pipes was poor dimensional accuracy, particularly out of roundness at the pipe ends. This led to problems of poor fit-up during field girth welding. Spiral line pipe, therefore, gained a poor reputation as a result of these early experiences and considered by many to be suitable for low pressure/lower critical applications. However, the opinion is changing and reputed manufacturers claim modern spiral line pipes to be of quality equivalent to straight seam welded pipe. The joint efficiency of both double vee submerged arc welded longitudinal and spiral welded pipes (100% radiographed), according to ASME B31.3, is also 1.0 [4]. However, API 5L takes joint efficiency as 0.95 for both longitudinal and spiral SAW pipes. Various aspects



Fig. 3.14 Spiral welded pipe sketch

of spiral welded pipe have been studied by TWI, in industry sponsored project and the report is available to the members [5].

Electric Resistance Welded (ERW) Pipe

Originally this type of pipe, which contains a solid phase butt weld, used to be produced using resistance heating to make longitudinal weld, but for better control and consistency, most pipe mills now use high frequency induction heating (HFI), above 100 kHz. However, the product is still often referred to as ERW pipe, for both the processes. The process consists of the starting strip, known as skelp, being passed through a series of rolls to progressively cold bend to the final round shape. After forming, heat is applied to edges to raise the temperature $\sim$1400 °C after which the open tube passes directly into the squeeze roller which applies correct pressure to bring the two edges 'a' and 'b' in contact as shown in Fig. 3.15. The pressure causes the metal to flow against each other at two edges to form a firm joint. The resultant deformation results in metal to extrude on both inside and outside of the pipe at the point of the weld, called *flash*. The flash on OD and sometimes on ID, are machined off. It may be mentioned that there is no fusion involved at the joint of ERW tube is like hot pressure welding.

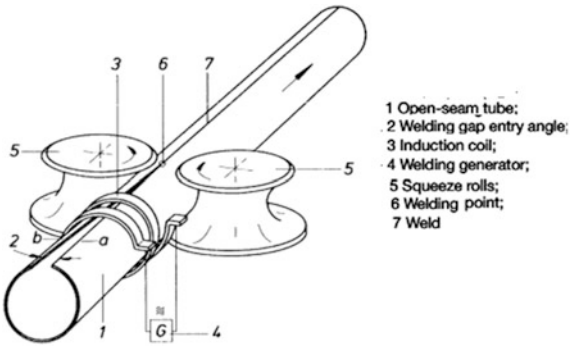


Fig. 3.15 High frequency induction welding

The defects that can occur in ERW/HFI pipe are primarily those associated with strip production, such as laminations and defects at the narrow weld line. Hook cracks can also form due to realignment of non-metallic inclusions at the two joint interfaces. Because the weld line is not visible after trimming, and due to the nature of the solid phase welding process, considerable lengths of weld with small discreet poor joint can be produced if the required parameters fall outside the set limits. In many cases such defects may go undetected. In addition, ERW pipe sometimes show in-service drop in hydrostatic pressure test from the original pre-service pressure test. This problem is caused by combination of low weld line toughness when small defects, grow with time, leading to derating (reduction in operating pressure) of the line.

Because of earlier poor experience, ERW pipe was generally regarded as a second grade pipe suitable only for low pressure and non-critical applications. However, prompted by a shortage of seamless pipe and the lower cost of ERW pipe, efforts were made in the 1980s to improve the pipe quality. The major factors which affect the quality were found to be the quality of the strip, its chemistry and metallurgical condition. Inspection of finished product was also found to have an important role. Ultrasonic, DP, eddy current and hydro test are specified for API quality steels for oil and gas service. Ultrasonic and eddy current inspections are carried out online during manufacturing. Accurate tracking of the weld line by automatic ultrasonic inspection equipment is crucial, since the weld line can rotate slightly during production. Thus by maintaining the quality of the strip with respect to the chemistry and metallurgical condition and proper heat treatment of the weld seam, it is possible to ensure good toughness. Further, for critical service like high-pressure gas line, ERW weld fusion line properties are checked using notched tensile specimens. This 'notched bar tensile test' developed by the American Gas Association is used to ensure acceptable fusion line ductility [6, 7]. While the use of ERW pipe in oil and gas industry has increased in the recent years, there is still some conservatism in the industry about its use in either sour or high-pressure gas service. However, use of ERW pipe or tube in hydrocarbon service in plant area is not permitted by many companies and engineering consultants.

Seamless Pipe

Seamless pipe, as the name implies, does not have a seam, and, therefore, is more reliable. The various methods used in manufacturing of seamless pipe are:

Piercing Mill

For manufacture of seamless steel and alloy steels pipes of higher diameters, piercing (a form of extrusion) process is used. Various techniques have been developed but the most popular one uses Mannesmann machine, having specially contoured rolls which both rotates and pushes the bloom forward. The round bloom of a predetermined diameter and length is heated and fed into the cross role piercing mill. The bloom passes over the mandrel with a piercing point to form a hollow

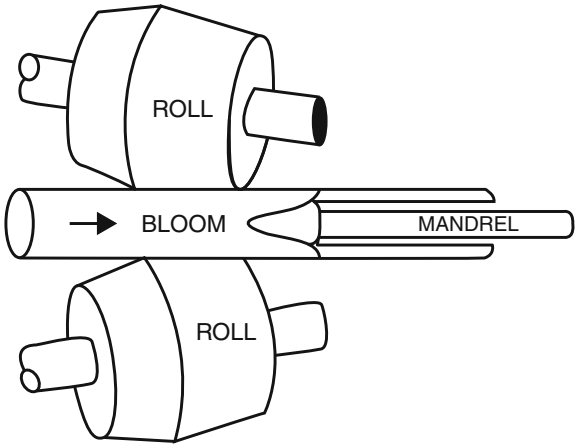


Fig. 3.16 Mannesmann piercing machine

shell with dimensional change of 1.5–2 times the length and 33–50% in cross section. Figure 3.16 shows schematically cross-roll piercing of bloom. This is followed by pilgering in pilger rolling mill to produce the final tube. During pilgering process 80–90% reduction in cross section takes place. The elongation ratio lies between 5 and 10.

Plug Mill

This process is used to make large (150–400 mm) diameter pipes. An ingot of steel is first heated and pierced and then enlarged on a rotary elongater to produce short thick-walled bloom. An internal plug, approximately the same diameter as the finished diameter of the pipe, is then forced through the bloom which is then passed between the rolls of the plug mill. Rotation of the rolls reduces the wall thickness. The final size of tube is then achieved passing it through a reeling mill and made ready for dispatch after heat treatment, final straightening, and inspection.

Mandrel Mill

This process is used to make smaller sizes of seamless pipe of 25–150 mm diameter. A mandrel is inserted into the hot pierced ingot and the assembly passed through a rolling (mandrel) mill. Unlike the plug mill, the mandrel mill reduces wall thickness continuously. The final diameter is achieved in reducing mill followed by heat treatment, final straightening, inspection and hydrostatic testing.

Extrusion

The process is used for small diameter tubes only. The bar stock is cut to length and heated to about 1250 °C before being sized and descaled. The billet is then extruded through a die.

UOE Process for Production of Pipe

Conventional pipeline is designed to withstand the internal pressure in the line. In addition to maximize the transport of product, especially gas, the present trend is towards higher pressure and higher diameter both of which result in increase in the wall thicknesses of pipes. For large diameter thick wall pipe, the Pilger process is not cost effective and these are more economically produced by what is known as UOE technique. Pipe produced by UOE technique is being used as land pipelines for number of years including the Trans-Alaska and Trans-Siberia pipelines. If such pipes are used for deepwater use, the external hydrostatic pressure becomes a dominant factor. This necessitates further increase in pipe thickness to prevent hydrostatic collapse particularly during installation of subsea trunk lines and long distance tie backs of 16″–20″. Use of these pipes has now been extended for deepwater service.

The UOE pipes have seam and made from plates which pass through a number of cold forming processes, some basic steps of which are shown in Fig. 3.17.

The basic steps are [8, 9]:

- The steel plate crimped at edge is first pressed into a 'U' shape with the help of a punch, the radius of which is similar to the outer radius of the final pipe which the 'U' shape acquires after the completion of the process.
- This is followed by pressing the 'U' into 'O' shape.
- The two edges are then tack welded followed by double-submerged arc welding.
- Once welded, the pipes are inspected using ultrasonic and radiography and then mechanically expanded for final sizing and improving roundness. Internal mandrel consisting of 8–12 segments is used.
- Through the optimization of crimping, U-press, and O-press operations, it is possible to control pipe diameter, wall thickness and ovality.

Because of various tensile and compressive strain cycles subjected during fabrication, collapse pressure of UOE pipe is however degraded as has been experimentally shown [10]. This result in providing additional wall thickness which makes it difficult for both manufacturing and lying of pipeline. However, introduction of

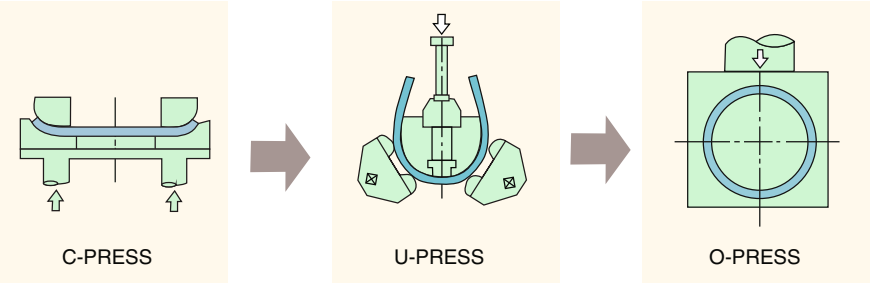


Fig. 3.17 Basic steps of UOE pipe manufacturing process

final compression step has been found to restore the degraded collapse stress. What is envisioned is that present expanders will continue to be used for land pipelines and the compression device would be used for deepwater pipes [11].

3.4.3.5 Drawing

Rod, wire and tubes of metals and alloys are produced by hot or cold working, depending on the ductility of the material. In drawing, the material is pulled through a die having conical hole resulting in reduction in cross section. To get the final cross-sectional dimension, the drawing is made through dies of various sizes with intermediate annealing. This process allows excellent surface finishes and closely controlled dimensions.

3.4.4 Production of Clad/Lined Material

In many cases, especially in process industries, resistance to corrosion plays an important role in specifying materials of construction. While corrosion-resistant material is used in many instances, for various reasons like strength requirements, thickness, possibilities of service related cracking, limitations in forming and welding and optimizing of the cost, a better option becomes the use of carbon or low alloy steel lined with a comparatively thin layer of corrosion-resistant alloy. In such cases, the strength bearing member is the base metal while the corrosion damage is taken care of by the thin corrosion-resistant alloy selected for the related service. There are mainly four processes by which such composite material (also known as *cladding*) can be produced. Cladding is normally done on flat products but techniques for production of clad pipes and other types of components have also been developed, some of which are discussed in Chap. 9.

3.4.4.1 Strip Lining

This is one of the common methods used for cladding of both new equipment and also as part of maintenance activities for local repair, if in-service experience shows high corrosion rates [12]. The method consists of fastening the sheets or strips of desired metal to the base metal to produce a continuous and non-penetrable liner cover. Various aspects of cladding have been discussed in a Nickel Institute Publication [13]. The lining is done after the fabrication is complete. The strips are generally of 100–150 mm width. In case of sheet lining, the size of each sheet depends on dimensions of opening available, geometry of the surface being lined and operating temperature. The first technique is important for service above 300 °C in instances, where a considerable difference exists in the coefficient of thermal expansion between the steel base and lining material, e.g. 300 series of stainless steel

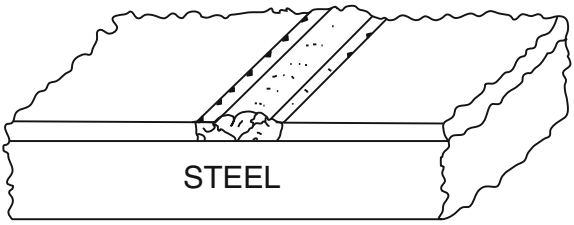


Fig. 3.18 Strip welding

THREE-BEAD METHOD

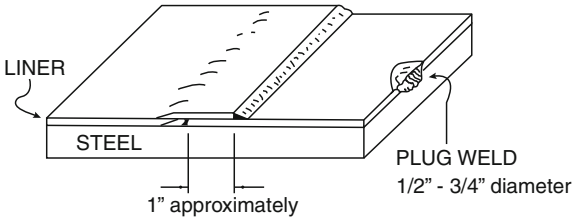


Fig. 3.19 Sheet welding

OVERLAP JOINT METHOD

lining on carbon or low alloy steels. Use of too large a sheet may result in bulging and failure of the weld joint. Except in cases of slight negative pressure, sheet or strip lining is not used for service under vacuum.

Lining requires that a good procedure is followed. The weld joints used are of two types, *three-bead and overlap joint techniques.* In three-bead method, each sheet or strip is fillet welded to the substrate followed by the third covering bead (Fig. 3.18). In case of overlap joint method (Fig. 3.19), each sheet is tack welded to the substrate steel by overlapping to the adjacent sheet and subsequently welding the two sheets. This method completely avoids the chances of diluted welds coming in contact with the environment and is preferred for aggressive environments. In case of lining of urea reactor with either UG 316L or titanium, overlapping weld is used. Plug welds, either using drilled or punched 10–16 mm diameter holes, are sometimes to be provided where (i) there are wide variations in temperature, (ii) there is large difference in thermal expansion between the clad and base metal, (iii) there is negative pressure excursion, and (iv) sheet width is quite wide. For strip and sheet lining welding can be done by using gas metal arc welding (GMAW), gas tungsten arc welding (GTAW) or submerged metal arc welding (SMAW) techniques. The method used depends on the extent of lining, type of lining and base material, shop or field welding, etc. For cladding of carbon steel with stainless steel types 304L or 316L lining, the following filler metals are recommended [13]:

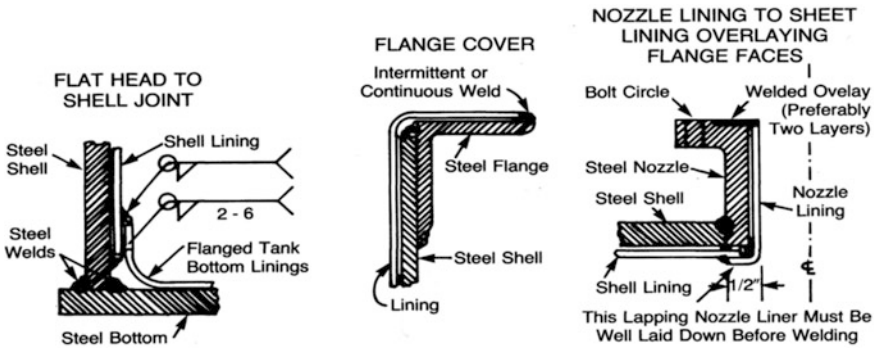


Fig. 3.20 Typical design for lining nozzles and flanges

Liner alloy	Liner to liner	Liner to steel
304L	ER 308L/309L	ER 309L/ER 312L
316L	ER 316L/309MoL[a]	ER309L[a]/309L

[a]If ER 309MoL is not available ER 316L can be used

For maintenance jobs, manual arc welding (MAW) is more commonly used. In case of stainless steels or other high alloy materials, one should use three-bead method to ensure that dilution effect of iron and carbon in the first two beads is compensated in the third bead to the desired composition. The integrity of weld is very important to avoid leakage of corrosive solution behind the lining as in such cases any corrosion of the base metal cannot be detected till the base metal develops leak. For early detection of any leak, therefore, tell tale holes are drilled in the base metal at low point of each sheet of lining joined by the overlap method. The two commonly used inspection methods for weld integrity are (i) visual and (ii) soap bubble test using light vacuum or light pressurization [14]. In case of nozzles, solid alloy (conforming to clad composition) is used for nozzles of $\leq 3''$ (75 mm), with larger ones being of cladded construction. Figure 3.20 gives the procedure for the lining of nozzle and flange.

3.4.4.2 Roll Cladding

The major tonnage of clad plates (about 90%) is produced by the hot-roll bonding process. For roll cladding, it is essential that both the base and clad metals

(a) Can be hot worked.
(b) Can be metallurgical bonded involving inter-diffusion of metals.
(c) None or minimum intermetallic brittle phase is formed between the cladding and the base metal, and

(d) Melting point of cladding metal is sufficiently above the rolling temperature of base metal.

The major manufacturing steps in case of roll cladding are:

(i) Grinding and chemical cleaning of surface to be clad,
(ii) Where required, electroplating or buttering the surface of base material with nickel to prevent surface oxidation and formation of intermetallic and/or carbide phases at the clad interface (nickel acts as a buffer layer),
(iii) Placing the clad plate over base metal and form an assembled pack 'sandwich' of two clad slabs, with clad surfaces placed one over the other. A uniform layer of Cr_2O_3 or ZrO_2 powder is spread to separate the two clad metal surfaces from coming in direct contact, and
(iv) Welding the two slabs together around the edges to prevent mechanical separation during rolling.

This is followed by the 'sandwich' (Fig. 3.21) to be heated and then rolled to the desired thickness.

Sometimes, before welding the 'sandwich' construction is evacuated or the air is replaced with argon to prevent surface oxidation. The actual step taken depends on the nature of the clad and base materials and facilities available in the mill. The original thickness to the base and cladding plate ratio is so selected that the extent of reduction would give the final required thickness of the base and clad metal. The rolling is done as per the normal practice for the materials in question. During rolling, only the base metal comes in contact with two iron rolls, avoiding any iron contamination of clad plates. The 'sandwich' rolling prevents the tendency for the clad plates to curl due to any differential expansion. After rolling the plates are separated, cleaned, cut to size and visually and ultrasonically inspected for de-bonded area as per ASTM A578 with acceptance criteria of Level C [15].

Roll cladded plates are available in 6–200 mm thickness, 1000–4400 mm width and up to lengths of 14–20 m. Roll clad has metallurgical bonding due to inter-diffusion between the two metals and, therefore, the composite plate can be formed to various shapes by normal methods. There is no adverse effect on material properties. The welding of such plate also does not give rise to much problem. However, roll cladding can be performed only on metallurgically compatible materials because of metallurgical bonding involved.

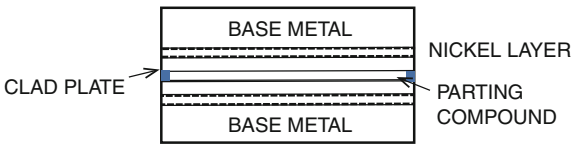


Fig. 3.21 Preparation for roll cladding of plate

3.4.4.3 Weld Cladding

One of the important methods of cladding is weld overlay and is used primarily on finished products. The post weld overlay step consists mainly of machining to get the required finish. Some of the important equipment/components where weld cladding is used are: cylindrical vessels, tube sheets, nozzles, flange faces, etc. Mostly, any two metals that can be successfully welded to each other can also be used for weld overlay. The selection of a process includes consideration of the purpose of overlay, thickness of cladding, size, cost and availability of the welding equipment and consumables. To decrease the cost of labour-intensive manual welding, automatic or semi-automatic processes, e.g. SAW, GMAW, etc., are being increasingly used. However, for small parts, repair works and where automatic equipment cannot fit, manual processes are used.

As weld cladding results in metallurgical bonding, due consideration is to be given to the composition of the base and cladding materials. In the case of carbon and low alloy steels, the most important factor is the adverse effect of dilution and pick up of carbon, which has adverse effect on the corrosion resistance of weld clad layer. The welding procedure used should take into consideration dilution or compositional variations on properties of cladding, stresses generated during welding which may cause either distortion or excessive stresses at the interface, deposition rate, type of flux, number of passes, etc. Present-day practice is to weld overlay directly on to the completed vessel shell, or to vessel dished ends. To avoid dilution effect, in some cases an intermediate layer of higher alloy or nickel is provided. For example, in case of hydrocracker having SS Type 347 weld overlay on 2.25Cr–1Mo, the first layer is of Type 309L. Alternately, a single pass weld of Nb modified 309L can be used. The higher Cr and Ni contents of SS 309 compensate for the dilution effect of base metal iron pick up and therefore the weld layer composition is nearer to the SS 347. In case of hydrocracker, any of these two processes used should meet the specified requirement of type 347 or higher chemistry up to minimum depth of 3.2 mm of weld from surface. Alternately, electro slag process has also been used to get a desired clad metal composition in a single pass. The process produces less dilution with base metal and is faster and more economical. The actual technique used depends on a number of factors including the facilities available with the fabricator.

For ferrous materials, weld cladding is normally done with stainless steels, nickel-based alloys and to some extent copper base alloy like Al-bronze and Si-bronze. Metals and alloys that do not tolerate significant amounts of iron contamination cannot be used for weld overlay of steels. Incompatible metals for overlaying steels are titanium, zirconium, magnesium, aluminium and pure copper.

3.4.4.4 Explosion Cladding/Welding

Explosion welding (EXW) was used for commercial application in early 1960 when Du Pont patented it in 1964, the operation of which was acquired in 1996 by DMC.

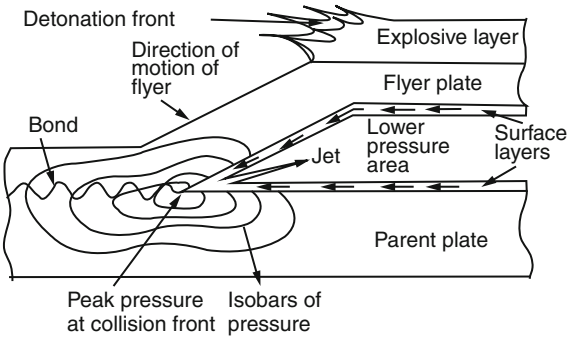


Fig. 3.22 Situation at collision front showing jetting mechanism

Today considerable advancement has taken place to make it one of the important processes of cladding. The principle of EXW is based on cold pressure welding where the pressure is generated by explosive charge, resulting in high-pressure collision of two components base and clad metal plates. The stress generated by explosion is sufficient to create a high-pressure jet between the metal plates so that contaminants and surface films are swept away to allow a metallurgical bond (Fig. 3.22). The collision region advances with a velocity equal to the detonation velocity, resulting in a flow of metal surface. A good explosively welded clad metal exhibits a regular wavy bond zone interface [16]. Sometimes localized high temperature occurs due to impact loading, leading to the formation of small pockets of solidified melt, but these discrete regions are completely encapsulated by the ductile material and the overall properties of composite are not affected.

The selection and quantity of explosive charge are dependent on strength and thickness of the material combinations, bond area and detonation velocity of the explosive, which may vary from 2655 m/s for ammonium nitrate (NH_4NO_3) to as high as 8190 m/s for PETN (Pentaerythritoltetranitrate, $C_5H_8N_4O_{12}$). The bonded plates are then cold rolled for flattening followed by cutting and ultrasonic testing for de-bonding. Sometimes explosion bonding is also followed by hot rolling. Unless bond ductility is an important consideration, heat treatment after explosion bonding is not necessary, as the process does not involve high temperatures. Changes in overall mechanical properties and that at the interface of clad material have been assessed as these are important for practical use. The change in hardness has been found to be confined to small depths at the interface. As regards the mechanical properties there is limited effect. EXW plates have been commonly used in chemical process industries for vessels and heat exchanger tube sheets. Explosive bonded slabs and billets have also been used to produce large tonnage of clad plate. Various other special uses of EXW have been identified, which include, tube to tube sheet joint, joining of large diameter pipe sections and for plugging of tubes.

Advantages and Disadvantages of Explosion Welding

The main advantages of these methods are:

(i) Formation of high quality mechanical bond without any diffusion of metals between the clad and base materials.
(ii) Brittle undesirable intermetallic compounds are not formed at the interface, e.g. titanium, tantalum, aluminium, etc., can be cladded to steel base.
(ii) While adequate ductility of both base and clad metals is prerequisite, large differences in melting points of the two are not that important.
(iii) Metals with tenacious surface oxide film can be more easily explosion clad than roll clad.
(iv) Both plate and cylindrical shapes like tube, pipes, nozzles, etc., can be explosion cladded.

The disadvantages of these methods are:

(i) Hazardous nature of storing and handling of explosives,
(ii) Some limitations of size/area of the component that can be cladded,
(iii) It is not amenable to automated and continuous production,
(iv) Bonding is difficult for materials with impact toughness below 20 J (15 ft lb).

3.4.5 Surface Defects of Worked Product

During working, surface or subsurface defects may be produced. If the defects are too deep, it becomes necessary to completely reject the material as some of these can become sites from which failure is initiated. To avoid quality problems later, the following steps are taken, depending on the desired end requirements of the user:

- The surface of rolled semi-finished products is inspected visually during different stages and the defects are removed by hand or machine chipping, grinding and scarfing. The major surface defects encountered are ingot cracks, scabs, seams and laps.
- The internal defects are more difficult to find easily. The internal defects may be due to elongated inclusions, insufficient welding of original blow holes or pipe during the process of working, lamination, etc. For normal service, these defects are examined only during the finishing stages as most of these either get manifested or disappear during the last stages of working. However, depending on the criticality, these checks can be done at intermediate stages also. Ultrasonic technique is extensively used for non-destructive testing. In modern mills, automatic scanning by ultrasonic technique is done in rolling stage itself to ensure good quality products.

- For ERW and fusion welded pipes, it is essential to have the integrity of the joints established, especially in services involving high pressures and hazardous materials. Eddy current, X-ray and ultrasonic methods are commonly used. Quality control is covered under ASTM and other standards. The user, depending on his requirements, can specify acceptability levels. Various ASTM standards cover procedure and acceptance level of internal discontinuities of plates [17, 18].

3.4.6 *Forming of Plates*

Plates need to be converted into usable product like vessel, pipe, reactor, etc., for which these are subjected to a process known as forming. Forming involves passing the plates through a roll or series of rolls, to bend into desired shape. The formability of a material depends on a number of factors and some of the important ones are strength, ductility, elongation, angle of bend, toughness, etc. The following formula is used for load required for bending [19]:

$$P = \frac{(0.833 \times Ut^2 \times L)}{W}, \tag{3.4.1}$$

where

P Estimated press load in tonnes
U Ultimate tensile strength (ksi)
t Thickness of plate (in.)
L Length of plate to be bent (in.)
W Width of die opening (in.).

Thus plates having higher yield strength would require higher press load compared to one having lower yield stress. Similarly, required load would increase with thickness of the plate. Thus the formability would also be dependent on whether the forming process is being carried out in cold, warm or hot condition.

3.4.6.1 Cold Forming

Forming of steel below 250 °C is called 'cold forming'. The important considerations in cold forming are:

- During forming the outer surface of the bend is stretched because of higher tensile stress to which it is subjected. Higher tensile ductility (% elongation) is therefore preferable to one having lower ductility.
- Cold forming of steel (i.e. forming below 250 °C) shall be carried out within the deformation range recommended by the steel manufacturer. For good quality pressure vessel steels intermediate stress relief should be carried out before

Table 3.1 Depth of HAZ in oxygen cutting of steel (mm/in.)

Thickness	Low carbon steel	High carbon steel	Alloy steel
<12.5/½	<0.8/1/32	0.8/1/32	≥ 1.6/1/16
12.5/½	0.8/1/32	0.8 to 1.6/1/32 to 1/16	≥ 3.1/1/8
150/6.0	1/8 in.	3.1 to 6.2/1/8 to ¼	≥ 6.2/¼

further working when the strain ratio exceeds 5%. The strain is calculated on the basis of formula given below:

$$\text{Percent strain} = \frac{\text{Forming mid thickness diameter}}{\text{Wall thickness}} \times 100$$

- Similarly, cracking tendency during forming will be reduced if material has better toughness. Thus compared to conventional grades, low sulphur, fine-grained, shape-controlled steels possess better formability because of their improved toughness.
- Bending transverse to rolling direction of plate is preferred over longitudinal bending because directional effect in case of latter can result in cracking.
- Plates are normally cut using gas or plasma before bending. The process leaves behind a HAZ with hard band adjacent to cutting edge, which results in cracking, if not removed prior to bending. The HAZ depth for different types of steel is shown in Table 3.1 [19].

3.4.6.2 Warm Forming

Warm forming above 500 °C considerably reduces the load on the bending machine and is preferable in case of plates of medium thicknesses. Important precaution in case of warm bending is not to go beyond 675 °C for annealed and normalized steels and 15 °C below tempering temperature in case of normalized and tempered and quenched and tempered steels.

3.4.6.3 Hot Forming

For thicker plates, it becomes necessary to carry out hot bending. In case of hot bending, it is important to control excessive oxidation of carbon and alloy steel plates and limiting copper content in steel to <0.3% to avoid a type of defect known as 'copper checking'. Hot forming temperatures of common stainless and duplex stainless steels along with that of carbon and alloy steels are given in Table 3.2 [20].

3.4.6.4 Forming of Clad Plate

Clad plates can be formed in both cold and hot conditions. It is important that during forming the clad side of the plate is in no case gets damaged or contaminated. In cold forming the procedure used will be similar to that used for normal plain steel plates. When the strain ratio exceeds 5%, intermediate stress relief need to be carried out before further working. For warm or hot forming of austenitic stainless steels and nickel alloys clad plates, the procedure will follow that for solid alloys whereby the sensitizing temperature range of 500–850 °C is avoided and forming completed above 850 °C.

3.4.7 Cutting Operation

Cutting of plates, pipes or any primary shapes is the first step in any fabrication process which can be done either mechanically or by application of heat. Except for small jobs and items of lower thicknesses cutting by use of heat is practiced using techniques depending on material composition, thickness, quality of cut (clean cut) and quantum of job. Three such processes are:

- Oxy-flame or flame cutting
- Plasma cutting and
- Laser cutting.

3.4.7.1 Oxy-flame Cutting

Oxy-flame cutting is the most commonly used method for cutting carbon and low alloy steels. During the process of cutting the steel does not melt, which would leave an uneven surface with blobs of metal on cut surface and edges. The cutting takes place indirectly by oxidizing the steel and as the melting of iron oxide is much lower than that of steel, the molten oxide is blown away leaving a clean surface. The oxy-flame process is therefore restricted to metals whose oxides have melting

Table 3.2 Hot forming temperature of some stainless steels of steel

Grade	UNS No.	Hot forming temperature range (°C)	Minimum soaking temperature (°C)
Lean DSS (LDX 2101)	S32101	1100–900	950
2205	S32205	1230–950	1040
2507	S32750	1230–1025	1050
304	S30400	1205–950	1040
316	S32600	1205–925	1040

points lower than that of the metals. Otherwise, as soon as the metal oxidizes it terminates the oxidation by forming a protective crust.

The oxy-flame process consists of heating the steel by oxy-fuel flame to around 900 °C when a stream of high-pressure oxygen is directed on to the hot metal which immediately oxidizes the steel and start cutting. If properly executed, the width of the cut (known as *kerf*) is clean and the edges remain sharp. The process can be used for a variety of purposes, from cutting scrap to cutting precision shapes, either manually or using automated system. Various gases can be used for cutting of which acetylene gives maximum temperature (1737 °C) along with shorter piercing time, ~1/3rd of that given by propane (1543 °C). Acetylene is costly and more efficient for thinner sheets. For underwater cutting, suitable gases are acetylene, hydrogen and MAPP™ which have sufficiently high flame temperature [21]. **M**APP™ gas is fuel gas based on a stabilized mixture of methyl acetylene and propadiene and belongs to Linde Group.

3.4.7.2 Plasma Cutting

Flame cutting cannot be used for stainless steels and high alloy chromium containing steels, aluminium and copper as the oxides of these elements have melting point higher than that of the element. These oxides prevent further oxidation by forming protective crust. Such materials can be cut using plasma arc. Electrically conductive gas transfers energy from an electrical power source through plasma. The gas is ionized in the nozzle and focused through the nozzle's special design to the material being cut. Plasma gas used is argon, hydrogen, nitrogen and their mixtures, plus air and oxygen. Here the metal is melted by plasma arc, which pierces through the metal. The molten material is removed from the bottom of the cut [22].

3.4.7.3 Laser Cutting

Laser beam produced in the resonator cavity of the laser cutting system travels from the resonator to the cutting head through the beam path system. In laser cutting, oxygen or nitrogen serve as cutting gas; oxygen for mild and low alloyed steel and nitrogen for stainless steel, aluminium and nickel alloys to achieve a clean edge and maintain the critical properties of the base material. The purity of both the gas is of at most importance.

3.4.7.4 Water Jet Cutting

Mechanical cutting with the use of water as a cutting tool has also been developed, where a jet of water pressurized up to 410 MPa (60,000 psi) is used with or without addition of some abrasives like garnet. With proper operation, a clean cut with close

tolerances and good finish can be obtained. The process is suitable for cutting many industrial materials including stainless steel, Inconel, titanium, aluminium, tool steel, ceramics, granite, and armour plate. A major disadvantage of the process is high decibel noise it generates [23].

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Chapter 4
Structure of Metals and Alloys

Abstract The metal from liquid state solidifies at a fixed temperature characteristic of the metal and atoms take up a definite geometrical position, the smallest of which is called a crystal. Most of the metals solidify in three crystal forms of face centered cubic (f.c.c.), body centered cubic (b.c.c) and close packed hexagonal (c.p.h.). The crystal undergoes no change till it melts except in some cases like iron where changes before melting occur in the order of b.c.c. (alpha ferrite) to f.c.c. (austenite) and again to b.c.c. (delta ferrite). On being alloyed, depending on the solvent and solute, complete or partial solid solution and intermetallic phases are formed. The phases formed as a function of solute concentration and temperature is depicted in phase diagrams. One important feature of all metals or alloys is the presence of grain boundaries. The different crystal systems, solidification and the process of evolution of grain boundaries, the factors governing the type of alloy formation, the phase rule and phase diagrams have been discussed briefly in this chapter.

Keywords Crystal structure · Phase diagram · Solid solution · Intermetallic phases · Grain boundaries

4.1 Crystal Structure

4.1.1 Introduction

Atoms are the basic particles of a matter, which may either be a metal, alloy or compound (both metallic and non-metallic). There are three primary states in which a matter can exist, i.e. gas, liquid and solid. These three states are temperature dependent and related to the number and arrangement of atoms in a given volume. In gaseous form, the atoms move about randomly, far apart from each other due primarily to thermal energy. On cooling, the thermal energy is reduced, slowing the movement of atoms, which then come closer to each other due to attractive forces between atoms. On continued cooling, a stage is reached when a definite closeness of packing is

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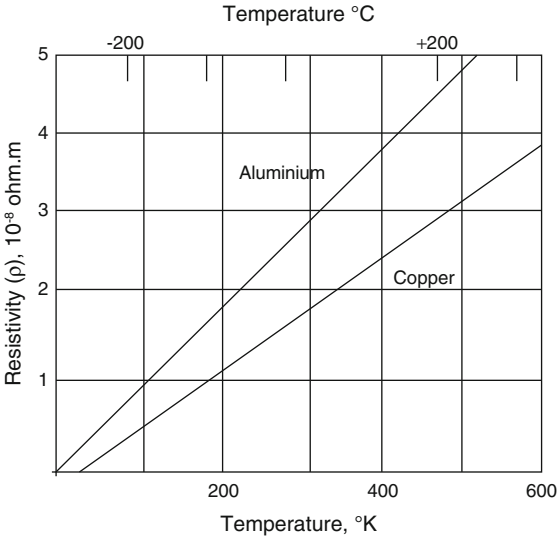


Fig. 4.1 Resistivity versus temperature

reached but still not sufficient for stable arrangement. This state is the liquid state. On further cooling the same atoms come very close to each other, their random movement is substantially suppressed and they take up a definite geometrical arrangement to form solids. Reverse change occur on heating. These transformations take place at a fixed temperature, which vary for different elements, and are known as boiling (condensation) and melting (solidification) temperatures, respectively.

From practical consideration for engineering metals and alloys, the two important states are liquid and solid. In the solid state, metals and alloys consist of atoms of the concerned metals arranged in regular patterns. In other words, these are crystalline in nature with a set of atoms forming a unit crystal. The three dimensional stacking of the unit crystals form the bulk material, though its external shape may be in any form like round, rectangle, elliptical, etc., The importance of crystalline nature of solids lies in the fact that many of the properties of a material are to a large extent related to this.

An atom consists of a positively charged nucleus with a cloud of negatively charged electrons revolving around it, in groups of orbit, called *shells*. The total system of an atom is electrically neutral. Atoms for practical purpose can be considered to be rigid spherical balls. The force, which holds the atoms of solid metals or alloys together is the metallic bond where each atom contributes its balance (outer) electrons to the formation of a negative electron cloud. Thus a metal can be considered to consist of positive metal ions surrounded by loosely bound electrons. These loosely bound electrons are free to move and this accounts for good electrical conductivity of metals and also its distinct property of increase in electrical resistance with increase in temperature (Fig. 4.1).The latter characteristic also

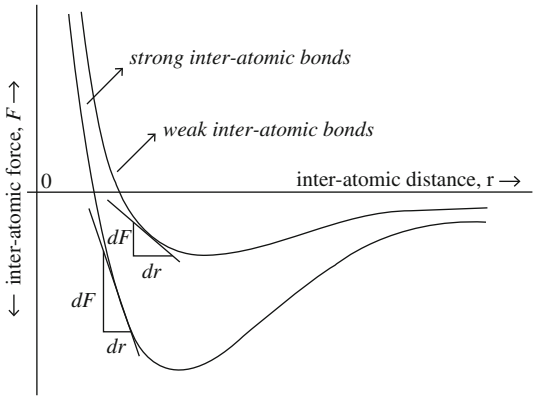


Fig. 4.2 Inter-atomic forces determine inter-atomic distance

distinguishes metal from non-metal which has high electrical resistance. In between the two there are elements, which are neither metal nor non-metal e.g. carbon which exhibit increase in conductivity with temperature.

When two atoms approach each other they are attracted by the mass effect. However, as they come too near each other, the repulsive force between charged nuclei and also electrons becomes dominant and thus the nearest approach of two atoms is related to balance of attractive and repulsive forces (Fig. 4.2). An arbitrary choice of atomic size is the closet distance of approach between two atoms of a particular metal and this atomic size varies from metal to metal.

While there are 32 modes by which the atoms can arrange in a regular crystalline pattern, most of the common engineering metals and alloys are arranged in two forms i.e. cubic and close packed hexagonal (c.p.h.). In the cubic arrangement, there are two sub groups viz. body centred cubic (b.c.c.) and face centred cubic (f.c.c.). These different arrangements are shown in (Fig. 4.3). Theoretically, the densest packing is with hexagonal lattice. The cubic arrangement is only slightly less dense, and of the two structures, f.c.c. is more densely packed than b.c.c. As the name implies, the inter-atomic distance along the three axes of cubic crystal is same, while in hexagonal metal, the *c*/*a* ratio is higher or lower than 1.0. Examples of metals that crystallize in different structures along with their melting and boiling points are given in Table 4.1 [1].

In crystallographic term, the three-dimensional array of atoms (or points) is termed as *space lattice* and to define the distribution, these points can be connected in different imaginary planes having some definite spacing. For example, in case of b.c.c. or f.c.c., typical planes are (100), (110), (111) etc. The planes are represented by *Miller indices*, which are smallest integers, proportional to the reciprocal of the intercepts. The crystal structure can be determined using the x-ray diffraction technique where the x-ray is reflected at different angles from the imaginary planes. Spacing of the atomic planes or lattice spacing (d), the wavelength of x-rays (λ),

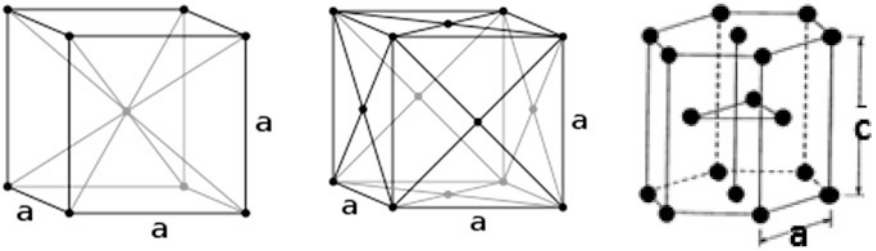


Fig. 4.3 **a** Body centred cubic (b.c.c.). **b** Face centred cubic (f.c.c.). **c** Closed pack hexagonal (c.p.h.)

Table 4.1 Room temperature crystal structure of some important metals along with their melting and boiling points

Name	Structure	Melting point (°C)	Boiling point (°C)
Aluminium (Al)	f.c.c.	660	2450
Beryllium (Be)	c.p.h.	1277	2770
Cadmium (Cd)	c.p.h.	321	765
Chromium (Cr)	b.c.c.	1875	2665
Copper (Cu)	f.c.c.	1083	2595
Gold (Au)	f.c.c.	1063	2970
Iron (Fe)	b.c.c. (RT)	1536	3000 ± 150
Lead (Pb)	f.c.c.	327	1725
Magnesium (Mg)	c.p.h.	650 ± 2	1107 ± 10
Manganese (Mn)	Cubic (complex)	1245	2150
Molybdenum (Mo)	b.c.c.	2610	5560
Nickel (Ni)	f.c.c.	1453	2730
Silicon (Si)	Diamond cubic	1410	2680
Tin (Sn)	b.c. tetragonal	232	2270
Titanium (Ti)	c.p.h.	1668 ± 10	3260
Vanadium (Va)	b.c.c.	1899 ± 25	3400
Zinc (Zn)	c.p.h.	420	906

the angle of diffraction (θ) and an integer can be related by using the following equation of Bragg's Law [2].

$$n\,\lambda = 2d\sin\theta, \text{ where } n \text{ is an integer and } \lambda \text{ is wave length}$$

The x-ray diffraction is a unique tool by which a number of structural characteristics of metals and alloys like unit size of cell, nature of phases, grain size, residual stresses, etc. can be found. It may be mentioned that William Lawrence Bragg at the age of 25 years got along with his father Nobel Prize in physics in 1915 for their work in determining crystal structures.

4.1.2 Structural Changes

The crystallographic structures discussed above mainly refer to the same at room temperature. Atoms in solids are not frozen at one place and some amount of movement always occurs. As the metal is progressively heated, initially the atomic movement increases leading to increase in dimensions of a unit cell, i.e. the lattice parameters increases. While in some metals, except for increase in lattice parameters, there is no transformation to other phase till melting, in some others a change in crystal structure occurs in the solid state at high temperatures. For example, copper and nickel retain f.c.c. structure till melting but iron changes from b.c.c. (alpha ferrite) to first f.c.c. (gamma/austenite) at 910 °C. On further heating this further reverts back to b.c.c. (designated as delta ferrite to distinguish it from alpha) at higher temperature (about 1400 °C). These solid-state changes in crystal structures are known as *allotropic modifications.* There are 28 elements which have allotropic forms, but out of these, except for iron other relevant metals are titanium (882 °C), cobalt (422 °C), zirconium (863 °C), and tin (13 °C).

4.2 Phase Diagram

When a metal is mixed with one or more metals or non-metals it is known as an *alloy*. The major constituent of the alloy is termed solvent and the minor ones as solute. For example, in case of copper rich alloys (cupro-nickels), copper is the solvent and nickel solute, but in nickel rich alloy (Monel™) nickel is the solvent and copper the solute. For alloying it is essential that the alloying elements are fully soluble in the liquid state. Iron and lead are not soluble in each other in liquid state and, therefore, they do not form a true alloy. On solidification of an alloy a number of changes may or may not occur, depending on the alloying constituents. The equilibrium states of changes (called, *phases*) as a function of composition and temperature are depicted in *phase diagrams or constitutional diagrams*. A phase is anything which is homogeneous and physically distinct. The phase diagrams give a picture of phases expected under equilibrium conditions at different temperatures and compositions. Knowledge of these is important because properties of alloys are very much dependent on the various constituents present and modification of these by heat treatment. J.W. Gibbs proposed phase rule (called Gibbs' phase rule) in the 1870s whereby stability of phase in any alloy system under equilibrium condition can be expressed mathematically by the *phase rule* [3]:

$$F = C + n - P \tag{4.2.1}$$

where

F number of degree of freedom i.e. number of variables
C number of components in the system

P number of phases in equilibrium
n number of external factors, e.g. temperature and pressure

In simple term, the degree of freedom is the quantity of external and internal variables (temperature, pressure and concentration) which may be changed without causing disappearance or formation of a phase in the system. For metal systems the effect of pressure is negligible and can be neglected and, therefore, temperature becomes the only external factor to be considered. The applicable equation thus becomes

$$F = C + 1 - P \tag{4.2.2}$$

Since the degree of freedom cannot be less than zero, the number of phases in a system cannot exceed the number of components plus one. Thus in a binary (two component) system, a maximum of three phases only can remain in equilibrium. In other words, a point will represent three-phase equilibrium. Similarly, a line will demarcate two phases. This basic approach of phase equilibrium can be used to explain the stability of different phases in an alloy system.

In considering phase diagrams the following important points are to be kept in view:

- In an alloy, solidification point, unlike in pure metal, is not sharp. The solidification takes place over a temperature range which is used to draw the phase diagram. The minimum temperature line at which an alloy remains completely in liquid state is known as liquidus and the maximum temperature line at which the alloy is completely in solid state is called solidus. Within these two temperatures both solid and liquid shall co-exist though each will have different composition. Similar change is manifested, when phase transformation takes place in solid state.
- Solute and solvent interchange their positions at different ends of composition axis. In Fig. 4.4 for Ag–Cu alloy, at the left end silver is the solvent and at the right hand end copper is the solvent.
- On alloying the resultant product can either be a solid solution or form a completely new phase like intermetallic compounds or mixture of both.
- In some alloy systems, at a definite composition the liquid solidifies at a fixed temperature similar to that in pure meal. This temperature is known as *eutectic temperature* and the composition as *eutectic point*, where three phases are in equilibrium of which one is liquid and other two solids. In some alloys, phase transformation similar to that at eutectic point occurs in the solid state also; this type of reaction is known as *eutectoid reaction*. At this point three separate solid phases are in equilibrium.
- Beyond the solid solution in alloy systems of limited solubility range, either intermetallic compound or a phase having different crystallographic structure (electronic or interstitial types) may form. In some systems, one or more intermediate phases or intermetallic compounds can also form beyond the solid

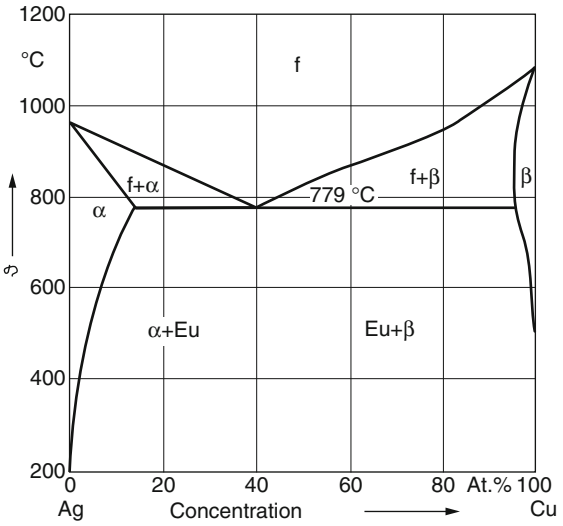


Fig. 4.4 Ag–Cu phase diagram

solubility range. Intermediate phases are either of fixed composition (e.g. Mg_2Sn, Fe_3C) or of variable composition (e.g. CuZn, Cu_3Sn, FeCr).

4.2.1 Solid Solution

Any solution is defined as a state in which more than one constituent, indistinguishable from each other are present, e.g. salt or sugar solutions in water. When solidification of an alloy results in the formation of crystal structure similar to that of the solvent, atoms of the metals present occupy the lattice positions randomly and cannot be differentiated from each other. This is known as *solid solution*. Solid solutions are of two types, *substitutional and interstitial*, depending on whether the alloying elements occupy the crystal lattice points or spaces between those of the solvent crystal.

The capacity of two metals to form substitutional solid solution has been explained by Hume Rothery [4]. In short, the empirical relationship states the followings:

– *Size factor*: Where the difference in atomic radii of the two metals exceeds 14–15%, the range of solid solution is very much restricted. A continuous solid solution (throughout composition range) is formed provided they have the same crystal lattice pattern and equal number of valence electrons and relative size factor is less than 8%. This would be evident from Fig. 4.5, which gives phase diagram of Cu–Ni alloy, where copper and nickel having the same f.c.c. crystal structure and difference of $\sim$2% in atomic radii, a continuous solid solution is

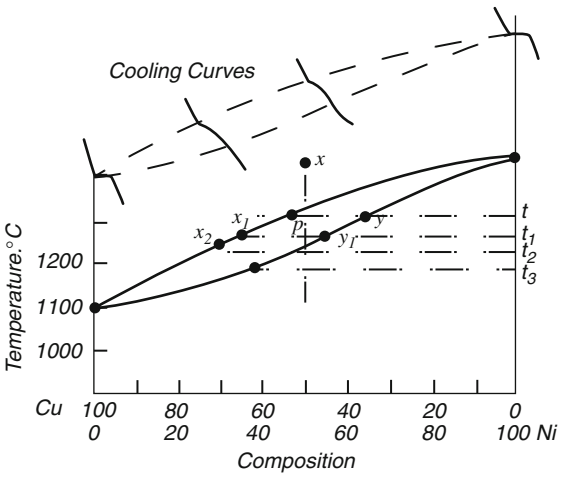


Fig. 4.5 Cu–Ni phase diagram

formed. With relative size factors between 8 and 15%, limited solubility is obtained.

- *Crystal structure effect*: The crystal structures of solute and solvent must match.
- *Chemical affinity effect*: the more electronegative the solute and more electropositive the solvent or vice versa, the greater is the tendency to restrict the solid solution ranges and to form intermediate compounds.
- *Relative valency effect*: a metal of lower valance tends to dissolve a metal of higher valency more readily than vice versa.

Interstitial solid solution occurs in those cases where the solute atoms like, carbon, nitrogen, boron, etc. has much lower atomic radii than the solvent. In such cases the only position the smaller atoms can occupy is the interstitial spaces of the solvent metal crystals. The solid solubility limit restriction due to relative atomic size difference between solvent and solute is primarily due to distortion of lattice structure introduced around the region occupied by solute atom. Further, interstices in the crystal lattice being much smaller, interstitial solid solutions normally have very limited solubility.

4.2.2 Grain Boundaries

The metal and alloys have a well-defined crystallographic structure, which is repeated in three-dimensional arrays. When molten metal solidifies or a new phase is formed in a solid, the initial step is the nucleation of small and stable crystals around which the three dimensional growth occurs. These crystals are randomly formed at various locations in the mass of molten or solid metal. However, due to thermal energy only a few of the small crystals form stable nuclei at the

transformation temperature. Thus at the actual transformation temperature not only the time taken for stable nuclei to form is large but the number of nuclei is also less. As the temperature decreases there is corresponding drop in temperature which makes it possible for larger numbers of stable nuclei to form and the transformation is hastened. The nuclei formed randomly have the same crystal structure but different orientation. When the well-defined transformed phase expands as grains around these points, the advancing faces from different points finally meet. However, because of different orientation of grains the interfaces do not match and a continuous line of atomic scale gap (mismatch) is formed in between adjacent grains (Fig. 4.6), which is termed as *grain boundary*. The grain boundaries play an important role in mechanical properties and kinetics of phase transformation.

The final grain size may be small or large depending on the number of stable nuclei around which transformation/change occurs. Greater the number of nuclei, smaller is the grain size and vice versa. The grain size in steel is controlled during production stage, primarily by judicious use of aluminium during de-oxidation and control of temperature during metal working. In cases of metals and alloys which do not show any change in phase with temperature, such as copper, nickel, and their alloys like Cu–Ni, Cu–Zn (solid solution range), etc. the grain size is controlled by subjecting the material to different degrees of cold working followed by annealing.

Mismatch of neighbouring grains results in grain boundary having deficient packing of atoms, leaving greater atomic size holes. The resultant higher internal energy makes the grain boundaries sites for precipitation, segregation of impurity atoms, phase transformation and passage for diffusion of atoms, etc. Size of grains (which is related to length of grain boundary in a unit area) therefore has an important role in not only causing changes in metals but also on mechanical properties, which has been discussed in this Chapter. The grain size for general engineering purposes is graded in the range of 1–9 as per ASTM [5] where grain size number "*N*" is defined by the following equation

$$n = 2^{N-1} \tag{4.2.3}$$

where "*n*" is the number of grains per square inch when viewed at magnification of 100X. It will thus be apparent that higher the grain size number (fine grain structure) smaller is the grain size and vice versa for large grains (coarse grain structure). It may be mentioned that ASTM grain size number covered in the standard is "00"–"14.0".

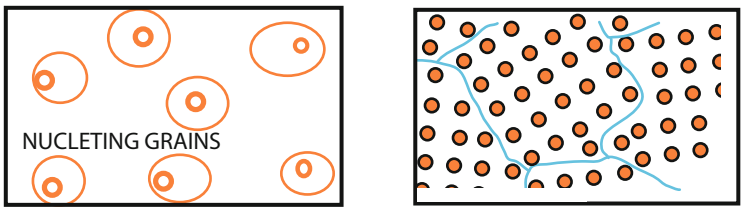


Fig. 4.6 Nucleation and growth of grains forming grain boundaries

4.2.3 Iron–Carbon Phase Diagram

As stated earlier ferrous materials are the most important engineering material. In all the iron base alloys, carbon is always present and therefore Fe–C phase diagram is very important for understanding the properties of various carbon and alloy steels. The Fe–C diagram is given in Fig. 4.7. Pure iron melts at 1539 °C, which on cooling first solidifies into as b.c.c. (delta iron). At 1390 °C, the b.c.c. changes into f.c.c. (gamma) which is stable up to 910 °C. On further decrease in temperature it again transforms into b.c.c. (alpha iron) phase. Below 910 °C the stable phase remains alpha iron. In practice, the actual transformation temperature (critical temperature) is lower during cooling compared to that during heating and are designated as A_r and A_c points, respectively. Sometimes A_e is used in equilibrium diagram in the designation of critical temperature.

When alloyed with carbon, the following major changes occur in iron with increase in the carbon content:

- Melting point of iron decrease reaching a minimum value (1146 °C) at about 4.27%C (eutectic point).
- Gamma to alpha transformation temperature decreases, reaching a minimum at about 0.8%C and 737 °C. Eutectoid reaction takes place at this point with the

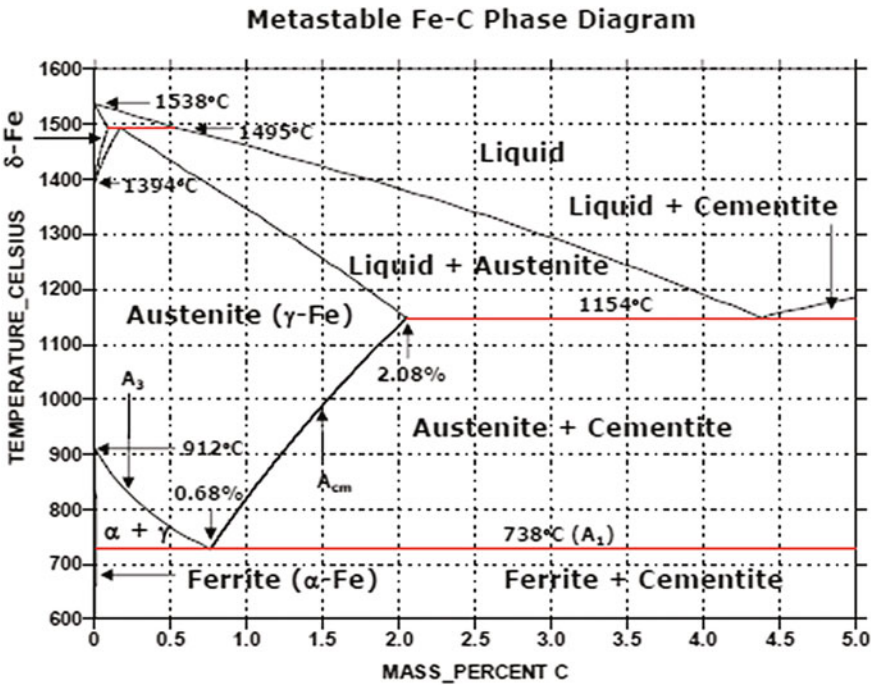


Fig. 4.7 Iron–carbon phase diagram

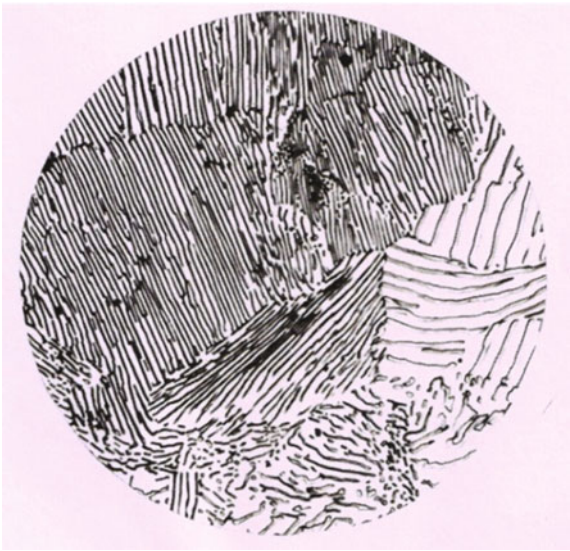


Fig. 4.8 Structure of pearlite [6]

formation of *pearlite*, which is a mixture of ferrite and cementite arranged in alternate layers (Fig. 4.8) [6].

- Solubility of carbon in alpha is very low (about 0.025% maximum at 727 °C, decreasing to as low as, 0.002% at room temperature).
- Solubility of carbon in austenite is comparatively very high (maximum 2.0% at 1146 °C).
- Under normal conditions, for commonly used steels (up to 1.2%C) the room temperature structure consists of ferrite + pearlite and cementite + pearlite below and above about 0.80%C, respectively. The former is known as *hypoeutectoid* and the latter as *hypereutectoid* steel.
- The phase diagram shows equilibrium condition, but in practice the phase obtained may be different because kinetics of transformation varies. These have been discussed in detail under heat treatment practices.

4.2.4 Binary Iron Alloys

Iron forms important alloys with a number of elements like Cr, Ni, Mo, V etc. In Fe–Cr binary diagram (Fig. 4.9) [7] chromium forms a complete solid solution with iron and stabilizes the alpha phase. Beyond about 15% Cr, gamma completely disappears and b.c.c. structure remains till the alloy melts. At about 50% Cr, a new phase sigma is formed (stable up to about 800 °C), which is an intermetallic compound of the Fe and Cr. In case of Fe–Ni alloy, on the other hand, the gamma

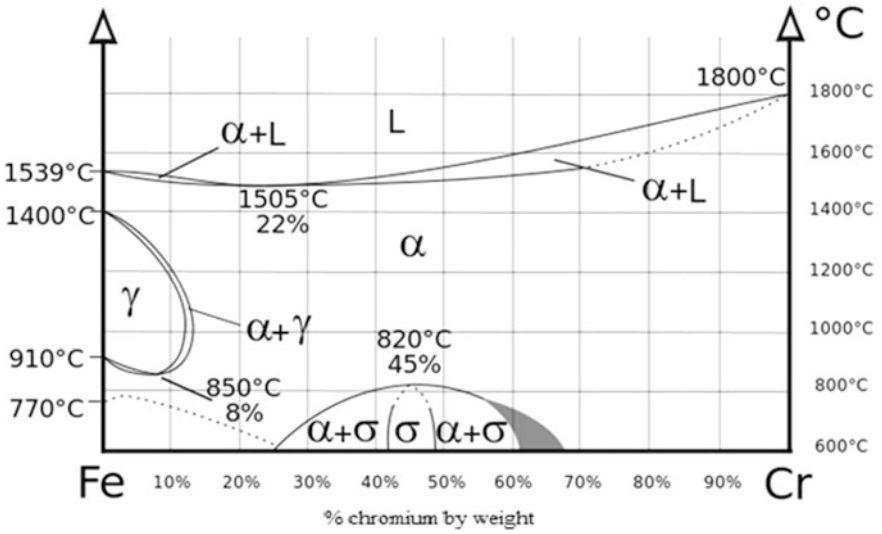


Fig. 4.9 Iron–chromium binary diagram showing gamma loop and sigma phase zone [7]

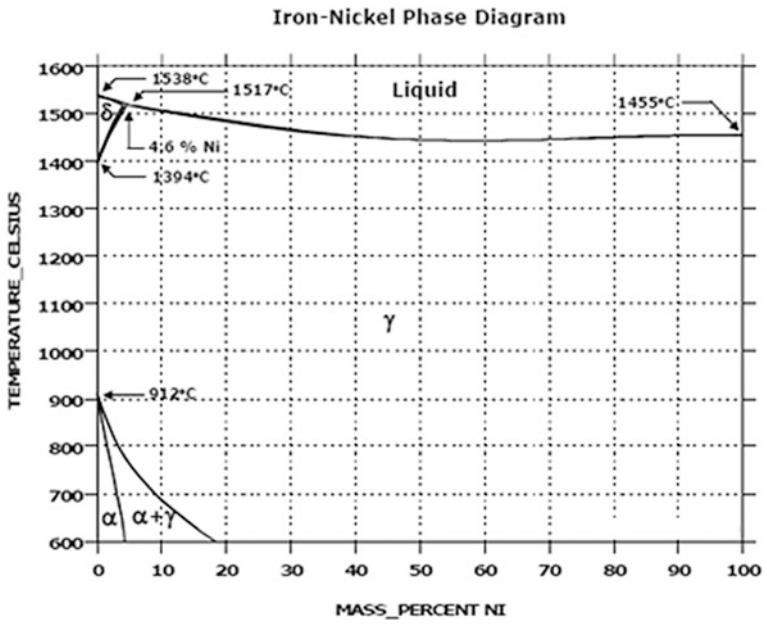


Fig. 4.10 Fe–Ni phase diagram showing gamma stability zone

transformation temperature is lowered and gamma stability area increases (Fig. 4.10) [8]. This is why in austenitic stainless steels with increase in chromium it becomes necessary to increase the percentage of nickel.

4.2.5 Ternary Phase Diagrams

Many of the alloys contain more than one alloying elements. The actual constituents present in these alloys may be quite different form those indicated in binary diagrams. Because of a number of possible combinations involved and difficulty in representing all the changes on a single plane paper, the ternary or quaternary systems have not been studied to the same extent as the binary ones. However, considering the importance of multi alloy systems, increasing number of ternary and other diagrams are being established. An outline of the important features of ternary diagrams is given below.

A complete diagram can be represented only by three-dimensional figures, i.e. a solid model and on paper this is plotted generally at one temperature only on equilateral triangle, with corner of the triangle representing the three pure metals. The location of a point within the triangle fixes the composition of a ternary alloy. The other method is to fix the composition of one alloying element and plot the temperature versus the concentration of the second alloying elements, similar to that in a binary alloy. Alternately, at each fixed temperature the ternary phase diagram can be plotted in a triangle.

In summary it can be stated that the effect of alloying elements can be divided broadly into two with respect to their effect on the Fe–C phase diagram. There are some elements like manganese, nickel, copper, cobalt (which have f.c.c. structure), carbon, nitrogen, etc. which enlarge the gamma field and are called *austenite stabilizers*. On the other hand, b.c.c. elements like chromium, molybdenum, vanadium, niobium and also titanium have the opposite effect of restricting the gamma field and are known as *ferrite stabilizers*. The alloying elements, *especially* those having strong affinity towards carbon, also have an effect on shifting the eutectoid point to lower carbon content and higher temperatures.

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Chapter 5
Mechanical Behaviour of Metals and Alloys

Abstract In service, metallic components are required to withstand stresses without failure and their ability to do this is dependent on their mechanical properties. Under the influence of stress metal undergoes deformation and finally fails in ductile mode. Deformation occurs by sliding of atoms along slip planes under the influence of stress and by movement of dislocations. Any hindrance in dislocation movement would increase the strength and this principle is used to increase the strength of material. In this chapter, the basic mechanism of plastic deformation, ductile to brittle transition, strengthening mechanisms and important mechanical properties for practical use have been discussed. These include yield and breaking strength, fracture and fracture mode, and toughness. The tests to be performed to determine these properties including hardness have been described. The chapter also includes fatigue failure of metals and the problem of irreversible damage caused due to creep at high temperatures.

Keywords Deformation · Dislocation · Ductile and brittle failure · Mechanical properties · Hardness · Creep

5.1 Mechanical Properties

The basic requirement of any engineering material is to be mechanically stable under stresses to which all components are subjected. The material should also have sufficient toughness so that any rupture or catastrophic failure is avoided. Finally, the material should be amenable to shaping, joining and machining for easy fabrication of components. Strength of a material is related to tensile stress at which it starts yielding and the stress at which it breaks. These are basically connected with permanent deformation along lattice planes and finally complete parting of the body under stress into two or more parts resulting in fracture.

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5.1.1 Deformation

When a metal is subjected to tensile stress the initial effect is elongation (strain) of the crystals in the direction of the stress, resulting in dimensional change. This elongation or strain is reversible up to certain level of stress, known as *elastic limit* i.e., if the stress is released the object reverts back to the original dimensions. Beyond elastic limit, any increase in stress would result in *plastic or permanent deformation*. The mechanism of plastic deformation and subsequent behaviour leading to break/fracture under stress are of utmost importance for utility of metals and alloys for engineering purposes.

5.1.1.1 Deformation Mechanism

To explain deformation and facture first it is necessary to establish how these phenomena occur. Deformation takes place by relative displacement of one part of the crystal with respect to the rest on a slip plane, resulting in elongation. At any particular stress, the elongation will take place only up to a certain extent and any further elongation would require increase in stress to cause further movement on another plane. From the orientation of the slip planes with respect to applied stress, it has been established that slip takes place as a result of shear stress. The shear nature of deformation along with the cup and cone fracture observed on round tensile bar during tensile testing are shown in Fig. 5.1. In case of perfectly arranged crystal theoretically fracture stress is a measure of strength, involved in parting of bonds between atoms on two faces of facture plane (Fig. 5.2). The stress required to achieve this has been theoretically calculated to be 100–1000 times the observed strength of material. To explain this discrepancy, the concept of *dislocations* in metals and alloys was postulated, which assumes that the crystals are not perfect and on solidification many of the atoms are either missing or out of position resulting in the distortion in the arrangement of atoms in crystals (Fig. 5.3). It has been estimated that metal on normal solidification may contain 10^4–10^6 dislocations per cm^2 and additional dislocations are generated during deformation, heating,

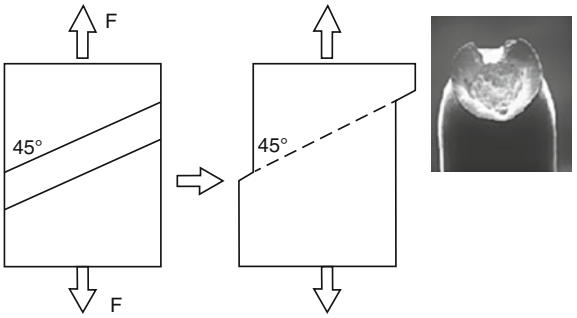


Fig. 5.1 Shear mode of deformation. *Inset* Cup and cone nature of fracture

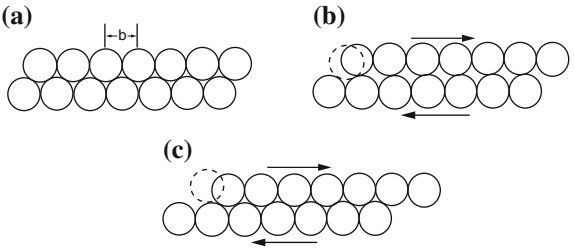


Fig. 5.2 Movement of atoms during the process of deformation

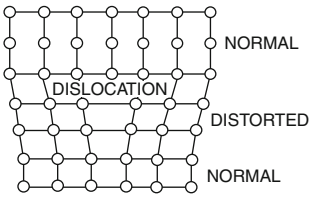


Fig. 5.3 Dislocation creates distortion in crystal plane

nuclear radiation, etc. The role of dislocation in allowing slip (plastic deformation) was independently explained theoretically nearly at the same time in 1934 by Taylor, Orowan and Polyani [1–3], though dislocations were physically observed only after the electron microscope was discovered. Without going into details it can be said that dislocations allow deformation to occur at much lower stress than in a perfect crystal.

Dislocations are disturbed regions between two perfect parts of a crystal and have two types of configurations, *edge and screw*. Many of the properties of metals and alloys can be explained on the basis of creation, multiplication and interaction of dislocations. On application of stress the dislocations initially move along the densest planes of atoms, because the stress needed to move the dislocation increases with the spacing between the planes. Thus in metals having f.c.c. structures, which have much more dense planes (larger number of points of contact of atoms) than those having b.c.c. structure, the dislocations move relatively easily and therefore these materials have higher ductility. The above considerations indicate that lattice structures play an important role on ease of deformation, as the slip system (combination of slip planes and slip directions) will vary with crystal structure. Materials with f.c.c. structure have total of 12 possible slip system consisting of four sets of (111) planes and three close packed direction in each plane and, therefore, their critical resolved shear stress for slip is low. Thus silver, copper, aluminium and gold are easily deformed. On the other hand, b.c.c. structures do not have such a well-defined slip system and therefore alpha iron (ferrite) has higher critical resolved shear stress and does not show the same high degree of plasticity. Metals having c.p.h. structures like zinc, titanium etc. fall under intermediate group because of the presence of three well defined slip systems.

The movement of metal occurring in blocks during deformation does not take place on the whole plane at a time, as stress is not uniformly distributed, but starts at

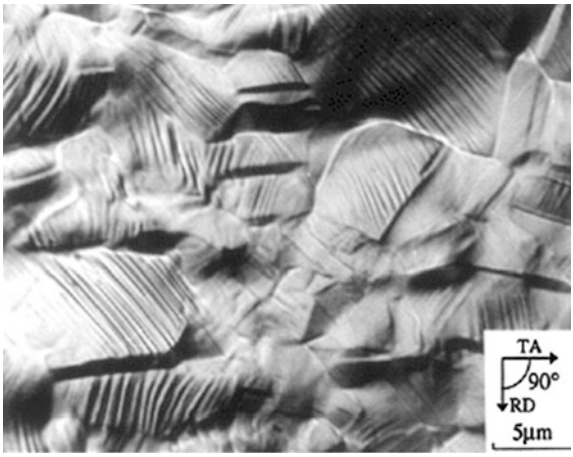


Fig. 5.4 Slip lines in polycrystallian copper [4]

the few places and finally covers the whole plane. After the dislocation reaches the free surface, steps are formed, which are visible under microscope as parallel lines (Fig. 5.4) [4] on a polished surface. If the surface is re-polished, the lines disappear. While slip starts occurring on a number of shear planes in different grains, continuous deformation would require increasing stress for slips to transfer from one plane to the other, from one orientation of crystal lattice to the next across the grain boundaries, overcoming the barriers of lattice distortion and presence of a second phase or inclusions. Thus deformation with increasing stress results in elongation and decrease in cross section till the material breaks. Breaking is due to fracture nucleated at sites of second phase or inclusion particles, which connect together resulting in final fracture The reduction in cross sectional area is an indication of ductility of the material.

5.1.2 Strengthening Mechanisms

From the knowledge of dislocation and its role in the deformation process, the strengthening mechanism of a metal by alloying and other treatments can be explained.

5.1.2.1 Solid Solution Strengthening

There are two types of solid solution. In one case the atoms of solute replaces and occupies the positions of the solvent atom. Such a solid solution is known as substitutional solid solution where total numbers of atoms originally present in the solvent remains the same but as that of solvent + solute. The 2nd type of solid solution is formed when the solute atoms are very small. The small atoms cannot

substitute a position of solvent atom because large strain produced on the adjacent atoms is not tenable. Such atoms being small in size, they enter the gaps between the solvent crystals. As the solute occupies interstitial position of the solvent these are known as interstitial solid solution. Carbon, nitrogen, oxygen and hydrogen atoms fall under this category. Because of arrangements of atom in alpha iron (b.c.c.), interstitial holes available for carbon and nitrogen are limited, resulting in sharp decrease in their solubility. On the other hand the solubility of both carbon and nitrogen in austenite (f.c.c.) is much greater than in ferrite, because of the larger interstices available. These substitutional or interstitial atoms distort the lattice, degree of distortion depending on the differences in atomic radii and the valency of the elements. This distortion impedes the movement of dislocations and thus raises the strength of a material. In this respect, interstitial atoms have greater effect in strengthening.

5.1.2.2 Grain Boundary Strengthening

Deformation occurs due to movement of dislocation along a plane. On loading, dislocations in a grain move along a plane but when they reach the adjacent grain boundary, their further movement is hindered because the concerned planes in the adjacent grains do not match (Fig. 5.5). Thus grain boundaries act as barriers for the movement of dislocations which pile up at grain boundaries. Any further deformation requires higher stress till it reaches a value to activate a favourable slip plane in the adjacent grain having different orientation or initiate a crack. As the number of dislocations in pile up of a fine grain is less compared to that in larger grain, it requires higher stress to push the dislocation to the adjacent grain in case of former than the latter. Further, number of grain boundaries that the dislocations would have to cross in unit length in fine grain metal would be much larger than that in coarse grain metal. Thus fine grained metals have higher strength than coarse grain metal. Theoretically this is related by Hall-Petch equation [5]:

$$\sigma_y = \sigma_i + k_y/\sqrt{D}, \tag{5.1.1}$$

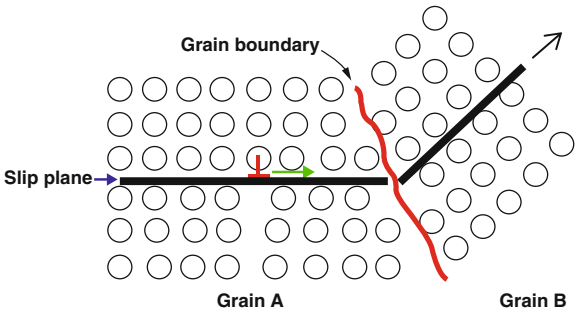


Fig. 5.5 Grain boundary as barrier for movement of dislocation

where, σ_y is yield stress, σ_i = back stress (a material constant) for dislocation movement, D = Grain size and k_y = Petch parameter.

In case of steel, fine grain size increases resistance to brittle failure and, therefore, suitable for use at sub-zero temperatures. If we compare ASTM A-515 and A-516 carbon steel plates we find that both have similar composition and mechanical properties but for low temperature use the right material is Gr. A-516, which has improved impact properties because it is manufactured using fine-grain practice of steel making.

5.1.2.3 Dispersion Strengthening

This is the most potent strengthening method and depends on the presence of particles of one or more phases in the metal matrix. These particles form obstacles to the dislocation movement where they can either pass through closely spaced small particles or loop between large particles (Fig. 5.6). The size, distribution and shape of particles affect the degree of hardening or strengthening. Thus finer the particles greater is the strengthening effect. At higher temperatures the particles tend to coalesce and form coarser particles, resulting in lowering of strength and creep resistance properties. In case of high temperature alloys, small amounts of alloying elements like Nb, W, Ti are added as carbides of these elements are more stable and do not easily coarsen. Addition of these elements therefore helps in improving and retaining their properties for longer time.

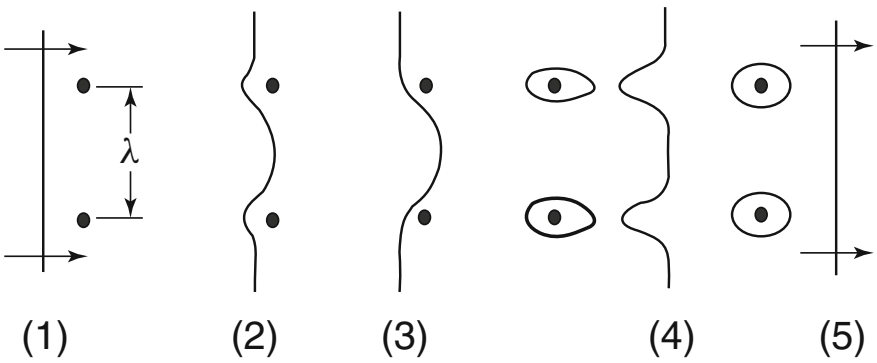


Fig. 5.6 Dislocation overcoming obstruction of dispersed phase

5.1.2.4 Work Hardening

The strength of a metal or alloy can be substantially increased by subjecting it to cold working. During cold working dislocation density is increased. It also results in the distortion of lattice and grains, making the dislocation movement more and more difficult with increase in degree of working, resulting in increase in strength. Increase in strength, however, results in sharp decrease in ductility. Very few alloys can be used in cold worked conditions, except where lower toughness can be tolerated. More ductile metals like aluminium and low carbon steels retain good toughness even when subjected to comparatively higher degree of cold working.

5.1.3 Fracture Mode

As stated earlier, final fracture mode may be brittle, ductile or combination of both. These modes are differentiated based on the extent of deformation a material undergoes before final failure. Materials like glass or martensite or ferritic materials below a certain temperature, fail purely in brittle manner without any plastic deformation. In other words, when shear stress is absent (preventing plastic deformation) and the applied stress exceeds the cohesive strain of the material, brittle fracture occurs. The failure may be *transgranular or intergranular*, i.e. traversing the grains or proceeding along the grain boundaries, respectively.

Brittle Fracture

For a purely brittle material like glass, the Griffith's formula is applicable. Griffith's theory [6] assumes that no material is free of defect and that the length of the cracks or crack like planner defects has an important role to play. The tensile stress which would lead to brittle failure is given by the formula:

$$\sigma = E\sqrt[\gamma]{c} \tag{5.1.2}$$

where

σ tensile stress
γ surface energy of fracture faces
E Young's modulus
c crack length

As very few metals are purely brittle, some amount of plastic strain always takes place ahead of the crack tip during which some amount of energy is dissipated. Orowan's equation modifies Griffith's formula by taking into account the role of plastic deformation [7]. The Orowan's equation states:

$$\sigma = \sqrt[E\gamma]{(\gamma + P)/c} \tag{5.1.3}$$

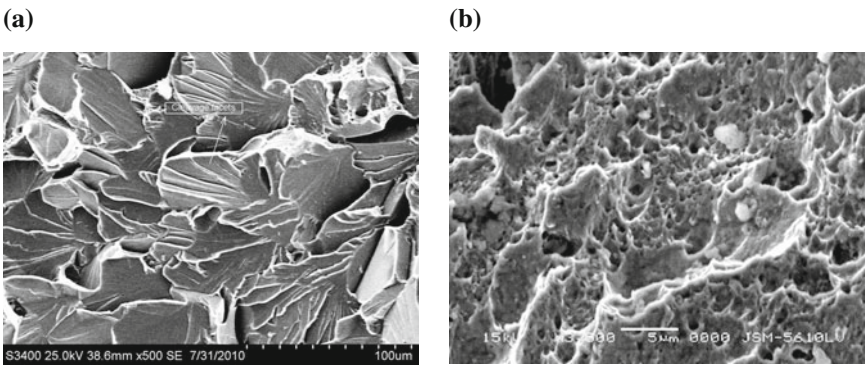


Fig. 5.7 **a** Brittle material shows planer mode of fracture [8]. X 1000. **b** A typical ductile fracture showing dimples [8]. X 3000

This includes the strain energy factor P to account for any plastic strain. Both equations show that stress required for a crack to grow decreases with increase in crack length and decrease in plastic strain energy factor.

Normally brittle fractures are transcrystalline in nature. However, cracking due to hydrogen embrittlement, creep, and temper embrittlement, separation along the grain boundaries take place without any marked permanent deformation. Ductile fracture on the other hand involves coalescence of voids formed by slip to form a continuous fracture surface followed by failure of the remaining material. The fracture appearance is fibrous and at high magnifications cup-like depressions, generally called dimples, along with the presence of a secondary material (e.g., precipitate, inclusions, etc.) is found at the centre of the dimples. Figure 5.7 shows typical SEM photographs of brittle and ductile failures [8].

5.1.4 Ductility of Material

5.1.4.1 Test Methods

From practical consideration it is important to know the toughness of a material which is determined by its ability to withstand impact loading. This property is determined from the amount of energy absorbed during fracture when impacted by weighted swinging pendulum released from fixed height. In such a case a ductile material will absorb more energy than a brittle one. Thus different materials can be characterized for their toughness by carrying out Charpy or Izod test. The difference between two tests is in the fixing of test specimen. In case of Charpy test the sample is held horizontally and the pendulum strikes opposite the notch. On the other hand in Izod test the sample is clamper vertically and struck on its free end as shown in Fig. 5.8a. ASME gives Charpy test values in material specifications.

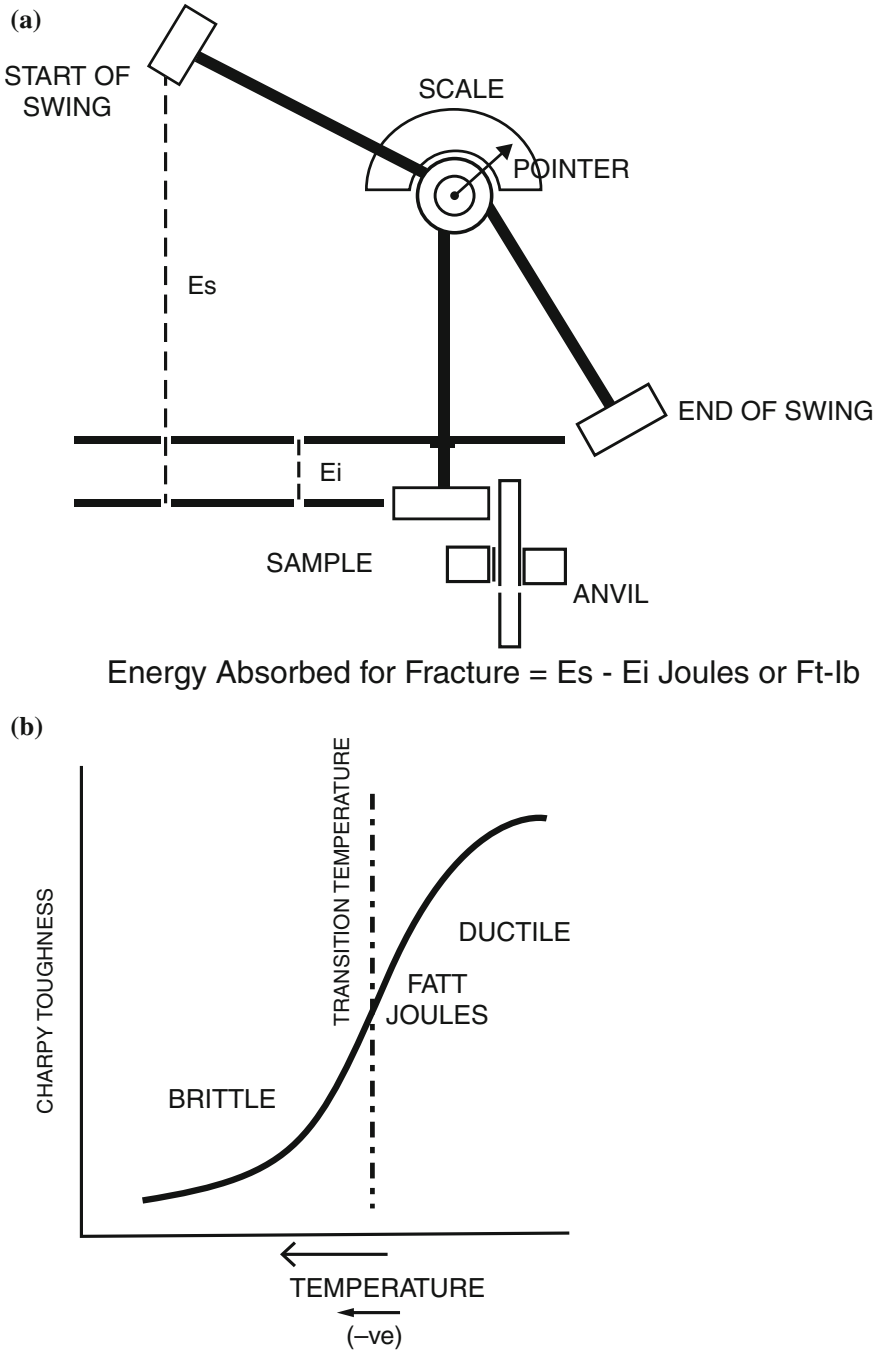


Fig. 5.8 **a** Schematic illustration of izod impact testing. **b** Ductile/brittle transition temperature

5.1.4.2 Ductile to Brittle Transition

Many ductile materials, under certain conditions fail in a brittle manner. Temperature has a large effect on this behaviour. The temperature at which the mode of failure changes from ductile to brittle is known as *transition temperature*. The phenomenon is more important for ferritic materials. This transition effect increases under the influence of impact loading; presence of planer/sharp defects; residual stresses; coarser grain and metallurgical structure. To determine the transition temperature, the commonly used Charpy test is carried out at decreasing temperatures and the energy absorbed versus temperatures is plotted as shown in Fig. 5.8b. The transition is evident in the plot and the middle of its straight line portion is taken as the *Ductile To Brittle Transition Temperature* (DBTT), measured as ft.lb or Joules. The fracture surface of the sample also show different brittle and ductile areas which can be easily distinguished and proportion of the two is also used to indicate the transition temperature. Therefore a 50:50 brittle and ductile area, known as *Fractured Area Transition Temperature* (FATT), is also used. The Charpy test is commonly used as a guide and quality control test for toughness but is inadequate for design purpose. The Charpy test is performed as per ASTM Standard [9]. There are various other methods e.g. 'nil ductility transition' (NDT) and 'crack arrest temperature' (CAT) by which ductile/brittle behaviour is expressed.

5.1.4.3 Practical Uses

Generally, for temperatures below −29 °C materials suitable for low temperature is required to be used, the range of which may vary from −33 °C (ammonia) to as low as −268.9 °C (helium). The material suitable for a particular service is dependent on temperature. The temperature range from −150 °C to ∼ absolute zero (−273 °C), where the molecular motion comes, as close as theoretically possible, to be completely immobile, falls under cryogenic range. The low temperature ductility of steel, for practical use up to about −45 °C, can be improved by grain refinement, increasing cleanliness, PWHT, and reducing sharp defects. Materials having faced centred cubic structures like austenitic stainless steels, copper and copper alloys and aluminium can be used at cryogenic temperatures down to −273 °C as they do not show any marked reduction in impact properties. These materials are used for various cryogenic services, such as, air separation, off-gas separation, production of helium, etc. Addition of nickel lowers the transition temperature of carbon steel and iron base alloys like Fe–2.25Ni, Fe–3.5Ni, Fe–8 & 9Ni, etc., have large scale industrial use for sub-zero and cryogenic temperatures e.g. for storage of ethane (−83.3 °C), ethylene (−103.8 °C), argon (−185.7 °C) or LNG. For the latter Fe–8 or 9% Ni steel is used.

5.1.5 Fracture Mechanics

For metals and alloys which are otherwise sufficiently ductile but also show brittle behavior under certain conditions, the suitability of the material cannot be assessed by normal impact tests. A sounder concept, based on fracture mechanics approach has been developed. This relates the stress and strain at the tip of a sharp crack or linear defect to the parameter K_1 (stress intensity factor, expressed in units of stress × length^{½} i.e. MPa × $\sqrt{\text{m}}$ unit). Crack growth occurs when this value reaches K_{1C} of the material known as fracture toughness. The science of fracture mechanics has advanced considerably in the recent years and can be applied to give a fracture-safe structure in the presence of a given defect size. Alternately, safe running regime of a pressure component with linear defects formed during fabrication or developed during operation can be established. The approach is based on determining the critical plane strain stress intensity factor K_{1C}, of a material under a particular condition (type, thickness, temperature) and the extent of degradation and then specifying the acceptance limits for sizes and shapes of defect when brittle fracture will not occur at the design or operating stresses. The end effect is that one can determine on the basis of critical crack length (CCL) whether a particular case falls under "*leak before burst*" (LBB) or "*burst before leak*" (BBL) situation. From point of safety LBB is preferred option because the operation gets sufficient time to take corrective action and leak can be controlled without causing large scale damage. Thus the fracture mechanics approach is a valuable tool and on its basis decision regarding continued service or early repair can be confidently taken. API 579-1/ASME FFS-1/BS PD BS 7910 (earlier BS PD 6493) are comprehensive consensus industry recommended practices that can be used to analyze, evaluate, and monitor defect in operating equipment [10]. The types of equipment mainly covered by this standard are pressure vessels, piping, and tanks. Evaluation can be carried out in 3 levels, as stated below:

- Level 1 Conservative screening on the basis of least amount of inspection which can be carried out by inspectors and plant engineers.
- Level 2 Study involves a more detailed evaluation including accurate flaw sizing and stress calculation. The assessment can be made both by plant engineers and engineering specialists.
- Level 3 Assessments involve detailed evaluation of components, accurate flaw sizing, finite element analysis, etc. Requires joint study by plant engineers and engineering specialists experienced in advanced stress analysis, fracture mechanics, etc.

A number of user-friendly Fitness-for-Service Software have been developed and used by industry. After analysis, if found safe, the equipment can be continued to operate, with or without de-rating (operating at reduced estimated safe pressure), if found necessary. It may be mentioned that the concept of fitness for service (also known as critical engineering analysis) was initiated by the utility power industries in USA, UK, and some European countries during 1960s.

5.1.6 Tensile Properties

There are five fundamental loading conditions: tension, compression, bending, shear, and torsion. Of these the behaviour of material under tensile loading is of primary importance as it determines the load carrying capacity in most of the cases. On being loaded in tension the two sections of material on either side of a plane are pulled apart (strain). Initially when stressed, the strain is small but reversible, but beyond a certain stress the material yields and permanent deformation starts. On further loading deformation will continue till the material fails. The maximum engineering stress at which the material shall not break is known as ultimate tensile strength (UTS). The tensile property of a material is determined by pulling a specimen of known and standard dimensions with two points marked at known distance in the gauge length at a slow and steady rate in a machine till fracture. During the process both stress and degree of deformation (change in distance between the two marked points) are recorded and the data plotted as stress versus strain curve (Fig. 5.9). From this curve the following properties of the material are determined, based on the original cross-sectional area of the sample:

Stress strain curve can be used to get many properties of material and some of the important ones are:

1. Increase in strain is proportional to stress till certain stress known as proportional limit. The relationship is expressed by Hook's Law which can be expressed by equation as:

$$E = \frac{\sigma}{\varepsilon} \tag{5.1.4}$$

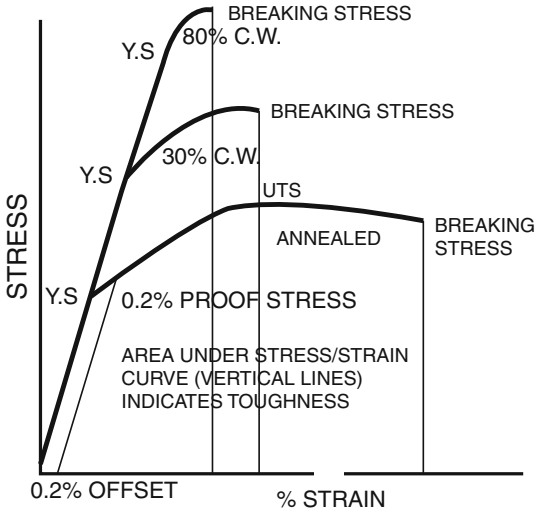


Fig. 5.9 Stress–strain curve

where,

E Young's modulus (Y) which is a constant
σ Stress (Pa)
ε Strain

2. Proportion Limit or Elastic Limit (PL/EL) is the stress beyond which strain is not proportional to stress and permanent deformation sets in.
3. Yield Strength (YS) is stress beyond which permanent deformation starts and continues till final failure. However, there is no relationship between increase in stress and corresponding increase in strain.
4. Proof stress (PS) is taken as approximate yield strength or elastic limit where sharp or definite yield point is not displayed during tensile testing. Here a line parallel to the initial straight part of the curve from a point slightly (normally 0.2% offset) to the right of the Proportional Limit is drawn and its intersection with stress versus strain curve is taken as proof stress.
5. Ultimate tensile stress (UTS) is the maximum stress beyond which there is rapid drops in stress occurs till failure (fracture).
6. Area under the stress strain curve gives an indication of the toughness of the material.
7. Total strain in the gauge length after failure is converted into % elongation (EL) and reduction in cross section to % reduction in area (RA). Both are indicators of ductility but % RA gives a better indication compared to % El because the latter is not uniform throughout the length and maximum deformation is near to the point of failure.

Characteristics of other properties of material are:

- Young's Modulus i.e. the ratio of stress to strain, is not affected by composition or heat treatment but decreases with temperature. In case of steels, a 25% decrease between 15 °C and 600 °C is observed. The springiness of the material is indicated by Young's Modulus and is considered when stiffness is to be taken into account in any design.
- Allowable stress for pressure vessel codes are determined by using design factor (safety factor) on specified minimum UTS and YS.

Normally under very few conditions a sharp yield point is obtained and it becomes difficult to get absolute value of yield stress. In such a case proof stress is determined, normally specified in the standards. Proof stress is generally based on a 0.2% offset or a permanent deformation and the value is a little higher than the actual yield stress. Detail examination of the curves in Fig. 5.9 would also show that for any particular material increasing cold work results in an increase in YS and UTS and decrease in %EL, %RA and degree of toughness. In case of highly cold worked material the difference between the YS and UTS becomes very small. This will mean that before its failure (fracture) almost no deformation will take place making it highly brittle. The other important observation is that the Young's modulus does not show any change with degree of working. If we take a case of

increasing temperature, its effect will be the opposite, that is lowering of YS and UTS and increase in %El and %RA.

Tensile properties of material are determined as per ASTM E8/E8 M Standard [11].

5.1.7 Hardness

Property of hardness of a material is measured on the basis of its resistance to penetration or wear or ability to scratch (Moh's scale), or the ability to cut. Four test methods used for determining hardness are, Brinell, Vickers, Rockwell and Shore. The first three are commonly used and these basically determine the extent of penetration of an indenter on application of a pre-determined load. Brinell measures the stress in kg/mm^2 of the spherical area of an impression made by a 10 mm ball at a load of 3000 kg for steel, 1000 kg for copper and 500 kg for aluminium. In practice, the average diameter of the impression is measured and related to hardness using a standard chart. Vickers hardness test, on the other hand, measures the diagonals on the impression made by a diamond square-based pyramid, the angularity of which is 136°. Loads applied, range from 5 to 120 kg, depending on the hardness and thickness of the material. BHN and VPN are practically identical up to the hardness number of 300. The Brinell number is not reliable above 600. Rockwell test measures the depth of penetration of a 1.58 mm steel ball with 100 kg load or a diamond pyramid at a load of 150 kg. A dial gauge records the depth of penetration and the value are termed as R_B (with ball) and R_C (with pyramid). This test is particularly useful for rapid routine test.

There is some degree of relationship between the hardness and the tensile strength as given in Table 5.1 [12]. A number of empirical mathematical relationships between hardness and yield and tensile strength have been attempted and one such relationship is given below [13]. It may be mentioned that these relationships do not give absolute values.

$$\text{HV} = 3.0 \times \text{YS} \tag{5.1.5}$$

where,

HV Vickers hardness
YS Yield stress in kg/mm^2

and

$$\text{UTS} = 3.45 \times \text{BHN for annealed steels and} \tag{5.1.6}$$

$$\text{UTS} = 3.24 \times \text{BHN for Q/T steel} \tag{5.1.7}$$

where,

UTS Tensile strength in N/mm^2

Table 5.1 Approximate conversion of hardness to tensile strength (Rm) values of steel

Tensile strength, MPa	Vickers hardness, HV10	Brinell hardness, HBW	Tensile strength, MPa	Vickers hardness, HV10	Brinell hardness, HBW	Rockwell hardness, HRC
350	110	105	770	240	228	20.3
370	115	109	785	245	233	21.3
385	120	114	800	250	238	22.2
400	125	119	820	255	242	23.1
415	130	124	835	260	247	24
430	135	128	850	265	252	24.8
450	140	133	865	270	257	25.6
465	145	138	880	275	261	26.4
480	150	143	900	280	266	27.1
495	155	147	915	285	271	27.8
510	160	152	930	290	276	28.5
530	165	156	950	295	280	29.2
545	170	162	965	300	285	29.8
560	175	166	995	310	295	31
575	180	171	1030	320	304	32.2
595	185	176	1060	330	314	33.3
610	190	181	1095	340	323	34.4
625	195	185	1125	350	333	35.5
640	200	190	1155	360	342	36.6
660	205	195	1190	370	352	37.7
675	210	199	1220	380	361	38.8
690	215	204	1255	390	371	39.8
705	220	209	1290	400	380	40.8
720	225	214	1320	410	390	41.8
740	230	219	1350	420	399	42.7
755	235	223	1385	430	409	43.6
			1420	440	418	44.5

Maximum use of hardness by a material engineer is made to determine indirectly the strength by a non-destructive method. It is used as a tool to control the quality or determine changes in mechanical properties during production, fabrication and heat treatment. It also indirectly indicates the structural changes, degree of cold work and strength of a material. In case of hydrogen related stress corrosion cracking, hardness measurement is made to ensure that the strength of the material or weld or HAZ is below the cracking susceptible range (usually below HRC 22). In case of fire or long period of high temperature service or carrying out too many PWHT cycles as a result of repeated weld failure a component's original structure may change, resulting in increase or decrease in strength. An idea of the extent of material degradation would require determining mechanical strength, which can

only be done by destructive testing. On the other hand one can get a rough estimation of the strength based on a relation between hardness and ultimate tensile strength.

The indenter size of different hardness tester is quite large. These tests give an average overall hardness of the material but cannot identify any change (low or high) in hardness confined in small areas or the individual phases present. Some of the examples are, decarburized or carburized narrow band; variations in hardness across the weld, HAZ and base metal; thin hard deposit or layer etc. cannot be determined by these instruments. For these, tests are to be carried out at very low load with small indenter (normally diamond) on samples under microscope having special attachments.

5.1.7.1 Field Hardness Tester

The above testing machines are not portable and hardness measurement in field on actual component cannot be performed. Earlier, for field application initially Poldi tester was used which was later replaced with the Portable Brinell Hardness Tester —Telebrineller System. In the two cases a load was applied manually by a light hammer. The results were not reliable, especially for measuring variations in hardness of weld and HAZ, due to the large size of indenter. The industry for a long time needed portable and reliable hardness testers. This has to a large extent been solved with the development of new instruments.

Advanced Field Hardness Testing Instruments

Recent developments have considerably facilitated field hardness measurements.

1. One popular device measures the frequency shift of a resonating rod with a Vickers-diamond tip as a result of its penetrating into the test material on application of a specific test load. The frequency shift is evaluated and electronically converted to a hardness value displayed on the LCD. Thus, higher is the penetration lower will be the hardness. The Microdur instrument works on the so-called UCI (Ultrasonic Contact Impedance) method shown in Fig. 5.10a [14].
2. Another well-known principle for portable hardness tester is based on the rebound method. Based on principle of Libb's rebound method, the hardness tester having spherical tungsten carbide tip measure the velocity ratio due to change in velocities before and after impacting the surface of the test object. The decrease in rebound velocity depends on the extent of loss of kinetic energy due to plastic deformation on impacted body. Softer the material greater will be the deformation (higher loss of energy) with subsequent greater loss in velocity. The situation will be opposite (less loss of energy and so less loss of rebound velocity) for harder material. The velocities after and before the impact are each measured using a small permanent magnet within the instrument the arrangement of which

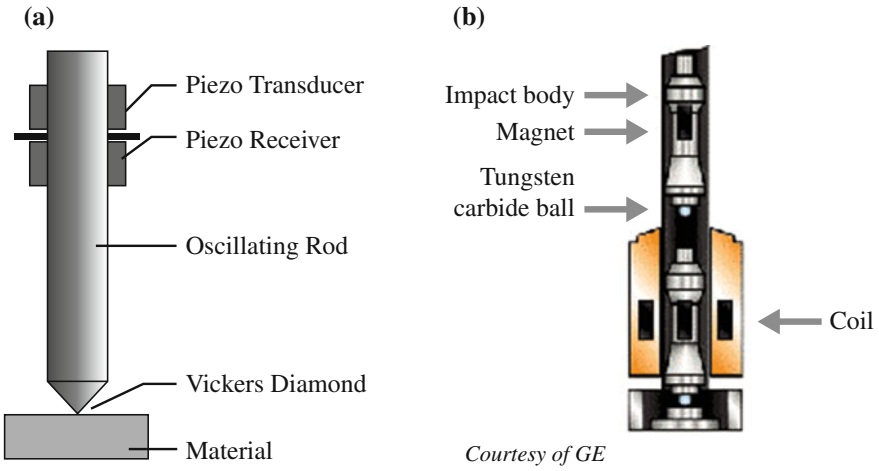


Fig. 5.10 **a** Ultrasonic contact impedence (UCI) hardness tester. **b** Cross section of rebound pocket hardness tester [14]

is shown in Fig. 5.10b. The ratio of the impact and rebound velocity is used to calculate Leeb's hardness value HL. However for actual use the HL values are converted into normally used hardness scale of HV, HB, HRC, etc. [14].

3. In an another method, Trans Pyramidal Indenter Viewing, or Through Diamond Technique (TDT), real Vickers hardness measurement under load can be made independent of the influence of the elastic properties of the test material [14]. The portable instrument has a graphical LCD display along with the TDT probe. When diamond penetrates on application of load, the length of the Vickers diamond indentation diagonals is automatically measured under load by viewing through the diamond with an optical system having a CCD camera. With the instrument performing data evaluation and display of picture on the instrument's LCD reliability of measurement can be ascertained.

The Equitop hardness tester is also covered by ASTM specification [15].

5.1.8 Fatigue

About 80% of fracture in rotating or reciprocating (sliding) machines occurs due to fatigue failure. This type of failure occurs when a component is subjected to repeated cycle of alternating stresses, much lower than that required for failure on a single application of load. Change in operating pressures and temperatures, start-ups and shutdowns, wave actions, also contribute to alternating stress. Broadly, there are three ways by which fatigue stresses can develop i.e. (a) reverse loading where tension, compression or shear stresses of the same magnitude

alternate, as in the case of rotating shaft (b) tensile, compressive or shear stress varying from zero to a maximum under unidirectional loading, typical of a punch or gear teeth and (c) where stresses change under unidirectional loading, between minimum and maximum without reaching zero, as in the case of cylinder head and connecting rod bolts. There are two categories of fatigue. (i) High cycle fatigue (HCF) and (ii) Low cycle fatigue (LCF). Traditionally the two are classified on the basis of number of cycles required for failure, i.e. failures occurring below 10^4 cycles as LCF and those occurring above that value as HCF.

In case of an un-cracked smooth surfaced component, the first step is initiation of crack, followed by its progress. Crack initiation is related to repeated slip and work hardening, finally leading to microscopic discontinuities (extraditions and intrusions) which develop into cracks. Once a crack is initiated, its growth rate depends on the magnitude of stress, stress gradient, notch sensitivity of the material etc. Variations in the cyclic load result in the development of small ridges or beach or striation marks that are clearly observed on the fracture surface (Fig. 5.11) [16].

As the cross section decreases with crack growth, a stage reaches when the remaining area is unable to withstand the load and ductile fracture occurs. This area is observed as granular area on the fractured surfaced. From the beach marks the origin of crack can be clearly identified. In the presence of a crack or crack like defect or a crack formed during service, its progress often obeys power-law relationship, known as Paris Law [17].

$$\log\left\{\frac{\mathrm{d}a}{\mathrm{d}N}\right\} = m\log(\Delta K) + \log C \tag{5.1.8}$$

Taking out the log gives the equation as

$$\frac{\mathrm{d}a}{\mathrm{d}N} = C\Delta K^m \tag{5.1.9}$$

This is because at constant load the cyclic stress intensity increase with time as the crack grows. In other words the final failure can be predicted on the basis of the growth rate and if critical length of crack is known. The fatigue failure consists of

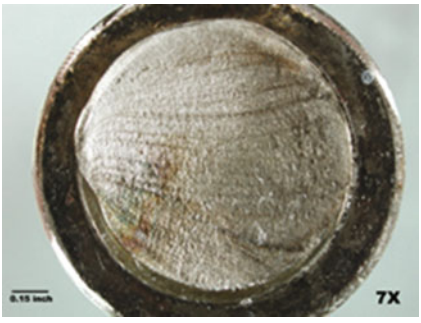


Fig. 5.11 Typical beach marks on fractured surface of a bolt head [16]

two steps, i.e. crack initiation and crack growth, represented as stage I and stage II. In HCF, at low stress the number of cycles required to crack initiation covers a major part of fatigue life, whereas at high stresses the fatigue life is related primarily to crack propagation period. Fatigue properties of a material are generally determined by subjecting a rotating or vibrating sample to known level of alternating stress. The test at different stress is continued till failure or until a limiting number of cycles has been reached (10^6–10^8 cycles). These results are plotted as stress versus number of cycles, as S–N curve. For most engineering ferrous materials, the S–N curves become almost flat at low stresses. This is for all practical purposes known as *endurance limit or threshold stress* below which failure will not occur (Fig. 5.12). Many materials, especially non-ferrous metals and alloys do not show any threshold value and the stress level corresponding to some arbitrary cycles is chosen (generally 10^8 cycles) for the fatigue limit. A safety factor is applied to the fatigue limit in designing of components subjected to fatigue.

The fatigue strength of a material is determined on samples having polished surface, because generally the cracks initiate at the surface and propagate perpendicular to the principle stress. However, the fatigue properties are affected by number of factors. For example,

1. Surface roughness decreases fatigue strength.
2. Fatigue strength is increased by increasing surface hardness e.g. case hardening, nitriding, and surface treatments like shot peening that introduce compressive stress.
3. Under aggressive environments fatigue strength is reduced (corrosion fatigue) and no endurance limit is observed.
4. Stress raisers have maximum effect in reducing the fatigue life. Some of the examples are (a) rapid/sudden change in cross section, e.g., change in shaft diameter; fillet welds; threads in bolts; keyways of shaft; grooves, bolt head, etc. (b) surface discontinuities, e.g. notches, corrosion pits, machining marks, etc.,

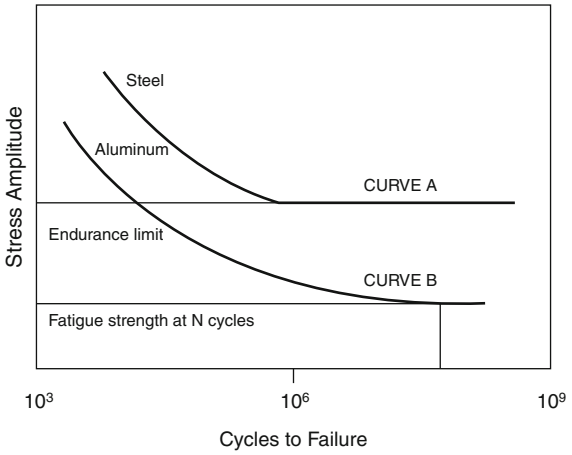


Fig. 5.12 Shows presence of endurance limit in ferrous but not in non-ferrous alloys

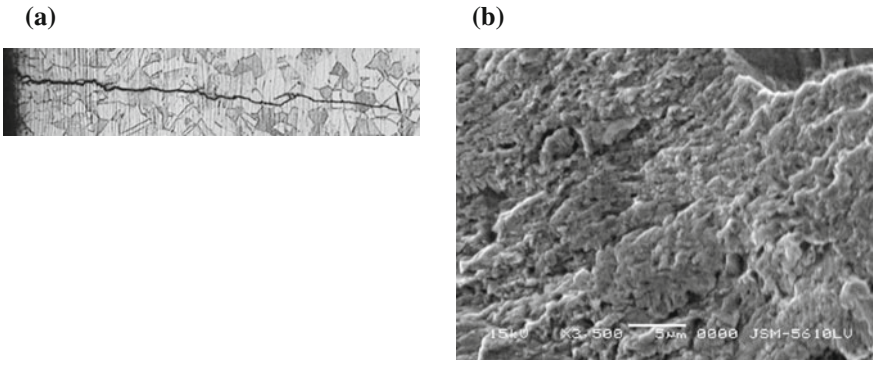


Fig. 5.13 **a** Fatigue crack of 316 stainless steel corrugated heat exchanger tube [18]. X 200. **b** SEM image of fracture face showing growth of fatigue crack [18]. X 3500

and (c) metallurgical discontinuities e.g. inclusions (particularly sulphides as stringers), micro cracks, sharp voids, etc. Fatigue limit increases with increase in the strength of material. The ratio of the fatigue limit to the UTS, known as the *endurance ratio*, generally varies from 0.5 to 0.6 but is drastically reduced to 0.2–0.3 in case of notched specimens. As regards the metallurgical structure, tempered martensite usually has better fatigue strengths than bainitic and ferritic-structure.

5. Fatigue cracks propagate transgranularly and are nearly straight with none or minor branching. Figure 5.13a shows the nature of fatigue crack which was the cause of failure of a corrugated stainless steel exchanger tube [18]. Scanning electron microscope (SEM) image of fracture face of the exchanger tube (Fig. 5.13b) shows typical beach mark.

5.1.9 Creep

At elevated temperatures all metallic materials deform slowly and continuously under the influence of stresses much below their yield stress at a particular temperature. This thermally assisted deformation under load is known as *creep*. The creep process occurs only above a certain temperature, which varies with the material. For example, creep occurs in case of lead at room temperature even at stress as low as its self-load. The critical temperature for creep is $\sim$40% of the melting temperature in Kelvin: and if $T > 0.40T_m$ then creep is likely to occur. Initial creep temperature for commonly used carbon and low alloy steels has been given in Table 5.2 [19].

It can be seen that the creep is likely to occur in carbon steels only above 425 °C. As a consequence of creep deformation, dimensional changes distortion or rupture of the components can occur.

Table 5.2 Initial creep temperature for commonly used alloys

Carbon steel	425 °C
Carbon + 0.5 Molybdenum	455 °C
1.25 Chromium + 0.5 Molybdenum	510 °C
2.25 Chromium + 1.0 Molybdenum	538 °C
Stainless steel	565 °C

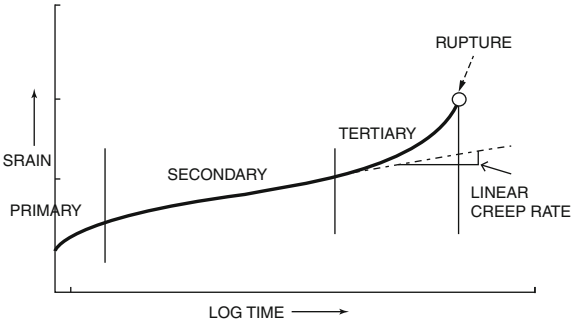


Fig. 5.14 Creep curve showing different stages of creep

For elevated temperatures in the creep range the design basis of any component is not its UTS or YS, but the creep properties, i.e. the time to rupture or the time to cause a given degree of deformation or strain. Creep properties at any temperature are generally determined by measuring the extension of strain of a specimen, subjected to a constant uniaxial stress, as a function of time. Normally the tests are carried out at different temperatures and stresses, by varying one of the parameters. Figure 5.14 shows shape of a typical creep curve. The creep curve can be divided into three stages, i.e. primary (Stage I), secondary (Stage II), and tertiary (Stage III). Of these, the primary one is a decelerating strain-rate stage; the secondary, a steady strain-rate stage; and finally the tertiary is an accelerating strain-rate stage. The duration of each stage is dependent on the temperature and stress. Under most of the practical conditions grater duration of creep life consists of secondary stage. It may be mentioned that similar trends in the creep curves are observed, if tests are carried out at constant stress but with varying temperature. Figure 5.15 shows stress vs. rupture/strain curves under different conditions.

The shape of the creep curves, discussed above, varies because of competing process like (a) strain hardening (b) softening process and (c) damage process. Of these, strain hardening tends to decrease the creep rate whereas the other factors tend to increase the rate. From the creep curves, creep rate rupture time and creep ductility can be determined. Worldwide, numerous commercial alloys from different countries have been tested and data generated. The data collected are sufficient to design for a life of 250,000 h, though the common practice (ASME and API) is to use 100,000 h as life criteria.

As the creep behaviour for any material is time, temperature and stress dependent, attempts have been made to use parametric techniques to incorporate all the three variables to facilitate extrapolation of data. Several parameters have been

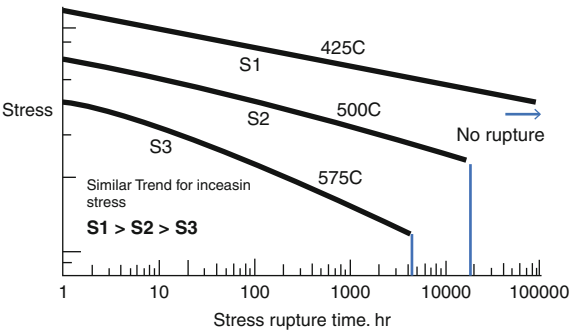


Fig. 5.15 Creep rate dependence on stress and temperature

evolved but Larson-Miller parameter (LMP) is the most preferred one by engineers, because it has been used successfully for long, is easy to understand and use, and has proved to be as accurate as others. LMP is expressed as

$$\text{LMP} = T(C + \text{Log}\, t) \times 10^{-3} \tag{5.1.10}$$

where T is temperature in degrees Kelvin, t is time in hours and C a constant. A value of C between 10 and 40 has been found to be applicable for different materials. Commonly $C = 20$ is used (e.g. by ASME and API) for ferritic alloys and 15 for high temperature austenitic alloys. The formula does not give a single plot of stress versus LMP but a scatter band width on the basis of which, two lines, minimum and means are drawn (Fig. 5.16). The reason for the variable constant is that creep properties for any particular material are dependent on a number of factors, e.g. grain size, phase distribution, etc. All of these cannot be individually controlled precisely in commercial products.

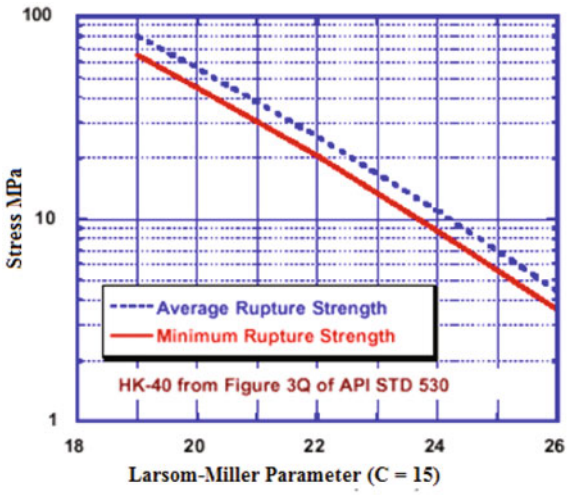


Fig. 5.16 LMP curve for creep rupture of alloy HK 40

5.1.9.1 Effect of Alloying Elements

Alloying elements influence creep properties and of the various elements, molybdenum has the most profound influence on creep strength. Normally within the accepted oxidation rate (up to 650 °C), 2 ¼ Cr–1 Mo steel is the most widely used alloy. For still higher temperatures, austenitic grades are used primarily from the point of view of oxidation and creep resistance. In the recent years use of 9Cr–1Mo (P9) and 9Cr–1Mo–1Nb (P91) has increased, especially the latter, for its excellent creep resistance properties.

Under normal conditions, creep occurs by dislocation climb through diffusion of vacancies or sliding of grain boundaries and, therefore, grain size has an important role to play. Vacancies diffuse more easily in the irregular structure of grain boundaries and hence creep is higher in fine grained material compared to coarse grained ones. Similarly, irregularity along the grain boundary results in first nucleation of cavities followed by their joining to form fissures and final failure. Figure 5.17 shows creep cavities in alloy 321H in a line carrying hot process air (about 700 °C) to secondary reformer of a hydrogen plant. Thus higher creep rate strength is attained by proper selection of alloying elements, control of grain size and distribution of phase which restrict the dislocation movement. Cracking is trans granular at high stress and inter-granular at intermediate and low stresses. The latter mode of failure is more common in actual situations.

5.1.9.2 Creep Based Design

Design Stress

The ASME Boiler and Pressure Vessel Code, Section 1Paragraph A-150 states the criteria used for determining allowable stresses [20]. As per the code the allowable stresses are not to be higher than the lowest of the following:

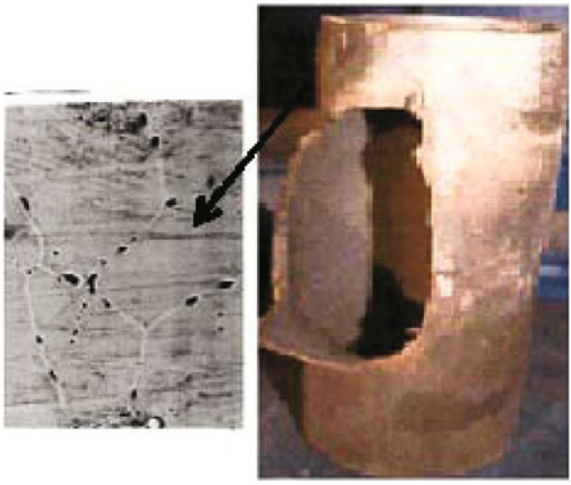


Fig. 5.17 Creep rupture failure of 321H stainless steel piping showing grain boundary voids near failure

- One-fourth of the specified minimum tensile strength at room temperature,
- One-fourth of the tensile strength at elevated temperature,
- Two-third of the specified minimum yield strength at room temperature,
- Two-third of the yield strength at elevated temperature,
- Stress to produce 1% creep in 100,000 h,
- Two-third of the average stress or four-fifth of the minimum stress to produce creep rupture in 100,000 h, whichever is minimum.

The design stress for vessel, piping, etc. operating in the creep range is given in ASME Section VIII Division 1 [21] in tabular form along with that for temperature operating below the creep range (elastic range). For fired heater tubes, LMP curves for different materials given in API 954 [22] form the basis for calculating the heater tube thickness.

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Chapter 6
Heat Treatment

Abstract Heat treatment is the process where requisite properties of formed and finished products are attained using predetermined heating and cooling rates. The treatment is most significant for ferrous materials because the phase transformation from austenite to ferrite can be controlled as the process involves nucleation and growth, which is reflected in time temperature transformation (TTT) curves of different alloys. The time being an important factor, rate of cooling (continuous cooling transformation, CCT curves) also plays an important role. Thus by heat treatment, depending on alloy content, it is possible to get different transformed products like martensite, bainite and pearlite. The major heat-treating processes for carbon and low alloy steels are annealing, normalizing and quenching where the distribution of ferrite and carbide are controlled by alloying and rate of cooling. Quenching which forms hard brittle martensite when tempered also improves the toughness of steel. Quenching is used also for surface hardening as well as for age hardening of some ferrous and non-ferrous alloys. For non-ferrous alloys, annealing is used. In case of austenitic stainless steels annealing requires quenching from high temperature. The chapter presents the mechanism of different heat treatment processes and discusses how the formation of different phases/transformation products can be explained. The role of alloying elements and cooling rates in controlling transformation and the importance of hardenability of ferrous alloys have been discussed. Austenitic stainless steels require solution and stabilizing annealing which involves rapid cooling unlike annealing of ferritic material, which involves slow cooling. The chapter also includes techniques of surface hardening by procedures other than heat treatment.

Keywords Pearlite · Martensite · Annealing · Normalizing · Solution annealing · Hardenability · Quenching · Surface hardening

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6.1 Introduction

For engineering materials heat treatment is one of the important steps in getting requisite properties of both the formed and finished components. Heat treatment, as the word indicates, consists of raising the temperature to ascertain level, depending on the type of material and cooling at different rates as required. The input of heat energy helps in hastening the diffusion process, relieving of locked in stresses, recrystallization of distorted grains, phase transformation, controlling the distribution of phases and impart specific properties for end use. For example, finished products are subjected to process of annealing, normalizing, hardening and tempering; welded fabricated components are subjected to intermediate and post-welded heat treatment (PWHT); cold working involves intermediate annealing during various stages of production; shafts and other components subjected to wear action are required to be surface hardened. There are thus many instances of useful application of heat treatment though heat treatment in some cases (if not properly carried out) can result in degradation of material property, e.g. decrease in corrosion resistance, temper embrittlement, sigma embrittlement, gain coarsening, quench cracking, etc. Understanding the role of heat treatment on material properties is, therefore, absolutely necessary. In this chapter, main emphasis will be on heat treatment of ferrous materials.

6.2 Heat Treatment of Ferritic Steels

The Fe–C binary phase diagram and other binary or ternary alloys containing carbon show the stability of various phases at different temperatures under equilibrium conditions. As discussed in Chap. 3, the stable phase in Fe–C system at room temperature are ferrite and cementite, where cementite, depending on carbon content is present as a part of pearlite or as pearlite + free cementite (beyond 0.8% C). However, in actual practice the equilibrium conditions are rarely attained. The heat treatments of ferritic materials in most of the cases consist of heating to temperature range of fully austenitic state and then cooling to room temperature. The changes occurring on cooling are not possible to be fully predicted form the Fe–C diagram. Any phase transformation involves diffusion, and is time/temperature dependent. Therefore, phases/structure formed and morphology of their distribution varies depending on the condition under which the transformation is occurring. Further, under practical situations, cooling from high temperature involves continuous cooling, and therefore the transformed structures formed are limited by cooling rate. The lowest rate of cooling is attained during cooling inside a furnace and the highest rate by quenching in water. Thus, the kinetics of the transformation of different phases from austenite shall determine the structural characteristics of the transformed products.

6.2.1 Constant Temperature Transformation

Structures formed during continuous cooling of steel from austenitic range cannot be ascertained from equilibrium diagram showing the solid state transformation zone of Fe–C diagram in Fig. 6.1. As a first step it is therefore necessary to establish the rate of transformation products formed and their distribution from stable austenite up to room temperature. Thus, the two variables, i.e. time and temperature with respect to the amount of transformed product is established for different materials. The method of doing this is to heat small steel samples to austenitic range followed by quenching these in a bath held at a predetermined temperature. The samples are maintained at these temperatures for different time to allow the transformation to take place isothermally and then quench the individual sample to room temperature after lapse of the transformation time. The samples are then microscopically examined to distinguish between the isothermally transformed constituent and that formed from the untransformed austenite after quenching. The data collected are plotted as temperature versus log time for different percentages of transformation from the beginning to completion to give the 'S–curve', also known as time–temperature-transformation (TTT) curve. From the curve, an overall picture of the transformation behaviour of austenite is obtained. Such a curve for carbon steel containing 0.6%C (hypo-eutectoid) steel is shown in Fig. 6.2 [1].

Comparison of binary and TTT diagrams shows that in both cases, the phases obtained are ferrite and cementite but the rate and the nature and distribution of phases in transformed ferrite/cementite aggregate vary with temperature at which the transformation takes place. The transformation products, consisting of ferrite/cementite aggregates are categories as (a) coarse pearlite, (b) fine pearlite,

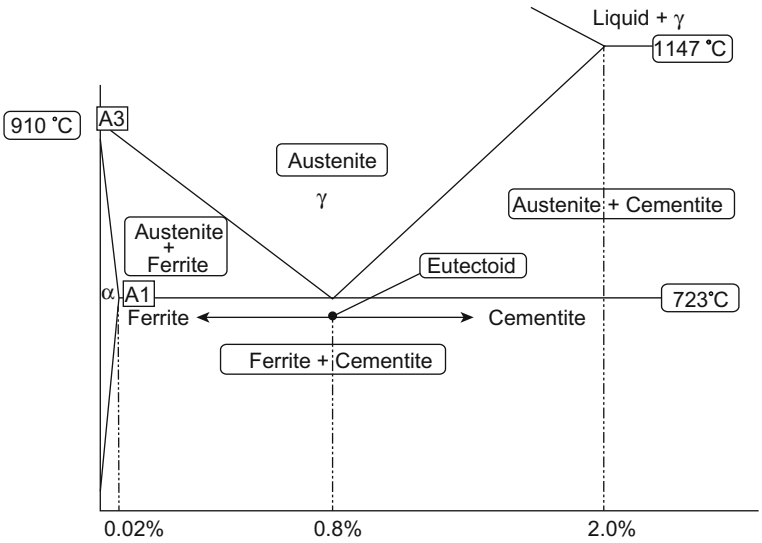


Fig. 6.1 Fe–C diagram showing the eutectoid region

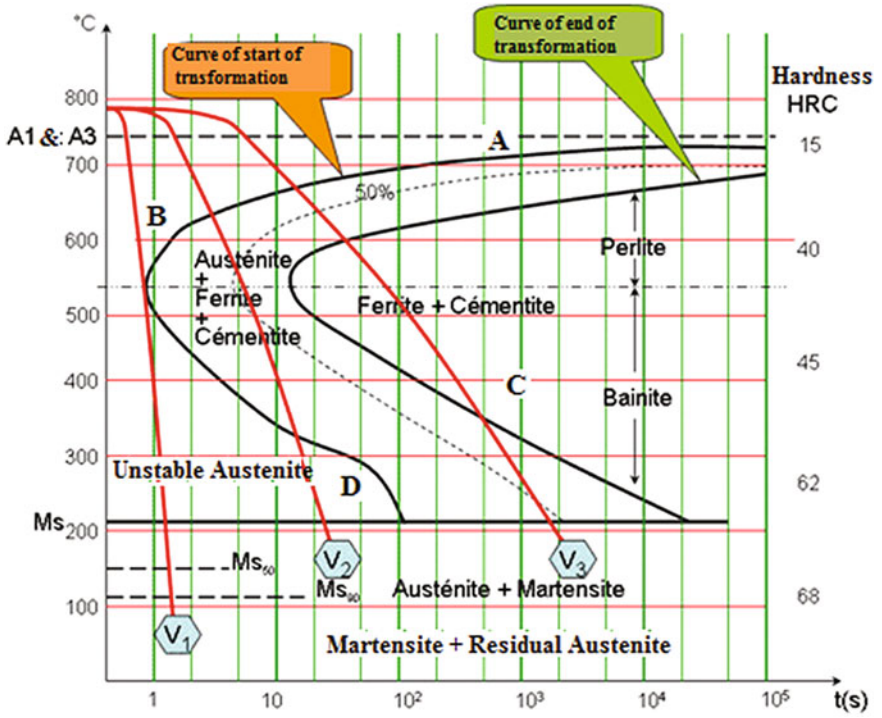


Fig. 6.2 TTT curve of 0.8%C steel [1]

(c) upper bainite and (d) lower bainite. In addition to the above four, a fifth transformation product, known as *martensite*, is formed below a certain temperature whose crystal structure is different from that of ferrite, austenite or cementite.

The salient features of transformation of austenite from TTT curve can be described as follows:

(a) Any transformation (other than martensitic) involves nucleation and growth, and therefore is time/temperature dependent. The start of reaction is controlled by nucleation reaction, which is slow at temperatures just below A_1/Ae_1 (eutectoid) as high thermal energy makes it difficult for a stable nucleus to form. Thus, both the start and finish of reaction are delayed. As the degree of super cooling from the equilibrium temperature (723 °C) increases, more and more nucleus are formed and there is corresponding increase in transformation rate and reaction is completed in shorter time [2].

(b) However, beyond a certain degree of super cool, growth rate decreases because of decrease in thermal energy at lower temperatures. Thus, the rate controlling factor changes from nucleation to growth. The overall effect of the two opposing reaction is that with increasing degree of super cooling, the reaction rate first increases and then decreases giving a C–curve shaped transformation versus time curve. To understand this phenomenon which controls many of the reactions, both

physical and chemical, we can consider simple case of formation of ice. Water solidifies at 0 °C but controlling factor for the time taken for the liquid water to be converted into solid ice depends on at what temperature below 0 °C the change is taking place. If we keep water at say −1 °C it will take much more time to solidify than if it is kept at ∼−20 °C in the ice box of a fridge. It is common to store food, perishable items, etc., in dry ice which is the general term used for solid carbon dioxide (CO_2), which solidifies at −78.5 °C. Suppose we now keep liquid water in dry ice chamber the formation of water will be very fast confirming the important role of super cooling in kinetics of reaction. As regards the TTT curve of 0.8%C steel given in Fig. 6.2 we can divide the same in four zones A, B, C and D.

- **A**: Just below the eutectoid temperature first reaction to start will be transformation of austenite into pearlite after reaching the start of reaction curve. The amount of pearlite would continue to increase till the time end of transformation curve is reached when 100% pearlite will be formed. As the temperature in this case will be high not only the transformation would take long time to start but the pearlite formed will also be coarser. However in case the steel contains lower carbon (hypoeutectic steel), then the TTT curve will have another transformation line prior to the start of formation of pearlite. In such a case, start of pearlite will be preceded by that of ferrite and the end product would consist of ferrite and pearlite.
- **B**: This reaction will be at higher degree of super cool and the same products, 100% pearlite or ferrite + pearlite, depending on carbon content, will be formed except that the time taken will progressively decrease. The pearlite formed will however be fine.
- **C**: In the temperature range between 560 and 300 °C, ferrite and cementite aggregates, called bainite, are formed having different structure than that of pearlite. The structure of upper bainite has feathery appearance and lower bainite resembles to some extent have needle like appearance with fine precipitates of carbide. The difference between bainite and pearlite formation is connected with low diffusion at this high degree of super cooling. In case of lower carbon steels both fainite and bainite are present.
- **D**: If the cooling is rapid enough so that the nose of curve is avoided then austenite stability, at such a high degree of super cool, is drastically reduced. At such low temperatures, the thermal energy is low for diffusion processes to take place within reasonable time. As a result the austenite gets athermally (constant temperature) transformed instantaneously below 300 °C into ferrite by shear action, a diffusion less reaction. The carbon in austenite is unable to come out, which is retained in solution in ferrite, which has solubility limit of only 0.002%. As a result the ferrite lattice is elongated along the vertical (c) direction. The degree of distortion, i.e. c/a ratio increases with increase in carbon content. It must be noted that complete transformation takes place athermally in steps and, therefore, martensite formation has also starting and end temperatures designated as M_s and M_f, respectively.

The structures of bainite and martensite are shown in Fig. 6.3a, b respectively.

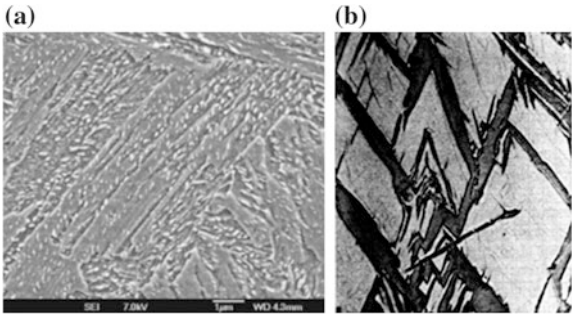


Fig. 6.3 **a** SEM microstructure of lower bainite obtained after isothermal transformation for 900 s at 355 °C. **b** Martensite "needles" in a matrix of austenite in a high carbon steel

6.2.1.1 Factors Affecting TTT Curves

The rates of transformation of austenite are affected by its composition, gain size and homogeneity. In general, increasing carbon and alloy content tends to decrease transformation rates. Similar effect is observed with increasing gain size of austenite as the transformation is nucleated preferentially at grain boundaries. Alloying elements have also profound influence on the TTT curves. The transformation curves can shift to the right, left and also up or down, depending on type of alloy. Further, the whole curves does not always shift in tandem and by alloying, curves for ferrite, pearlite and bainite can be affected in different ways. Three types of curves are obtained, i.e. transformation controlled by the (a) ferrite curve (b) pearlite curve and (c) bainite curve as shown schematically in Fig. 6.4 for some of the alloys. In addition, Ms point can also move up or down.

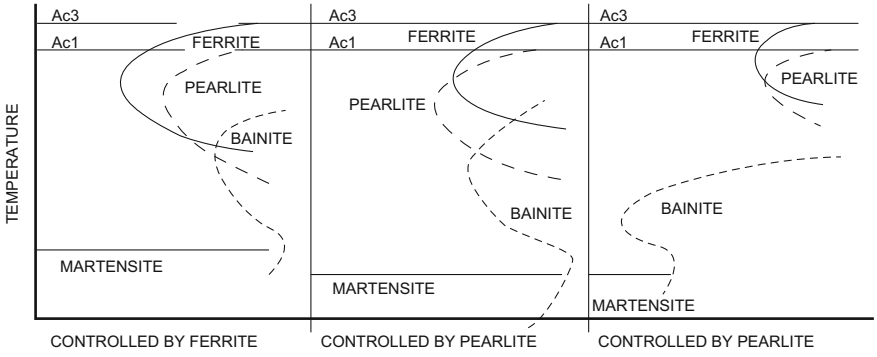


Fig. 6.4 Shows possible shifts in TTT curves of different steels

The effect of some of the important alloying element can be summarized as follows:

(i) Carbon, nickel, manganese, silicon and copper move both pearlite and bainite formation curves to the right. For example, in case of a 0.35%C steel, the start of both ferrite and pearlite reactions cannot be suppressed, but in case of eutectoid steel (0.8%C), the nose does not touch the zero time axis. In other words, in case of former theoretically it is not possible to get 100% martensite as ferrite formation precedes formation of martensite.

(ii) Molybdenum, chromium and vanadium move the pearlite curve to both right and up; on the other hand the bainite is only displaced downwards. Thus, there may be two or three noses for different transformation reactions.

(iii) By combination of alloying elements, lines for different reactions can also be separated.

TTT curves of some common alloy steels are shown in Fig. 6.5. TTT curve of wide varieties of steels are available which is normally used as reference [3].

6.2.2 *Transformation on Continuous Cooling*

The transformation products formed in actual situation can now be derived from the superimposition of cooling rate on TTT curve. The cooling rate may vary within slow to extremely fast rates, cutting the TTT curve at various points as shown for Fe–0.8%C steel in Fig. 6.6. These are known as *continuous cooling transformation (CCT) curve.* From the intersection points of the two curves, the type and extent of transformed products that can be obtained by any particular mode of heat treatment can be predicted. Referring to Fig. 6.6, the following the following transformation products are expected when cooled from austenitic temperature:

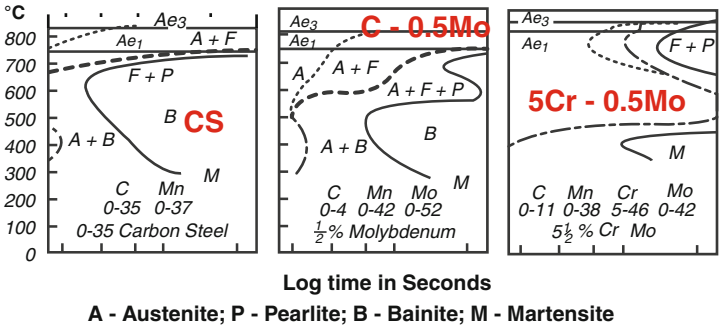


Fig. 6.5 Effect of alloying elements on TTT curves. Alloy containing 5%Cr shows shift of ferrite and pearlite to right and that of Ms upward

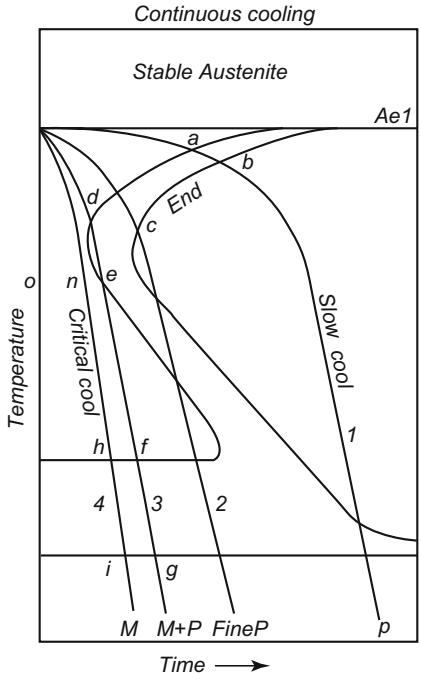


Fig. 6.6 Continuous cooling transformation (CCT) curve of 0.8% carbon steel

- Curve 1, i.e. very slow cooling, e.g. furnace cooling, will give fully pearlitic steel because the line cuts both start and end of pearlite transformation at high temperature. However, as the transformation takes place at high temperature over a longer period, the nucleation is slow but growth rate high. As a result coarse pearlite is formed.
- Curve 2, e.g. air cooling in still air, will also give 100% pearlitic structure. The line cuts nearer the nose of the TTT curve, where the temperature is much lower than eutectoid temperature, the nucleation rate will be high but growth slow. As a result, fine pearlite will form.
- Curve 3, obtained by faster cooling, as in quenching, will give fine pearlite along with martensite as the line crosses start but not the end of transformation line. The residual austenite on further will be transformed to martensite below "f".
- Curve 4 which involves highest cooling rate will completely avoid the nose of the curve, retaining 100% austenite at Ms temperature "h", forming fully martensitic structure below 'i'. The minimum cooling rate by which the nose of the transformation is avoided is known as *critical cooling rate* of the particular alloy.

Thus from the nature of TTT curves for either plain or alloyed steel, it is possible to derive the type of structure obtained and thus also the required final property. Similarly, cooling rate curves can be superimposed over the various TTT curves of steels shown in Fig. 6.5 to predict the presence of different transformation products.

For example, if we consider the TTT curves of 0.3%C steel and 5Cr–0.5Mo, given in Fig. 6.5 and superimpose different cooling rate curves, it will be observed that

- It will not be possible to get martensite in 0.3%C steel under normal quenching conditions as tip of the nose is absent in TTT curve and transformation to ferrite and pearlite shall occur.
- On the other hand, the nose of 5Cr–0.5Mo is shifted so much to the right that the critical cooling rate will be very low and formation of martensite can be avoided only if cooling is done at very low rate.
- Thus in case of many alloy steels where the nose of the reaction shifts to the right a fully martensitic or bainitic structure is obtained with much less severe quenching.
- Atlas of transformation needs to be consulted to achieve the required properties [4].

6.2.3 Important Heat Treatment Processes

Heat treatment forms an important process by which large changes in the properties of material can be achieved along with alloying with different elements. Some of the commonly performed heat treatments are discussed.

6.2.3.1 Annealing

Annealing is an important process which is used for both ferrous and non-ferrous metals and alloys. Annealing has different purpose for different materials but the main objective is to bring it in a state where equilibrium structure exists, strength is reduced but ductility is improved and internal stresses are minimized. Annealing is required under the following conditions:

- In case of non-heat treatable non-ferrous alloys grains are elongated during cold working due to plastic deformation resulting in increase in strength and loss in ductility. Further working becomes possible only by restoring the ductility by intermediate annealing. In cold working, a number of intermediate annealing steps may be involved. Final annealing is done to improve material properties. The reduction in internal stresses in the material also reduces chances of stress related in-service mechanical or environment related failures.
- For non-ferrous castings like bronze, inhomogeneity or coring is more persistent than in brass and, therefore, these require longer time for annealing. Coring affects uniformity in mechanical properties and reduces corrosion resistance.
- Plain carbon steel is annealed to get homogenous ferrite pearlite structure with good ductility but lower strength. Low and medium alloy steels having strong tendency to martensite or bainite formation even during air cooling, require to be annealed to improve the mechanical properties before use.

- For steel casting, annealing is carried out by heating below the eutectoid temperature, mainly to remove internal stress and quite above A3 (about 80 °C) to reduce inhomogeneity and for grain refinement.

Annealing Temperature and Time

Annealing is a time and temperature dependent process and, therefore, both are to be controlled. In case of carbon and low alloy steels, the full annealing temperature is 20–50°C above the upper critical temperature of concerned composition. As an example annealing temperatures and hardness for some of the carbon and low alloy steels are given in Table 6.1 [5]. Too high annealing temperature should be avoided to prevent austenite grain growth which may result in decreased strength and ductility.

Recrystallization

In case of low carbon steel and non-ferrous metals, especially those having single phase structure, annealing is carried out to refine the grains, remove the cold worked structure and restore ductility. Cold work elongates the grains and on heating beyond a certain temperature, which is specific for different materials and known as *recrystallization temperature*, new equiaxed grains are nucleated. With increase in temperature and time these grains grow by absorbing each other, reaching an equilibrium size which is specific for the particular temperature. The changes taking place during the process of recrystallization and annealing are shown in Fig. 6.7.

The recrystallization temperature and grain size also depend on prior degree of cold work. If percent cold work is low, the points at which new grains can nucleate are fewer in number resulting in coarse grains. On the other hand, with heavy cold working very fine grains can be produced. With proper control of degree of cold work, temperature and time very large size grins or single crystals can be successfully produced. In low carbon steel recrystallization temperature is around 500 °C and annealing (known as *process annealing*) is carried in the sub-critical region of 550–700 °C.

Table 6.1 Annealing temperature of some steels

Alloy designation	Annealing temperature (°C)	Hardness after annealing (BHN)
1020	875	121
4130	865	156
4140	815	197
5140	830	167
5150	825	197

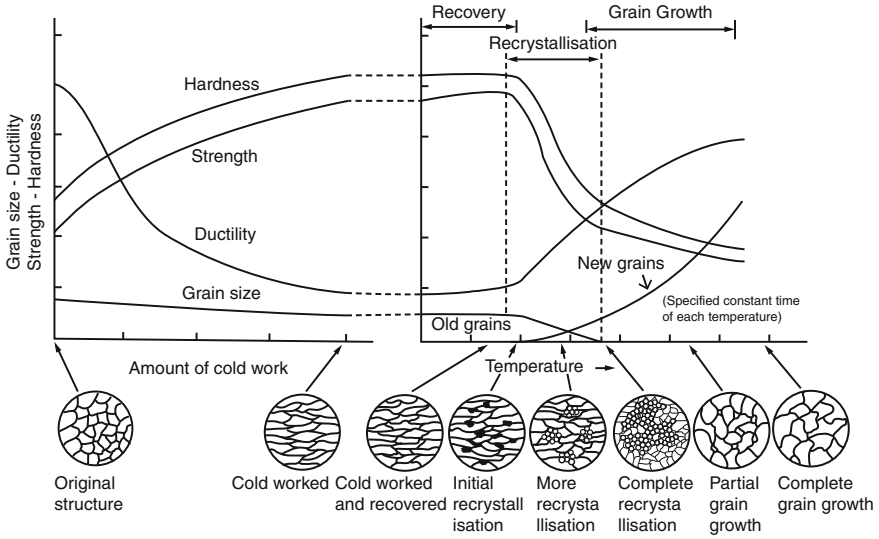


Fig. 6.7 Changes in grain size and mechanical properties on recrystallization

6.2.3.2 Normalizing

Normalizing is done on steel where the material is heated to a temperature, little higher than (30 °C) that for annealing, soaked for some time which increases with thickness as shown in Table 6.2 [6] and then cooled in still air. For steels containing carbon above 0.25%, tempering after normalizing is preferred. This reduced the chances of hard spots formed due to uneven cooling rates. In addition, it helps in increasing toughness. Normalized and tempered steels are, therefore, specified (including those having higher thickness) in many cases. Air hardening grade of steels, cannot be normalized. The strength and impact values of normalized steels are higher than these obtained by annealing. Carburizing grade alloy steels, e.g. 3310 and 4320 are usually normalized at temperatures higher than the carburizing temperature to avoid distortions during carburization.

Table 6.2 Approximate soaking time for hardening, annealing and normalizing of steel

Thickness of metal (in.)	Soaking time (h)
Up to 1	½
1–2	½
2–3	¾
3–4	1.0
4–5	1.0
5–8	1½

6.2.3.3 Quench Hardening

Quenching from austenitic range is an important method by which hardening of steel is achieved. In this connection both the mechanism of heat removal during quenching and hardenability of steel are two important considerations. As evident from earlier discussion, if critical cooling rate is reached, which involves high rate of cooling, hard transformation structures like martensite and bainite are formed. However, this does not mean that the whole cross section develops the same structure, the reason being difference in cooling rate from core (centre) to the surface. On quenching, cooling starts from the external surface coming in direct contact with the coolant. Further, severity of cooling on the external surface also varies during the course of cooling, which in case of liquid coolant can be divided into three stages, A, B and C, as shown in Fig. 6.8. During stage A, the quenched surface is very hot and a continuous vapour film is formed around the article due to DNB (deviation from nucleate boiling) condition. During this period the cooling is slow due to the insulating effect of vapour. On decrease in temperature during Stage B, nucleate boiling (NB) starts operating when continuous collapse of vapour film on metal surface takes place. Highest rate of cooling is the attained due to violent boiling of quenching liquid around the article occurs. The rate of cooling is related to the boiling point of quench liquid. Finally in stage C, cooling takes place at a much slower rate by conductance. Through thickness cooling is therefore by transfer of heat from inside to outside. The overall effect is that cooling rate would be highest at the surface and progressively decrease with depth becoming minimum at the centre as shown in Fig. 6.9.

Accordingly, the nature of transformed products and hardening effect across the cross section would vary, depending on the TTT curve of the concerned alloy.

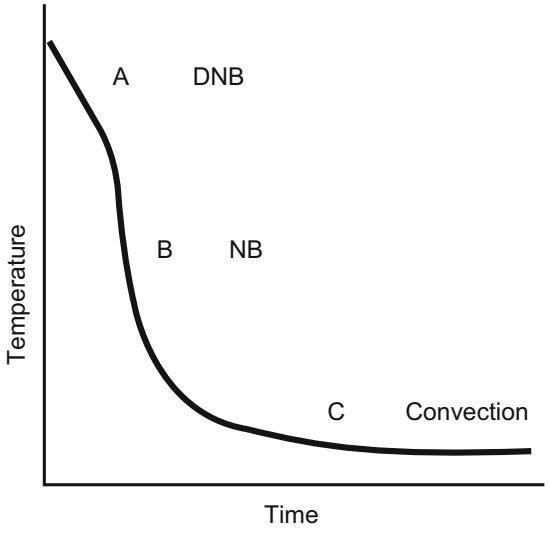


Fig. 6.8 Intensity of cooling during three different stages of quenching

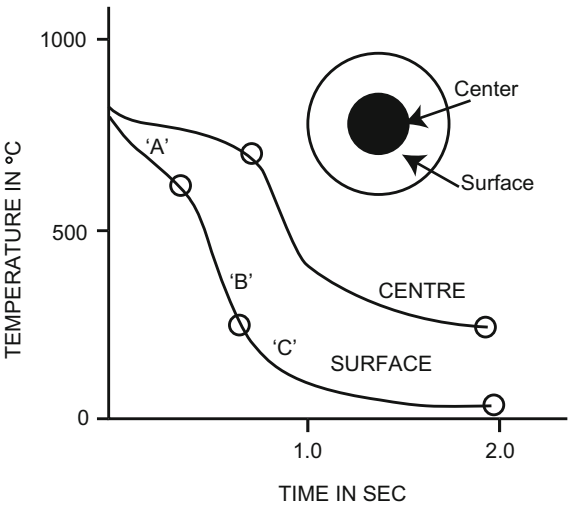


Fig. 6.9 Variation in temperature between centre and surface of a circular bar

As example hardness across the cross section of two grades of steel of different diameters quenched in water (giving different cooling rates), is shown in Fig. 6.10.

Hardenability

We have discussed earlier the transformation of austenite in carbon or alloy steels to transform into pearlite, bainite or martensite, products having different hardness. Depending on heat treatment and composition of steel, different properties can be achieved. Here hardenability of alloy steel concerned is important where hardenability can be defined as measure of depth and distribution of hardness to which steel will harden on quenching from austenite.

Grossman Test

Systematic work on hardenability was first taken up by Grossman and co-workers [7]. It has been discussed earlier that on quenching, variations in the hardness and transformed product occur across the cross section. A microscopic examination of the structure shows that maximum hardness is more or less constant till the martensite content remains $\geq$ 50%, which gets lightly etched compared to portion towards centre of specimen where ferrite/pearlite structure predominates. Grossman test consists of quenching several cylindrical bars of different diameter of the steel under consideration followed by taking hardness measurements on transverse section of different bars and find out maximum diameter where 50% martensite is obtained at the centre. This diameter is designated as critical diameter D_O, for the particular steel in a particular coolant. However, critical diameter would vary with the severity of quench and for this Grossman Quench Severity, or H-factor was

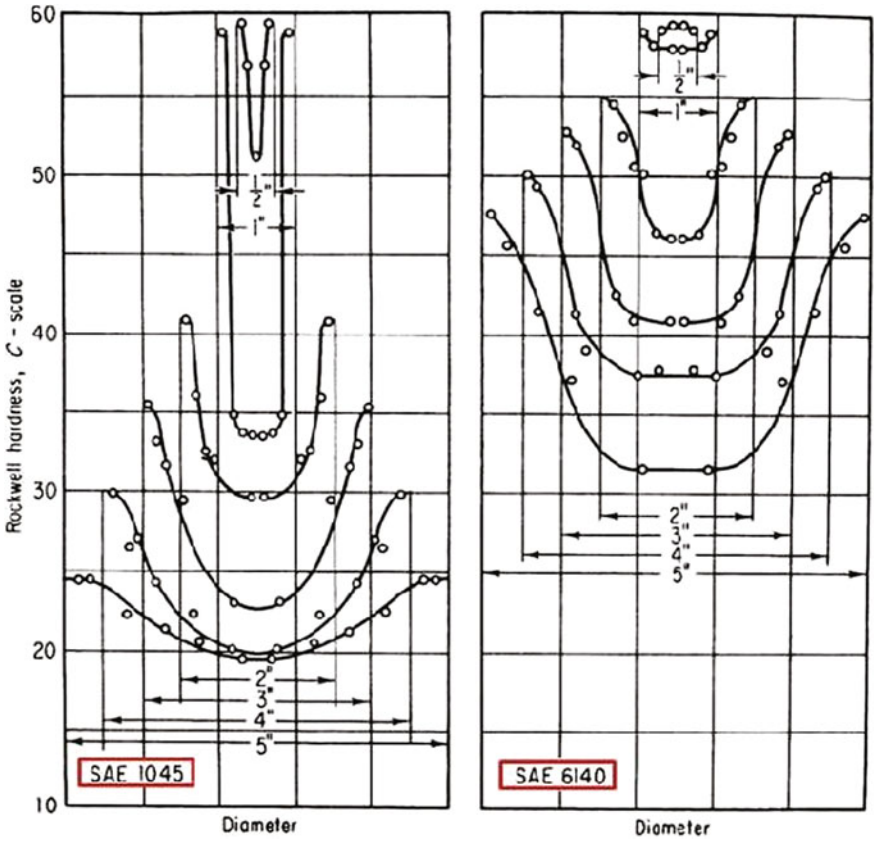


Fig. 6.10 Hardness across cross section of two grades of steel of different diameters heat treated in same quenchant

introduced which is defined as the ratio of the effective heat transfer co-efficient (h) at the part's surface divided by twice the thermal conductivity (k) of the metal:

$$H = \frac{h}{2k} \tag{6.2.1}$$

Table 6.3 [8] gives traditionally used Quench Severity Factor (H) values for still and agitated brine, water, oil and air. The severity in still water is considered as 1 and an H-factor of 5.0 is about as high as is practically achievable.

With development of different oils and polymers as quenchant, the range of severity of quench has been widened.

Brine gives faster cooling rate than water because on vapourization salt crystals are formed on metal surface which in turn breaks the vapour film and thus cause faster cooling during stage B. Salt also raises the boiling point causing less severity in quenching. Chances of soft spots are minimal and the process does not require

Table 6.3 Quench severity factor 'H' compared to water at 65 °F (18 °C)

Circulation or agitation	Quench severity factor, 'H'			
	Brine	Water	Oil	Air*
None	2.0	0.9–1.0	0.25–0.30	Still 0.02
Mild	2.0–2.2	1.0–1.1	0.30–0.35	Circulated air 0.032
Moderate	–	1.2–1.3	0.35–0.40	
Good	–	1.4–1.5	0.40–0.50	
Strong	–	1.6–2.0	0.50–0.80	
Violent	5.0	4.0	0.80–1.10	

*Reference: Quenching Media, http://www.tpub.com/steelworker1/12.htm

vigorous agitation which normally is to be done in case of water. Oil, on the other hand, is a comparatively mild quenching agent and if hardness is sacrificed to some extent, this can be used without any distortion or cracking of components. In alloy steels where considerable shift in nose of TTT curve takes place, oil quenching will give better full thickness hardness.

Thus D_0 can be determined under various H-factors for a particular alloy. Further assuming $H = \infty$, that is, infinitely rapid rate, ideal critical diameter (D_I) can be determined which has minimum. 50% martensite at the centre of the bar. Plot of actual critical diameter D_0, against ideal critical diameter D_I for different H-factor is then plotted. For any alloy on the basis of a quenching experiment D_0 is measured and then from the plot critical diameter is estimated. This value is the measure of the hardenability of given steel independent of the quenching medium used [9].

Jominy End Quench Test

The accelerated test by which the hardenability is determined is known as Jominy End Quench test, shown schematically in Fig. 6.11. This is a standard test [10] where one end of the 1" dia. × 4" length (25 mm × 100 mm) round specimen, heated to proper austenitizing temperature, is subjected to a jet of water impinging on one end of the sample as shown in Fig. 6.11. The jet of water impinging on the surface is standardized so that there are no variations in the rate of cooling. After the test, the sample is taken out and hardness taken at 1/16" intervals along the quenched bar. Prior to taking the hardness two parallel surfaces are ground to a depth of 0.015" (0.38 mm). Hardness readings are taken in Rockwell C. The results are plotted, starting from quench end, as a curve of hardness versus distance. The plot can also be considered as hardness versus cooling rate since each distance is also equivalent to a certain actual cooling rate. The results plotted in Fig. 6.12 show hardness against distance and cooling rate for various grades of steel. In practical situation it is also important to know the depth at which 50% martensite will be achieved (considered as fully hardened). Thus critical diameter (D_O) can be determined for different severity conditions from Jominy test results. Percentage martensite against distance is also included in Fig. 6.12. It is important to keep in mind that Jominy test gives a band within which all data of distance versus hardness fall for a particular grade of steel. The band width is controlled by the range of alloying elements specified in chemical composition of concerned specification.

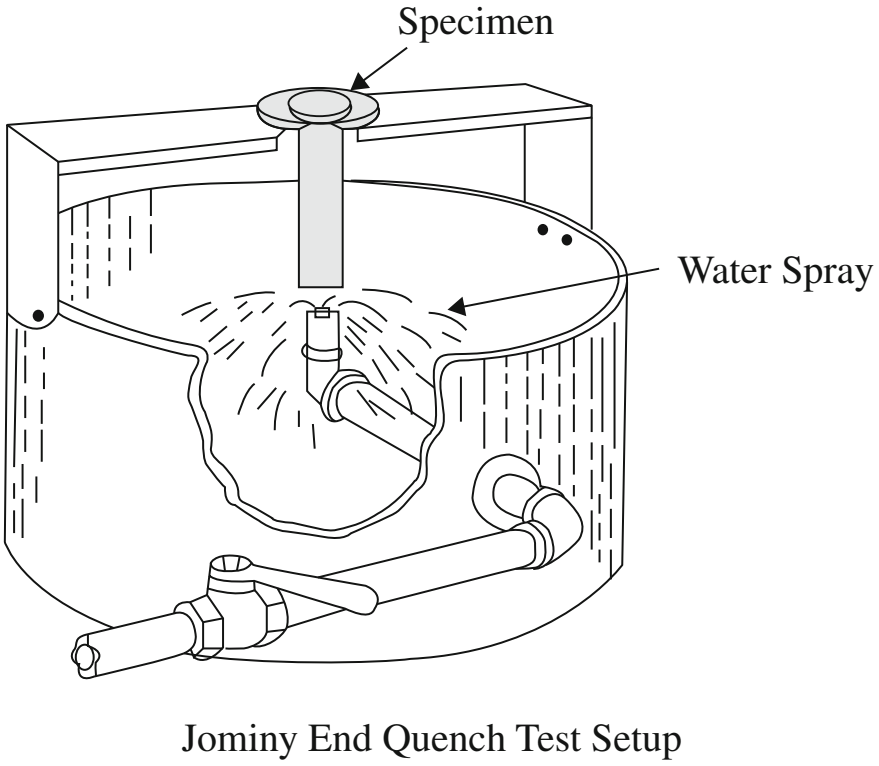


Fig. 6.11 Set up for determining hardenability of an alloy

Alloying increases the depth of hardening of steels. In situations where a tough core with shallow hard surface is required, normal carbon steel (with small amounts of Cr, Ni, if necessary) is sufficient. On the other hand, addition of 3% Ni and 1% Cr will considerable increase the depth of hardening even if oil quenching is used. It has been shown that small additions of a number of elements are more effective than equivalent total addition of one element. In some instances, bainite is the preferred transformation product. This is achieved by proper selection of alloying and quenching procedure.

Tempering of Hardened Steel

Hardened steel after quenching has high internal stresses is hard and brittle and therefore not suitable for direct use. To make the quenched component usable, it is reheated to different temperatures, depending on desired final properties. The process is known as tempering. Depending on the end use, quenched material is tempered by reheating at different temperatures (normally between 250 and 700 °C)

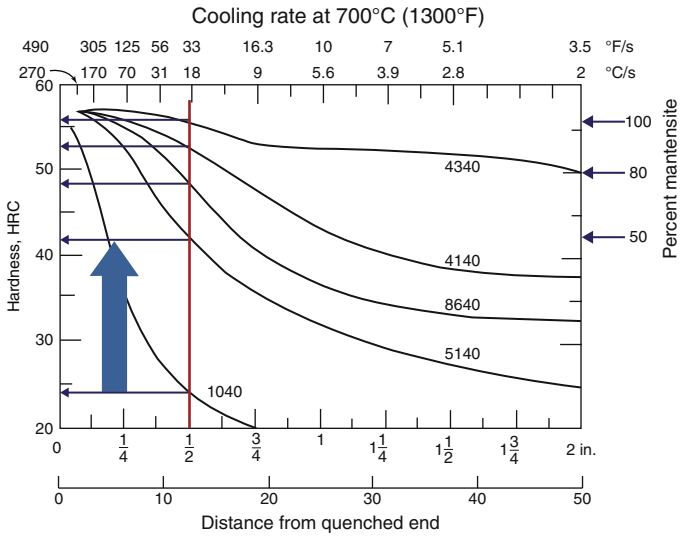


Fig. 6.12 Hardenability curves for five different alloy steels, each containing 0.4 wt%C

and for different time to relieve stress, reduce hardness and impart ductility to allow the saturated carbide to precipitate out, depending on the desired use. The various changes occurring can be stated as follows:

- **Stage 1.** 50–200 °C. Martensite breaks down to a transition precipitate known as Є-carbide + a low carbon martensite. Slight increase in hardness occurs.
- **Stage 2.** 205–305 °C. Decomposition of retained austenite to bainite takes place along with increase in hardness (known as secondary hardness).
- **Stage 3.** 250–500 °C. Conversion of low carbon martensite and Є-carbide into ferrite takes place and cementite gradually coarsens resulting in rapid softening.
- **Stage 4.** 400–700 °C. Carbide types change in alloy steel. First cementite is formed and then the alloying element diffuses into it to form equilibrium carbides which in case of chromium containing steel will be in order: Fe_3C–Cr_7C_3–$Cr_{23}C_6$.

Some typical structural changes occurring while tempering of martensite along with some of the uses are illustrated in Fig. 6.13.

Temper Embrittlement

This phenomenon reduces the notch impact strength when alloys containing Mn, Ni and Cr are slowly cooled or held for a long time in the temperature range of 350–550 °C. Other mechanical properties are not affected. Sb (0.001%), P (0.008%), As, Sn, Mn increase while Mo and W decrease susceptibility of steel to temper

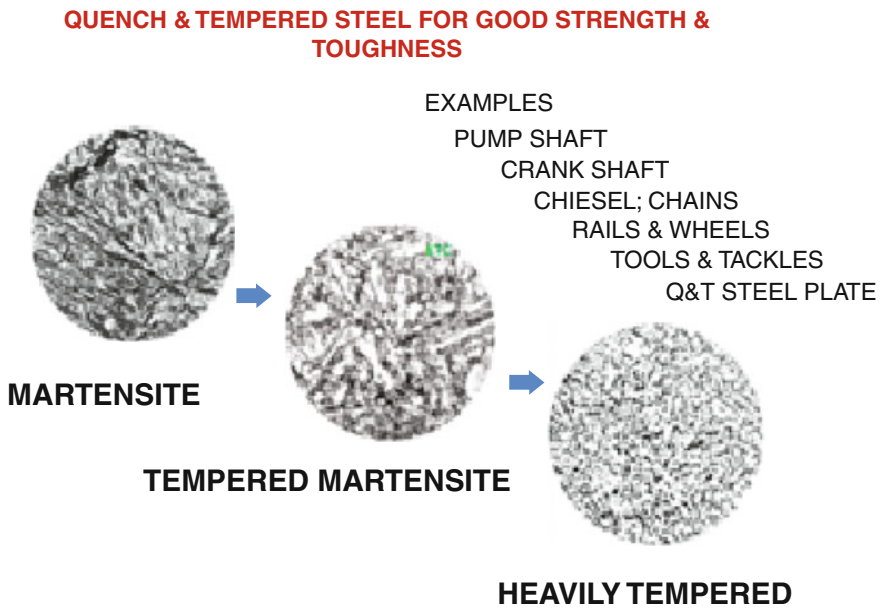


Fig. 6.13 Changes in microstructure on tempering of martensite

embrittlement. Grain boundary segregation is considered to be the main cause. That is why all chromium containing low and medium alloy steels contain minimum 0.5% Mo though this does not ensure complete freedom from embrittlement. Tungsten is another element which helps in reducing temper embrittlement. This phenomenon has been discussed in greater detail in Chap 8.

6.2.3.4 Age Hardening

In some alloy system, it is possible to harden and increase strength to various degrees by solution treatment followed by ageing at a temperature where precipitation of intermetallic compounds takes place. Such treatment is also known as precipitating *hardening*. This method is of considerable importance in Al–alloys like A1–Cu and Al–Mg–Si, Cu–Be, and precipitation hardening (PH) stainless steels. In this method, the advantage is taken of decrease in solubility of solute with decrease in temperature and separation of an intermetallic compound form the solid solution. Figure 6.14 explains schematically the age hardening process of Duralumin (Al–4%Cu alloy).

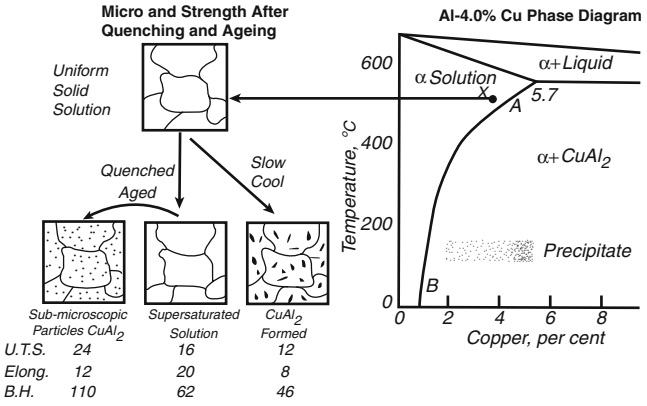


Fig. 6.14 Enhancing strength by precipitation hardening heat treatment

6.3 Surface Hardening

6.3.1 Carburizing

In many components like shafts, roller bearings, chains, etc., a combination of tough core and a hard surface against surface wear is required. To meet these requirements, various methods are available and one of the widely used one is *case carburization.* In this case, low carbon steel or low alloy steel is selected to meet the strength and ductility requirements of the component. This steel is then treated to enrich the surface with carbon. The components are heated above 900 °C in a carbon rich solid, liquid or gaseous media for some time whereby carbon enters steel and diffuses to a certain depth to enrich the surface layer with carbon. Treatment in solid is known as pack carburization. Roughly machined sections are packed in wood or bone charcoal containing 10–15% barium carbonate as an energizer to promote rapid reaction. The box is sealed and heated at 900–950 °C in the austenitic range where carbon solubility is very high. Because of diffusion of carbon from the surface, carbon gradient is established between surface and the core. After the process is completed the article are cooled down in the box. Liquid baths consists essentially of sodium cyanide and soda ash heated to 900–950 °C. These are particularly suited for thin case of 0.08–0.25 mm thickness on articles subjected to wear and fatigue, e.g., gear and shafts of automobiles. Addition of barium chloride activated cyanide bath is used to get a case depth of up to 1 mm. It gives faster penetration with surface content of up to 1%C and 0.24% nitrogen. Gas carburizing, on the other hand, uses propane or natural gas and is carried out in gas-tight container in an atmosphere of neutral carrier gas. In this case, it is possible to keep a close control of the carbon potential which plays a major role in the carburizing process.

6.3.1.1 Heat Treatment After Carburizing

After completion of carburization, suitable heat treatment is given to impart the final required properties to case and core. A two-step heat treatment is necessary after carburizing because of carbon gradient between surface and core. In the first step, the core is heat treated to give requisite structure by heating above upper critical point followed by quenching to give a mixture of ferrite and martensite. At this temperature all the cementite in the case goes in solution and forms brittle coarse martensite. Reheating to a temperature just above the critical range corresponding to the carbon in the case, followed by quenching, leads to the formation of hard but less brittle martensite. This treatment also tempers the core. Plain carbon steels containing less than 0.2%C are normally used for case hardening. In case of alloy steels, nickel and chromium are commonly used. Boron (0.004%) is sometimes used along with manganese.

6.3.2 Nitriding

To get a thin hard surface, enrichment of surface with nitrogen is carried out by heating low alloy steels in dissociated ammonia at about 500 °C. Normally, Cr–Mo steels with small addition of aluminium are nitrided. A surface hardness of 900–1100 VPN can be attained. Bearing surface of shafts are hardened for wear resistance by carburizing, nitriding or carbonitriding.

6.4 Heat Treatment of Stainless Steels

In this section, heat treatment of austenitic and duplex stainless steels has been discussed as these are the main grades used in process industries. The major difference between these stainless steels and carbon and alloy steels is the allotropic modification shown by later alloys. This results in formation of different types and amounts of phases and structures having properties varying within wide range. Such changes do not take place in austenitic and duplex stainless steels, and therefore not of much concern. However, changes do take place in these alloys when exposed at high temperatures in the range of 400 and 815 °C (see Chap. 7) which generally prohibits any heat treatment which involves exposure in this temperature range. These changes are basically related to precipitation of carbides or formation of intermetallic compounds, affecting the performance.

6.4.1 Austenitic Stainless Steels

6.4.1.1 Solution Heat Treatment

For getting optimum performance, austenitic stainless steels should be free from stresses and presence of precipitated chromium carbides. To meet these two main requirements all stainless steel plates, pipes, forgings, etc., are to be annealed by heating to temperatures of 1050–1120 °C to remove stress and dissolve all precipitated carbides. This is followed by rapid cooling so that the material is exposed to shortest possible time in the susceptible temperature range of 400–815°C. Rapid cooling is done either by water quenching or forced circulated air (severity compared to water is 0.032) [11]. This type of heat treatment is known as "solution annealing" or "quench annealing" to distinguish from annealing of ferritic steels like carbon or low alloy steels. Both hot and cold worked products are to be subjected to annealing. Heat treatment of stainless steels increases its resistance to corrosion and also their creep strength.

6.4.1.2 Stabilizing Heat Treatment

In stabilized grades of stainless steels, titanium and niobium carbides also go in solution. These steels are slowly cooled to temperature ~900 °C when titanium and niobium carbides get precipitated out in preference to chromium carbide. This reduces the chances of knife-line attack or poylthionic acid cracking.

6.4.2 Duplex Stainless Steel (DSS)

DSS requires full solution anneal which consists of heating to high temperature, as in case of austenitic stainless steel, followed by rapid cooling. This treatment helps in getting optimum mechanical and corrosion resistance properties. The solution annealing temperatures vary with the grade and specification of DSS. The minimum and range of temperatures quoted by International Molybdenum Association (IMOA) [12] and M/S Outokumpu [13] are given in Table 6.4.

Table 6.4 Solution annealing temperatures of duplex stainless steels

Alloy	Solution annealing temperature (°C) (IMOA)	Solution annealing temperature (°C) (Outokumpu)
LDX 2101	–	1020–1080
2304	980–1040	950–1050
LDX 2404	–	1000–1120
2205	1020–1120	1020–1100
25 Cr Duplex	1040 (Gr. 255)	–
2507	1025–1125	1040–1120

6.5 Other Surface Treatment Processes

There are number of special surface treatment processes which have been developed to meet specified service requirements. Some of these are described next.

6.5.1 Shot Peening

Shot peening is a cold working process in which a surface is bombarded with shots of metallic, glass or ceramic balls of 0.18–0.36 mm diameter at high speed. The striking balls stretch the metal surface and form small depressions or dimples. The tensile stress induced on the surface due to stretching action results in producing below the dimple a hemisphere of high compressive stress (Fig. 6.15). Overlapping dimples develop a uniform layer of residual compressive stress on the metal surface up to a certain depth, which is the intersection of applied tensile stress and peening generated residual stress which consists of both compressive and tensile components along the thickness as shown in Fig. 6.16. The compressed layer is about 0.25 mm deep in case of shot peening.

Benefits obtained by shot peening are the result of compressive stress and the induced cold working. Compressive stresses are beneficial in decreasing the possibilities of tensile stress induced damages [14, 15]. Shot peening is therefore used to

- Increase fatigue life.
- Increase resistance to SCC and hydrogen assisted cracking.
- Decrease fretting and galling.
- Increase resistance to cavitation erosion.
- Reduce welding stresses of repair weld in situ when PWHT is not possible.

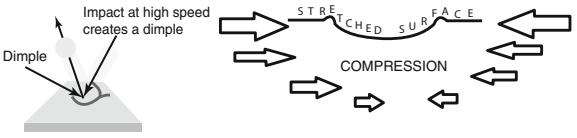


Fig. 6.15 Shot pinning results in depression and as a result a thin layer of compressive stress is developed

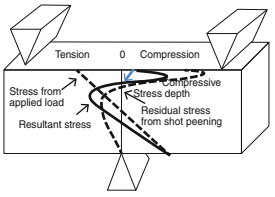


Fig. 6.16 Effect of shot pinning on stress across the thickness. Compressive stress up to *dotted arrow*

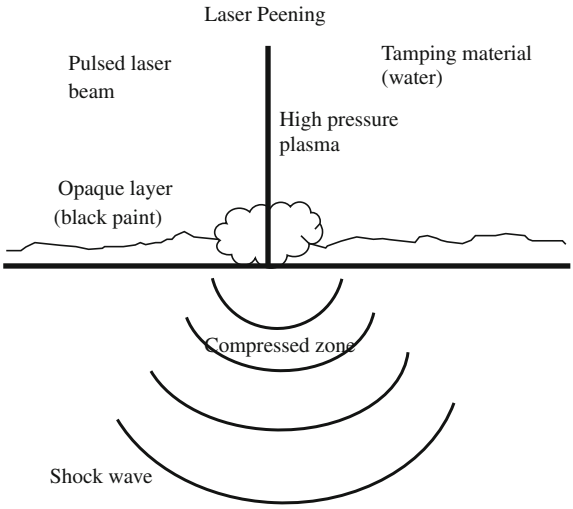


Fig. 6.17 Laser peening process

6.5.2 Laser Peening

In the recent years, advances in technology have made it possible to use streams of laser beam to get the effect of shot peening. This is also known as *Laser Shot Peening System*. In laser peening, a black tape or paint is put on the surface and bombarded with powerful laser beam. When the pulses of energy from the laser are absorbed by the opaque material, the heat generated vapourizes and forms high temperature plasma. The plasma gas trapped between the work piece surface and the transparent water layer limits the thermal expansion of the gas resulting in increase in the gas pressure to extremely high value. The high pressure is transmitted to the work piece producing a shock wave, which travels through the part of material and generates compression stress as shown in Fig. 6.17. The stress waves passing through the material produces a layer of residual compressive stress, similar to shot peening. The process is repeated till the desired thickness of compressive layer is obtained, which can be as deep as 1–2 mm, which is much higher than what is achieved in shot peening.

The advantages of laser peening are same as those of shot peening but the process is economical only for precision and critical components.

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Chapter 7
Metallurgical Aspects of Welding

Abstract Welding is the commonly used method for joining of metals. The process consists of filling the gap between the two ends with liquid metal which when solidifies forms a strong bond. During the process the base metal attains high temperature at the liquid/solid interface and a temperature gradient on both sides of the weld is formed. In case of ferritic steels, martensite or bainite or pearlite is formed adjacent to the weld at different cooling rates, depending on TTT and CCT curves of the alloys. Martensite and bainite are hard, and on cooling cold cracking occurs due to hydrogen pick up during welding. Cold cracking is avoided by taking steps to prevent hydrogen pick up, reducing the rate of cooling, and tempering of brittle structure by post-weld heat treatment (PWHT). In case of austenitic stainless steels welding is easy as no phase transformation is involved. However, to avoid hot cracking small amounts of ferrite in the consumable is necessary for which WRC 1992 constitution diagram is used. Duplex stainless steel (DSS) alloys are required to follow a procedure which ensures weld deposit to have equal ferrite/austenite phase mixture that provides good corrosion resistance and ductility. In this chapter, various metallurgical aspects of welding of ferritic steels such as the phenomenon of cold cracking and its avoidance by controlled weld procedure, dehydrogenation of weld prior to cooling at room temperature, use of low-temperature intermediate PWHT and other stress relieving methods have been detailed. The methods to avoid PWHT such as temper bead welding, buttering technique, friction stitch and seam welding have been described. Welding of austenitic stainless steel along with the allied problem of HAZ cracking, welding of DSS steels, titanium and of dissimilar metals and outlines of underwater welding have been provided. Use of friction heat for joining, used in nuclear and offshore industry, has also been described.

Keywords Cold cracking · Welding stress · Post-weld heat treatment · Temper bead welding · Stainless steel welding · Hot cracking

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7.1 Introduction

Welding as a joining method for fabrication of pressure components replaced riveting in the early 1930s. In conventional fusion welding, joining is achieved by applying heat, with or without the addition of the filler meal, to produce a localized union through fusion. Weld metal has a cast structure against worked structure of the base metal. Ideally, the filler metal should match the composition of the base metal but a closer matching of mechanical properties (tensile, impact, creep, etc.), freedom from cracking and, in some cases, resistance to corrosion are of greater importance, which because of the structural differences are not always attained. The present chapter does not cover the topic of welding per se but discusses some of the important metallurgical aspects of fusion welding primarily with respect to fusion welding of carbon, alloy and stainless steels.

7.2 Welding of Ferritic Steels

During welding, the base metal around it is heated in the range where ferrite transforms to austenite. On the other hand, fused weld deposit also transforms to austenite on cooling. When the component is cooled after completion of welding, phase transformation takes place in both the weld and the base metal adjacent to the weld (known as *heat-affected zone* or HAZ in short). The nature of the transformation products depends on chemical composition and cooling rate.

7.2.1 Structure of Weld Deposit

During the process of fusion welding, it is essential that fusion extends to some distance into the base metal or the previous pass, when multipass is used. This is also known as depth of penetration of weld. The completed weld forms different zones as shown schematically in Fig. 7.1. The admixture of filler metal and melted

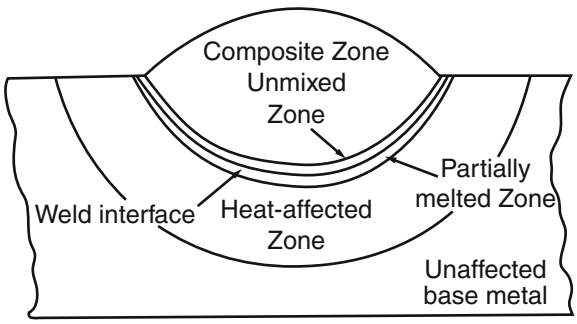


Fig. 7.1 Different zones formed in weld

base metal forms a completely melted and homogenous weld fusion zone. This is followed by a narrow melted layer of essentially the base metal composition and partially melted zone. Low melting inclusions and impurities normally tend to segregate in the latter region. This is the main cause of hot cracking of welds. Finally, between the solid parent metal and the weld there exists the HAZ. This zone does not undergo melting but passes through a high temperature cycle which, in turn, causes metallurgical changes. The structural characteristic of the weld and HAZ depends on the nature of material being welded. The HAZ consists of number of zones, and the one nearest to weld interface has a coarse grain structure. While basic effect of heat involved during welding is similar, no major changes occur in HAZ in metal and alloys which do not show allotropic modification. In case of austenitic steels, however, the problem with the HAZ is related to corrosion.

Temperature gradient exists on both sides of weld and the HAZ, which remains solid throughout welding. In this region the temperature surpasses temperature of the ferrite to austenite transformation. When the weld cools down, transformation of austenite to ferrite takes place. The transformed structure formed in the weld or HAZ depends on the chemical composition of the base metal and the rate of cooling. The TTT curves of base and weld metal determine the types of transformed structure that can form during the process of cooling. For carbon steels, up to 0.3% C, the structure will consist of ferrite and pearlite mixture. However, in case of higher carbon and low and medium alloy steels, the transformation product will be martensite, bainite or mixture of martensite + ferrite or bainite + ferrite, depending on the composition and rate of cooling. In most of such cases the solidified weld and HAZ will have hard and brittle constituents. This high strength, low ductility structures have a large effect on not only the completed weld but also on in-service performance of weld.

7.2.2 Cold Cracking

This is the most common and important type of failure associated with welding of ferritic steels. The welds are susceptible to cold cracking due to the combined effect of stresses produced due to (a) constraints of parts being welded and shrinkage of weld (inducing tensile stresses), (b) crack sensitivity of transformed constituent of HAZ, and (c) hydrogen picked up by the weld and base metal, during the process of welding. The hydrogen plays most important role in this type of cracking, as stated below:

1. The molten weld pool absorbs hydrogen from consumable flux and from the surrounding environment due to the reaction of hot metal with any moisture present in these:

$$Fe + H_2O = FeO + 2H_2 \tag{7.2.1}$$

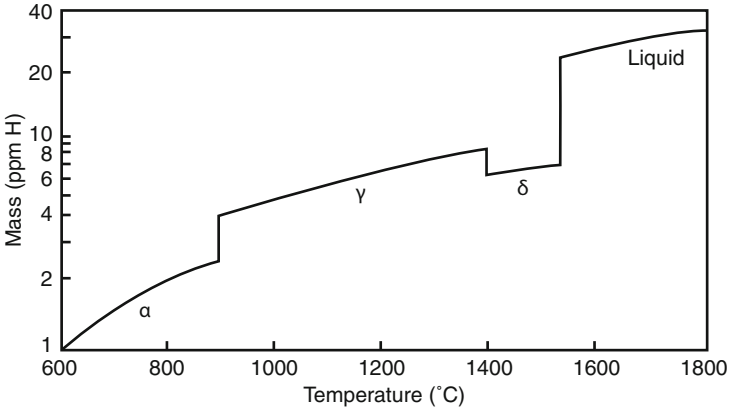


Fig. 7.2 Solubility of hydrogen in iron

2. Solubility of hydrogen in molten and solid iron changes with temperature and its crystal structure as shown in Fig. 7.2. The solubility at atmospheric pressure drops from ~30 wppm at 1800 °C to below 1 wppm at room temperature [1]. Maximum solubility in δ ferrite and austenite has been reported up to 8.0 and 9.5 ml per 100 g, respectively [2].
3. Much of the hydrogen absorbed by weld pool escapes as it solidifies but a part of it also diffuses into the HAZ and adjacent base metal.
4. Austenite has higher solubility for hydrogen than ferrite. As the cooling is faster than the rate at which the hydrogen will diffuse out, the transformed products formed from austenite remains supersaturated with hydrogen.
5. If the transformed microstructure of weld and HAZ is crack sensitive and the temperature below embrittlement temperature, cracking due to hydrogen-assisted embrittlement (HE) occurs.

Cold cracking is, therefore, a hydrogen related embrittlement phenomenon. The mechanism can be broadly described as follows considering that the cracking is due to hydrogen enhanced de-cohesion. As discussed earlier it is now universally accepted that no material can be considered as free of defect. In the presence of a notch like defect triaxial stress is created at crack tip when subjected to tensile stress. This increases the stress and makes the dislocations immobile at crack tip. Hydrogen picked up by the metal (during welding or any other process) has a tendency of migrating towards the high stress area at crack tip and form a cloud of hydrogen around it, also called 'Cottrell Cloud' [3]. This area of metal becomes liable to develop a crack. When local crack tip opening stress exceeds the cohesive strength, a crack is initiated which stops beyond the hydrogen cloud as illustrated in Fig. 7.3. The stress concentration point is then shifted at the tip of extended crack and the process is repeated. If such a process leads to cold cracking then the crack progresses in steps and not at one go.

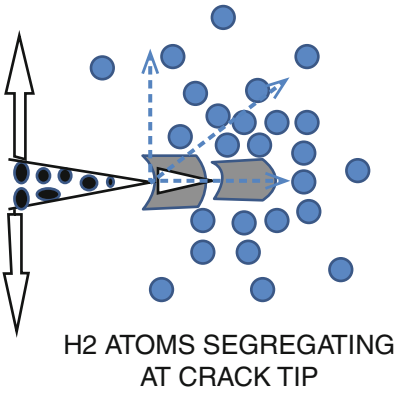


Fig. 7.3 Mechanism of H embrittlement due to absorption of H atoms

The delayed nature of crack initiation and propagation has been established experimentally by measuring the change in electrical resistance or sound (acoustic) emitted where qualitative assessment of progress of crack can be made [4]. As crack occurs after some lapse of time subsequent to welding, this is also known as *delayed cracking*. Cold or delayed cracking can occur within minutes, hours or days after welding. The delayed cracks developed after inspection (radiography or ultrasonic) of weld go undetected which sometimes lead to in-service failures. For alloys, highly susceptible to delayed cracking, equipment fabricators inspect the welds after minimum 48 h of the completion of welding. American Welding Society Code [5] also requires a delay of 48 h for inspection of weld in case of high strength Q/T steels having crack sensitive HAZ like A514, A517, A709 Gr. 100 steels. In conclusion, it can be stated that the ability of ferritic steels to tolerate the level of hydrogen is dependent on strength (indirectly on composition, structure and hardness) of the material. Higher the strength, lower is the tolerance level of hydrogen. The critical hydrogen content also depends on plate thickness and the welding parameters. With increase in thickness, tolerance for hydrogen decreases.

7.2.2.1 Carbon Equivalent

As cold cracking is related to crack sensitive microstructure, propensity of cracking depends on the composition (hardenability) of steel where carbon along with the other elements (deliberately added or present as impurity), determine the nature of transformed structure as indicated from TTT curves. In this connection the CE formulas have been developed by normalizing the chemical composition of a material into a single number to indicate its hardenability. The simplest model of CE is a linear model where critical cooling rates of individual alloying elements on hardenability have been converted to equivalent effect of carbon and the sum total of these added to the actual carbon content. Thus finally it is the CE and not the

carbon content which is considered in welding of steel. Plain carbon steels contain, in addition to carbon, manganese and silicon which affect the phase transformation behaviour. Initially the CE has therefore been expressed on the basis of these two elements in steel as

$$\mathrm{CE} = \%\mathrm{C} + \frac{\mathrm{Mn}}{6} + \frac{\mathrm{Si}}{4} \tag{7.2.2}$$

The above formula ignored the effect of other elements present in small amounts as alloying element or as impurities. To take this account a number of formulas have been suggested but presently the commonly used relationship is:

$$\mathrm{CE} = \%\mathrm{C} + \frac{\%\mathrm{Mn}}{6} + \frac{\%\mathrm{Cu} + \%\mathrm{Ni}}{15} + \frac{\%\mathrm{Cr} + \%\mathrm{V} + \%\mathrm{Mo}}{5} \tag{7.2.3}$$

For assessing weldability, in addition to CE carbon content of steel is also important and the relationship between the three can be expressed in typical Graville diagram shown in Fig. 7.4. The three zones can be defined as follows:

- Zone I—Steels have low carbon and low hardenability and can be easily welded.
- Zone II—Steels having higher carbon level but lower hardenability. In this case welding can be performed without possibility of cracking by some preheat and through control of heat input.

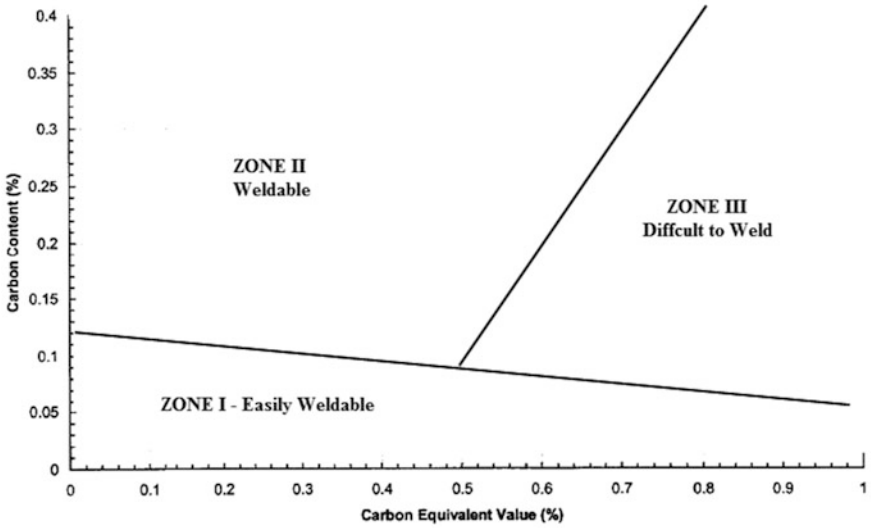


Fig. 7.4 Graville diagram for steel showing three zones of weldability

- Zone III—Steels with high carbon and high hardenability produce crack sensitive micro structure under all conditions. Welding procedure here would require close control of preheat and PWHT.

7.2.2.2 Prevention of Cold Cracking

To minimize cold cracking, one or more of the following steps are taken:

1. Reduction/elimination of crack sensitive microstructure:
   - Preheating: It is an extremely effective method, used to reduce the cooling rates of weld and HAZ to form a more favourable microstructure. With preheating, the temperature gradient and the thermal conductivity (in case of iron) are reduced. Both of these ensure slower cooling rates because the heat is conducted from the welding zone at a lower rate. Thus, the preheated weld is more likely to have lower hardness than a weld made without preheat. The latter is important for low alloy steels where transformation to martensite takes place readily.
   - Interpass temperature should not be below preheat temperature and should also not be very high especially to avoid restriction on heat input and grain coarsening in the HAZ, which adversely affect toughness/ductility of the weld. Maximum preheat and interpass temperature normally should not exceed the recommended minimum for particular steel by more than 80 °C.
   - A proper control over the CE is highly desirable; not only to avoid in-services cold cracking but also to avoid hydrogen assisted stress corrosion cracking. It is a general approach to limit the CE 0.43–0.48 (as per ASME SA-20), depending on the thickness; CE increasing with thickness. However, the best performance is obtained with CE of <0.4.
   - Various codes give the basis for determining preheating temperature but a broad approach can be stated as follows:
     - CE less than 0.45%—Optional preheating
     - CE more than 0.45% but less than 0.6%—93 to 204 °C
     - CE more than 0.6%—204 to 317 °C
2. Reduction in pickup of hydrogen:
   - Here basically one has to tackle the source of hydrogen and the following steps would ensure reducing the hydrogen picked up during the process of welding. The important steps are as follows:
     - Avoid as far as possible high humidity periods.
     - Avoid use of cellulose covered electrodes and hydrogen in shielding gases.
     - Make the surface of the component to be welded moisture free by warming ($\sim$60 °C) in case preheating is not being done during the course of

welding. In case of maintenance welding inside equipment, this should be considered a must because of high humidity environment in closed area.

- Use low hydrogen electrode and fused instead of agglomerated slag. Electrodes are available with different diffusible-hydrogen contents. The International Institute of Welding (IIW) designation system for hydrogen potential of welding consumables is 'very low' for up to 5 mL/100 g; 'low' for 5–10 ml/100 g; 'medium' for 10–15 mL/100 g; and 'high' for more than 15 mL/100 g of weld metal deposited. The American Welding Society, on the other hand, assesses electrodes via a logarithmic scale for diffusible-hydrogen levels in a weld deposit. H16 is for 16 ml/100 g of weld metal (17.6 ppm), H8 is for an electrode producing less than 8 mL/100 g (8.8 ppm), the common upper limit for 'low hydrogen' and H4 is for less than 4 ml/100 g or 4.4 ppm [5].
- Preheat (dry) the electrode before use as per manufacturers recommendations. It is considered a good practice to dry only required number of electrodes for the day to avoid re use of those dried once.
- Bake out hydrogen from equipment under hydrogen and sour service before the start of weld.
- In case of alloy steels of higher thickness subject the welded article to low-temperature hydrogen bake out or intermediate heat treatment before cooling prior to carrying out NDT and PWHT.

3. Reduction in residual stress:

– It is a common experience that many failures occur at weld or in the HAZ, under the influence of stress. There are many reasons for the weld joint to be in stressed condition, e.g. applied/operating stress, joint restrain, weld of insufficient area, welding stresses, etc. Of the various factors responsible, the most important one is the welding stresses. In other words, the welds develop stresses after completion of the job. The stress can be as high as the yield stress of the material. Welding stresses do not go above this because stresses beyond are released due to local yielding (strain).
– Why stresses develop during welding can be explained on the basis of changes occurring during the welding. When weld is deposited on the surface, the area below the bead is heated and tends to expand. However, this expansion is localized and a temperature gradient exists around the heated zone. Thus, the bulk of the material resists this expansion. On the other hand, when the completed weld cools, it contracts but the bulk of the material which is at higher temperature stops it from contracting freely. As a result the opposing stresses between welds and the base metal the area below the weld develops compression and the rest tension. As the built-in or residual stresses are related to expansion and contraction of the metal, the welding stresses in austenitic steels will be higher compared to ferritic steel. The welding stresses are both in the longitudinal and transverse directions but the extent of stress is greater in case of the former.



Fig. 7.5 Rupture of thick wall converter during hydro test after fabrication [6]

– To reduce the stresses the following steps are followed:

  Reduce joint restrain.
  Modify weld procedure to minimize residual stresses.
  Subject the welded component to post weld heat treatment (PWHT), which forms an important part of welding process. This treatment is mandatory as per ASME Section VIII Div. 1 beyond certain thickness. The basic objective is to increase resistance to brittle fracture by improving notch toughness and reduce stress by PWHT.

Post Weld Heat Treatment (PWHT)

Post weld heat treatment forms an important part of welding process by which varieties of metallurgical objective can be achieved. Some of the important effects of PWHT are: (a) stress relieving (b) tempering of hard structure to improve toughness and mechanical properties, and (c) effusion of hydrogen absorbed by weld and HAZ. The PWHT temperature generally varies from 590 to 720 °C, depending on composition of steel and final hardness requirements, but in any case the temperature should always be below the eutectoid transformation temperature or tempering temperature of quenched and normalized steels. In the latter case, too high a temperature may adversely affect the desired mechanical properties due to softening effect. Normally a temperature below the tempering temperature is also preferred during post fabrication PWHT.

PWHT, as per code, can be carried at lower temperature and ASME Section VIII allows PWHT up to a temperature of 480 °C for P-1 materials provided the time is increased. The required microstructural changes can, however, be obtained in most of the cases only at higher temperatures, especially where the important controlling parameter is maximum limit on hardness of the weld and the HAZ. While selecting PWHT temperature the latter requirement should be kept in view. Figure 7.5 shows a thick walled vessel, which failed during hydro test after fabrication [6]. In this

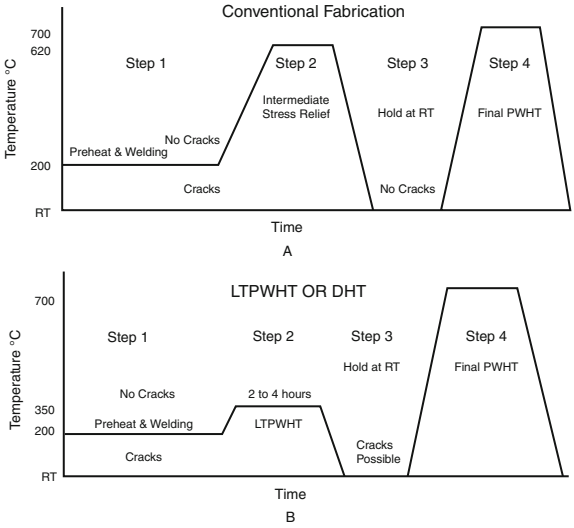


Fig. 7.6 Comparison of conventional and LTIPWHT procedure

case the investigation showed the failure was due to combination of factors, such as, pre-existing crack located at the weld between shell and forged nozzle, low notch toughness of weld metal and inadequate PWHT.

Intermediate (IPWHT) and Low-Temperature Dehydrogenation Heat Treatment (LTDHT)

For Cr–Mo and high strength quenched and tempered low alloy steels, where plate thicknesses are high, intermediate PWHT (IPWHT) is given during welding to avoid hydrogen related cracking. The conventional IPWHT for 2.25Cr–1Mo steel is carried out at ~600 °C. To reduce the time factor, in early 1980s a new low-temperature intermediate PWHT (LTIPWHT), also known as *low-temperature dehydrogenation treatment* (*LTDHT*), was developed to meet the primary aim of IPWHTT, that is, reducing hydrogen to a safe level to avoid cracking. Figure 7.6 compares schematically heat treatment by the two methods of PWHT. LTIPWHT, unless properly conducted to reduce dissolved hydrogen below the threshold limit, can cause in-service cracking. Sometimes, hydrogen induced micro cracks, can grow and coalesce over a period of time during operation, into macro cracks, leading to failure. This approach is also applicable for repair welds. Table 7.1 gives a summary of two incidences of failure of identical ammonia converters having wall thickness of 125 mm, using inadequate LTIPWHT in conjunction with hygroscopic agglomerated welding fluxes [7]. This resulted in higher hydrogen pick up during welding. Eleven other converters of essentially the same design, welded with low hydrogen fused flux with a 600 °C IPWHT followed by stress relieving in a furnace, did not show the presence of any cracks even after 16 years of service.

Table 7.1 Comparison of failed ammonia converters

Alloy	France 2.25Cr–1Mo	Germany 2.25Cr–1Mo
Start-up	1985—Built in France	1982—Built in Germany
Leaked after	4 years	8 years
Final PWHT	H_2–N_2–16% NH_3	H_2–N_2–11% NH_3
Temperature	750 °F	750 °F
Pressure	2600 psi	2600 psi
Welding	Submerged arc, agglomerated flux + LTIPWHT	Submerged arc, agglomerated flux + LTIPWHT
Repair	Weld removed; weld repaired using agglomerated flux with LTIPWHT	Weld removed; weld repaired using agglomerated flux with LTIPWHT
Subsequent cracking	1-in/year	Unknown

LTIPWHT or LTDHT should, therefore, be carefully implemented to ensure absence of any cracks during fabrication or weld repair. There has been an instance, where failed weld of an ammonia converter cracked after only nine months of operation. Investigation showed that the temperature during final PWHT was low and the structure was crack sensitive.

As already mentioned, the maximum PWHT temperature is dependent on the nature of alloy and final desired hardness of the weld and HAZ. It is to be ensured that during PWHT the mechanical properties do not fall below the minimum specified. This care is all the more necessary when necessity arises for re-PWHT, either after re-welding to remove any defect in the original weld or for repair welding as a part of maintenance activity. The number of heat treatment cycles to which particular equipment can be subjected to is, therefore, to be pre-determined. It is presently a common practice to order thick plates meeting the minimum mechanical properties when subjected to tempering of total hours equivalent of four PWHT cycle at little above the PWHT temperatures. In such a case it is assumed that two cycles of PWHT would be required during fabrication and two required for any weld repair during the operation of the equipment. In case of such a requirement from fabricator/user, samples taken to determine the mechanical properties (included in material data sheet) is subjected to the requisite period of tempering by the steel manufacturer.

7.2.3 Stress-Relief Cracking

Many welded alloy steels containing strong carbide formers, e.g. chromium, molybdenum, vanadium, niobium, titanium are susceptible to cracking during PWHT or when put in service at elevated temperatures. These cracks, also termed

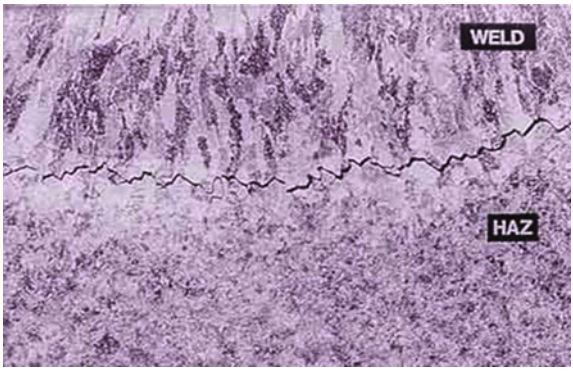


Fig. 7.7 Reheat cracking. Cracks are intergranular [8]

as *reheat cracking*, usually run parallel to the weld (Fig. 7.7) in the HAZ and sometimes in the weld metal itself [8]. As already discussed, the HAZ nearest to the weld has a coarse grain structure. This area retains almost all the alloying elements in solid solution and, therefore, develops higher strength but creep ductility is adversely affected. During PWHT, the locked in residual stresses are released by a creep/strain relaxation process. It is now accepted that the presence of strong carbide formers and the presence of impurities segregated at grain boundaries, enhance susceptibility to reheat cracking. It may be noted that the same composition factors also adversely affect creep ductility and temper embrittlement.

7.2.4 Other Methods of Reducing Weld Residual Stresses

Residual stresses are reduced during PWHT to a level near the yield point of the material at the temperature of PWHT. Final residual stress remaining at room temperature, however, depends on the uniformity and rate of cooling, PWHT temperature and holding time as will be evident from Fig. 7.8 [9]. It will be also evident from the figure that residual stress is also dependent on yield strength of the material.

7.2.4.1 Peening

Peening has been used by the welders for many years. When used correctly, peening reduces the longitudinal stresses of butt welds due to compressive stresses introduced in the peening process. For maximum effectiveness all weld layers are to be peened except the first and the last layer. The restriction of the first run is imposed to avoid any damage of the root run and sideway displacement of the members. As regards the last layer there are possibilities of degradation of material property as a result of cold working. Normally peening is not suitable for weld deposits of 6 mm or more.

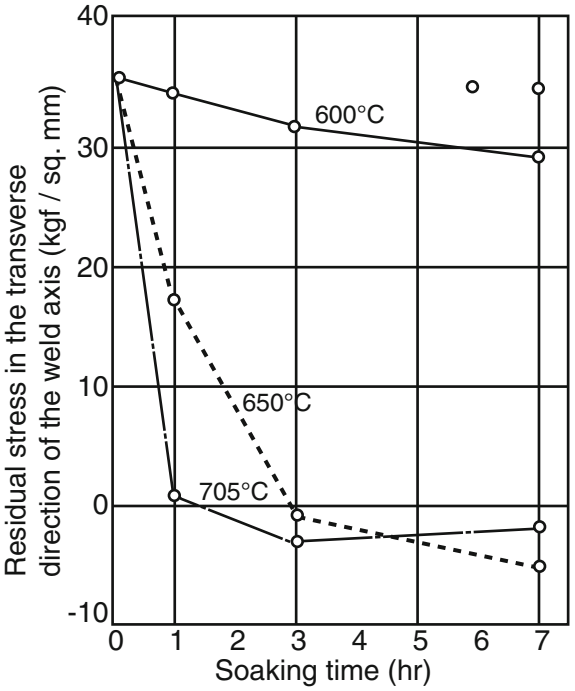


Fig. 7.8 The effect of time and temperature of PWHT on stress relief of 2.25Cr-1Mo steel welds [9]

7.2.4.2 Vibratory Stress Relief

Considerable interest has been shown by many practicing engineers in post weld stress relief by using low- and high-frequency vibration with the assistance of an oscillating or rotating wave generator. The technique, also known as Ultrasonic Impact Technology (UIT), was developed in Russia during the 70s. When properly applied, local plastic yielding takes place releasing the peak stresses. It is claimed that it imparts compressive residual stress up to a depth of 6 mm and the ultrasound travelling through the treated material softens and alters the grain structure in the HAZ [10]. The technology is commonly used to treat the toes and surfaces of welds. The UIT methods have been successfully used to control distortion and to improve fatigue life of welded structures. The range of materials and industries where the technology has been applied is quite diverse, from mild to high strength steels and in industries such as infrastructure, mining equipment, offshore structures, aerospace, and others. By UIT technique it may be possible to reduce distortion in parts machined after welding and minimize damages induced by high level of residual stresses. Vibratory stress-relief treatments is still not generally accepted technique and it will not be effective in changing mechanical properties which depends on the change in the metallurgical structure of welds and HAZ. Vibratory stress relief is still a controversial subject and opinion of expert on its effectiveness varies from very effective to no effect at all. This method has been

specially found effective in case of casting and is used to avoid in-service cracking often experienced because of locked in stresses.

7.2.5 Residual Stress Measurement in Weldments

A number of techniques have been developed for residual stress measurement which may be classified as either destructive or semi destructive or non-destructive. Non-destructive techniques include X-ray or neutron diffraction, ultrasonic and magnetic Barkhausen noise (MBN) tests. Non-destructive methods are preferable but their use is restricted primarily due to the following:

- Size of measuring instruments which limits their field use
- Requirement of proper calibration
- Interference of microstructure signal.

In practice, however, the destructive and semi destructive residual stress measurement methods are preferred because these require comparatively less specific calibrations and have a wide range of applications. In the destructive and semi destructive techniques, also called mechanical method, measurement of the residual stresses are based on stress relaxation, using electric or mechanical strain gages and photo elastic coatings. These techniques are based on the fact that strains occurring during the release of stress (unloading) are elastic. The three such techniques are as follows:

- *Sectioning technique of a plate using electric resistance strain gages*. It is simple, reliable, and has high accuracy.
- *Mathar–Soete drilling technique*. Causes little damage to the component and convenient to use on welds and adjacent material. Suitable for field and laboratory but requires to be used with care.
- *Gunnert drilling technique*. Robust, simple and semi non-destructive. Any damage is repairable.

A summary of some of the techniques is given in Table 7.2 [11].

7.2.6 Avoiding PWHT

It may be mentioned that it is only in case of pressure equipment in process industry that PWHT has a major role in assuring equipment integrity. No PWHT requirement, except in case of a few joints, is mandatory in case of off shore jackets. Similarly this requirement is not included in structural welding standard [12]. As already discussed, the primary objective of PWHT is to relieve welding stresses, refine the coarse grain at HAZ/weld interface, and in many cases also to modify the metallurgical structure of HAZ to prevent cracking subsequent to welding or during

Table 7.2 Comparison of residual stress measurement techniques

Technique	Advantages	Disadvantages
Hole drilling	Fast; Easy use; Generally available; Hand-held; Wide range of materials	Data interpretation; Semi destructive; Limited strain sensitivity and resolution
Deep hole drilling	Deep interior stress measurement; Thick section components; Wide range of materials	Data interpretation; Semi destructive; Limited strain sensitivity and resolution
Sectioning	Economy and speed; Hand-held; Wide range of materials	Destructive; Data interpretation; Impossible to make subsequent slices close together
X-ray diffraction	Ductile; Generally available; Wide range of materials; Hand-held systems; Macro and Micro RS	Lab-based system; Small components; Only basic measurements
Ultrasonic	Very quick; Low cost; Hand-held; Generally available	Limited resolution; Bulk measurements over whole volume

service. However, in some situations, especially for maintenance welding, performing PWHT is either not possible or presents considerable difficulties. The industry experience is that in some cases a PWHT in situ may result in a worsened situation. Industries facing considerable problem in repairs involving PWHT are nuclear, power, petrochemical and offshore industries. To circumscribe the problem, a number of methods have been developed, standardized and successfully used. These are as follows:

1. Preheating Method
2. Temper Bead Welding
3. Buttering
4. Friction Stitch Welding

7.2.6.1 Preheating Method

According to API 510, PWHT of steels of P No. 1, Group 1, 2 and 3; P No. 3, Group 1 and 2 (excluding Mn–Mo steels in Group 2) can be avoided by maintaining a minimum pre heat temperature of 150 °C with maximum interpass temperature maintained ≤ 350 °C. The welding is, however, to be limited to the shielded-metal-arc (SMAW), gas-metal-arc (GMAW) and gas-tungsten arc (GTAW) welding processes [13].

7.2.6.2 Temper Bead Welding

Due to temperature gradient in the base metal adjacent to the weld during welding, the grain size in the HAZ varies, with that at HAZ/weld interface being coarse. The

brittleness of the weld is related to both the presence of this coarse grain and hard structure (where transformation products form). The primary approach of temper bead welding is to refine the grain during welding itself by using a proper multipass welding technique. The work on temper bead welding was first initiated in 1980s for the repair work in nuclear industry where PWHT after repair weld is not possible. The technique has since been further modified and refined. The well-known techniques are as follows:

- Half-bead technique
- Consistent layer temper bead technique
- Alternate temper bead technique
- Controlled deposition technique

Of the above four, the controlled deposition technique is the preferred one. A broad outline of the three layer controlled deposition process is described below.

1. The first layer of weld is deposited using small electrodes with a low heat input. The angle of the electrode is adjusted to limit penetration and steps are taken steps to avoid hydrogen cracking and weld defects. Attempt should be made to have a 50/50 overlap of beads which helps in reducing the coarse grain area. Maintenance of proper preheats and interpass temperatures is also an essential part of the process.
2. For the second layer larger bead is deposited on the top of the smaller ones so that its refined zone overlaps the coarse area of first run.
3. The third layer is also by controlled deposition when required grain refinement and tempering of the HAZ are achieved.
4. During depositing the final bead it is ensured that deposition is made in the middle of the cap away from the parent metal.

Details of the different layer given in TGN-PE-02 of Welding Technical Institute of Australia are given in Fig. 7.9 [14]. On closer examination of the figure it will be apparent how weld pass 14 tempers the HAZ at the toe of the weld pass 7 and weld pass 16 achieves the same purpose with weld pass 9. Correct placement of beads 14 and 16 is crucial to a successful outcome. Some important parameters to be maintained in depositing the different layers are stated as follows:

1. Heat input ratio layer 1–2 = 1.7
2. Heat input ratio layer 2–3 = 1.22
3. Aim is to increase heat input 30–70% with each layer

It may be mentioned that though the technique appears to be simple, it is not so. Prior to carrying out the job, the procedure is to be developed by carrying out many weld simulations along with the confirmation of the desired structure by metallographic examinations. Experienced welders, certified to carry out the actual job, are essential to maintain all the required parameters.

API 510 permits use of controlled deposition, temper bead or half bead technique after the details of the three different processes are examined before taking up

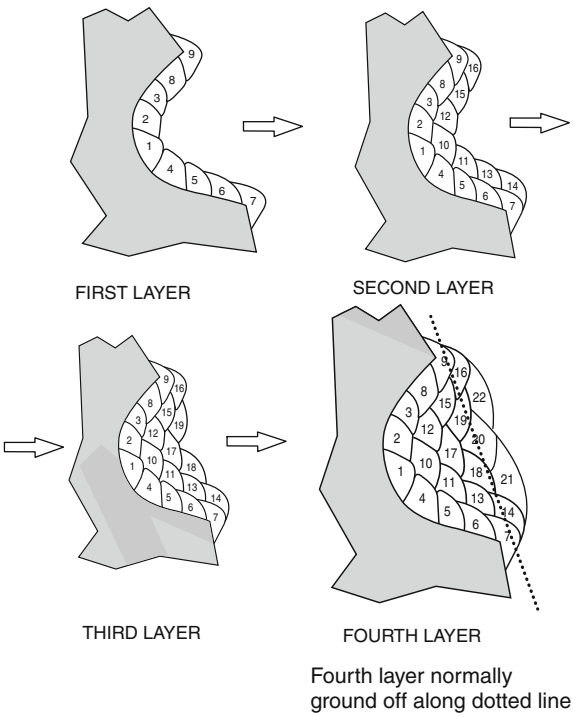


Fig. 7.9 Temper bead welding. Cross section of structural characterizes of different layer [14]

the repair [13]. The 2004 edition of Section IX of the ASME Boiler and Pressure Vessel code has also dealt with temper bead welding under clause QW-290 'Temper Bead Welding' [15]. In case of P No 1, P No. 3 and P No. 4 steels, API 510 [clause 8.1.6.4.2.3] recommends controlled deposition technique where notch toughness testing is a requirement. The said clause gives requirements for getting good weld and tests to be carried out on samples used for weld procedure qualification. Some important points mentioned are as follows:

(i) Without allowing the temperature to fall below pre heat temperature, weldment temperature shall be raised to 260 ± 30 °C and held for a minimum period of two hours to assist out-gassing of any weld metal hydrogen picked up during welding.
(ii) Hydrogen bake out would not be necessary if the electrode used is classified by the filler metal specification with an optional supplemental diffusible-hydrogen designator of H4 (such as E701S-H4).
(iii) Adequacy of the toughness of the weld metal and the heat-affected zone of the base metal in the as-welded condition shall be determined at the minimum design metal temperature (ASME Section VIII: Division I, parts UG-S4 and DCS 66), and
(iv) If special hardness limits are necessary (NACE RP 0472 and NACE MR 0103) for use in refinery sour service, the same shall be included in hardness tests.

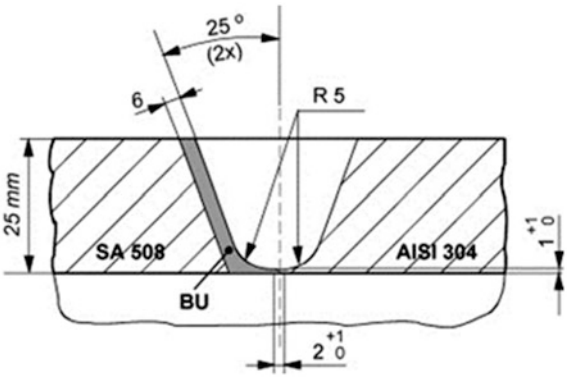


Fig. 7.10 Buttering for joining ferritic and stainless steel

7.2.6.3 Buttering Technique

To avoid PWHT in repair of hardenable low alloy steels, welding with austenitic stainless steel consumable (Type 309) is quite common in industry. The technique of buttering can also be confidently used to get better quality weld joint. In this case, ferritic steel components are first buttered on both side with either Inconel or SS 309L, followed by final closure using the consumable of the ferritic steel. The advantage is that there is no dilution effect on the closure weld and minimum adverse structure formed on alloy steel. Thus, PWHT is avoided provided the buttered layer is of sufficient thickness. Figure 7.10 shows buttered joint details between SS 304 and SA 508 ferritic steel for a reactor pressure vessel. As per ASME section IX, the PQR is required to be qualified for buttering. It must be mentioned that some hard structure will from at the butter layer/alloy steel interface which in many cases may not be harmful. In situations where this is not permissible, the components to be joined are given PWHT treatment prior to closing weld. The method is costly but necessary in some situations. The method of buttering is also necessary while performing DMW.

7.2.6.4 Friction Stitch and Seam Welding

In the recent years stitch welding has come into prominence because unlike fusion welding, temperatures attained in this case are much lower. The technique first developed and patented by TWI [16] is based on principal of utilizing heat of friction to heat and soften the metal (not to melt) to fill up any gap. The development of such a technique initially was for repair jobs in special situations where normal technique like welding cannot be used. In situation like underwater welding, the importance of this technique is much greater and for the last decade many improvements have been made and further refining of the technique is being investigated jointly by off shore companies and welding specialists. Efforts to use robotic techniques for welding at larger depths and also in offshore platform, FPSO

(Floating Processing Storage and Offtake) are in progress and have to some extent proved successful [17]. The scope for the use of this technique in both production and repair in nuclear, shipping, automotive, manufacturing industry, etc. has been found to be successful and is being used [18].

As stated the process utilizes friction as an efficient thermo-mechanical source. The joining is carried out in solid state, which makes the conditions thermally less serve. Three techniques, such as, friction stud, friction hydro pillar processing and friction taper stitch, are commonly practiced. In taper stitch welding tapered holes are made through the full thickness of components to be welded. A tapered plug with a similar included angle is then friction welded into the hole. The stud (consumable) is rapidly rotated under axial stress and once sufficient plasticity is developed, the hole is filled with plasticized metal. The impurities are expelled at the top of the weld. Figure 7.11 show the basic principles of taper stitch process. It is possible to use similar basic technique for seam welding whereby V-shaped groves in work pieces (as in welding) can be joined together without melting. Heat is generated by friction between the work pieces and a rotating consumable bar is axially pressed into groove and the work pieces moved underneath the rotating consumable which fills up the groove as shown in Fig. 7.12.

Process to weld double V-shaped groove has also been developed. The procedure uses what is known as bobbin tool technique [18].

The process of friction welding has also been used for providing sleeve and butt-welding of pipes or plates, though its maximum use is in repair of thick vessels. The friction stitch processes have number of advantages:

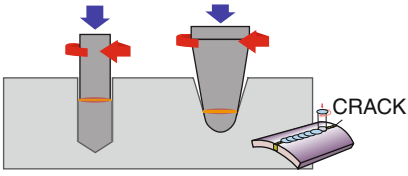


Fig. 7.11 Friction stitch welding of crack

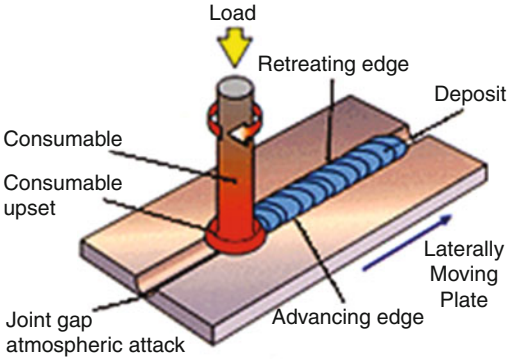


Fig. 7.12 Friction seam welding

- The maximum temperatures attained are much lower than with electric arc welding. Formation of hard microstructure is avoided because of less severe temperature gradients.
- Unlike underwater welding, significant amounts of hydrogen and oxygen are not evolved from the surrounding water though no dry habitat is used as required in case of arc welding.
- For repair in nuclear and offshore oil and gas production industries, approach to the job site normally raises considerable problem because of radiation and limited depth to which (350 m) a diver can dive. Development of robotic machines nowadays allows the work to be executed with remote control. For underwater jobs the system is fixed on a modular advanced tie-in system (Matis) frame and operated by remote control up to 3500 m depth.

7.3 Underwater Welding

Underwater welding of ships, submarines, piers and offshore platforms and pipelines presents a great challenge. The most important requirements of normal welding, like avoiding presence of moisture on the surface to be welded and surrounding atmosphere, controlled cooling to avoid hard weld and HAZ, etc. either cannot be met or only partly met. In addition, with increasing water depths, characteristics of arc, power required, consumption of consumables, etc. drastically change for the worst. In spite of these, under water welding is being successfully performed by using special techniques and trained welders.

The following methods are normally adopted for under water welding, depending on the desired weld quality:

(i) **Welding in Wet Environment**: This is the earliest method used for emergency repairs and salvaging work. However, in performing open water welding the depth to which a diver can work is limited because of accessibility. Due to welding being performed in open water, hydrogen and oxygen atmosphere envelops the weld, resulting in porosity and hydrogen cracking; both the weld and base metal cool rapidly forming hard crack susceptible microstructure; the electrode and electrical leads require water proofing; visibility under the water is poor making it difficult for the welder to perform well; and the welder has to spend a large part of time in chipping off of the solidified slag after each run. As a result the time taken is longer and the quality of job is normally not adequate to meet the requirements specified for an onshore job. Open water welding is, therefore, used primarily for emergency short-term repair or jobs which can tolerate substandard weld. This is later corrected by a proper execution of the job, where possible. It may be mentioned that in spite of the limitations, good quality weld can and are made by experienced welders.



Fig. 7.13 View of underwater welded taste plate for offshore

Underwater welding always raised the problem related to hydrogen (under bead cracking of HAZ) and weld porosity. Wet welds were therefore not attempted on base metals with carbon equivalents (CE) greater than 0.4. This led to the formation of a Global/CSM Joint Industry Underwater Welding Development Program (JIP) to study various aspects of underwater welding. The work carried out at Colorado School of Mines with different fluxes showed "addition of $CaCO_3$, ZrO_2, and Fe–Mn to the flux coating, several experimental electrodes performed exceptionally [19]". In terms of porosity, 10 out of 24 welds met AWS D3.6 Class A (dry) weld classification [20], while 12 welds met the requirements for Class B (wet welds). In terms of Charpy-V-notch impact testing all four welds passed and exceeded the AWS D3.6 Specification requirement of 15 ft-lbs (20 J) at 0 °C (32 °F). For wet underwater welding shielded-metal-arc welding is employed with the electrode having special flux coating with waterproof electrodes. Presently, such electrodes are easily available in international market. Figure 7.13 shows the condition of a plate welded under water.

(ii) **Welding in Dry Environment**: A quality weld, meeting X-Ray and code requirements, can be better achieved in under water welding if the job is executed out of contact with water. Both GTW (up to depth of 61 m) and meal arc welding (up to depth of 55 m) have been successful used. For under water dry welding two methods are used.

- In *habitat welding*, the welding chamber is sealed around the welding part. The chamber bottom is open forming a water seal. However, the atmospheric pressure inside the chamber remains equal to water pressure at the operating depth. The diver is provided with all necessary equipment in a dry environment and he gets clear view of the weld and can manipulate the electrodes in all positions. If required, both pre and post heat treatment can be carried out. This type of dry system is known as hyper baric (high pressure) and is normally used for deep-sea jobs.

- The second method, *chamber welding*, involves fittings of a waterproof chamber completely isolating the water from the work area. In this case, the interior of chamber is maintained at atmospheric pressure. The chamber is connected to surface atmosphere by a pipe. However, these are mainly used for comparatively shallow depth. The welder can work in the chamber without diver dress and has good approach to the work piece.

Under water welding operations are limited by the depth to which a diver can dive and time taken for habituating divers with various pressures. A quality weld, meeting the X-ray and code requirements, can be achieved in underwater welding if the job is executed out of contact with water. The quality of underwater welds can be ascertained by using most of the techniques used for onshore jobs. Visual inspection using good lighting and televisions camera is a preferred method. Here the viewing is done on the surface where all angles can be covered which a diver cannot see. Radiograph, FMPI (in case of chamber welding) and U/S inspection are the preferred methods. In spite of the advances made in underwater welding, the limitations remain, specially the depths to which a welder can work. Greater emphasis is presently being put on perfecting the solid state methods like stitch welding which is a mechanical process and can be performed by remote control from platform or ship/boats.

7.4 Welding of Components Showing Magnetism

It is not uncommon for problem faced in welding due to pipes having magnetism, which results in deflection of arc. According to John Anderson of Diverse Technologies [21], "*Magnetic arc blow occurs because there is a force on the plasma that is perpendicular to the current flow in the arc and the magnetic field direction. For a pipe weld, the magnetic field direction is axial with the pipe, the current will be radial to the pipe and the resulting arc deflection will be circumferential. As magnetic field levels increase, the arc becomes progressively more unstable and difficult to control* (Fig. 7.14). *The result is often poor quality welds that have to be ground out. At higher magnetic fields the arc blows out. In severe cases the arc is to be immediately extinguished and no welding can take place. No wonder some welders think of this as black magic. The belief that the problem can be solved by heating up, hitting with hammer, trailing the weld set cable over it, or sun to go down before welding can be stated as old wives' tales. The solution is into understand scientific reason behind it and then act accordingly*".

7.4.1 Causes for Magnetism of Plant Piping

A number of factors including, natural, material composition, NDT, welding current, etc. are responsible for the presence and strength of magnetism in ferritic materials.

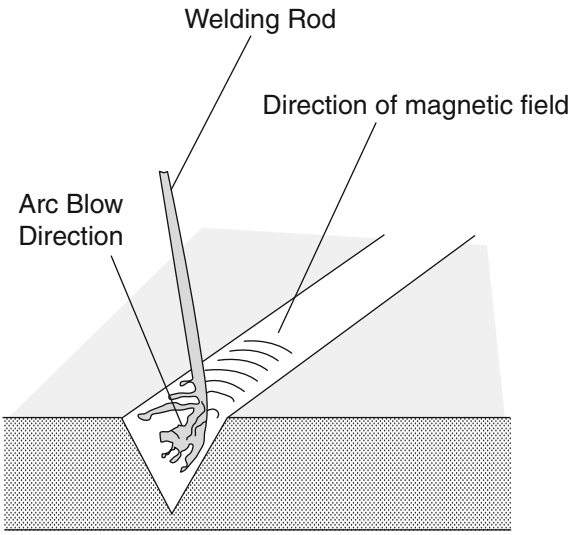


Fig. 7.14 Shows how arc blow occurs

Some of the causes identified for structures and piping [22] are summarized below:

1. Magnetism is frequently observed during welding of ferritic iron, nickel or cobalt alloys which show magnetism, but not in non-magnetic stainless steels or non-ferrous alloys of copper, aluminium, etc.
2. The Earth's magnetic field can magnetize large equipment in process plants connected together in the direction of north to south by pipes. Though the Earth's magnetic field has strength of less than 0.1 mT it occurs because large steel structures pull in the Earth's magnetic field and it becomes concentrated in the pipes which link the main parts together. High strength alloy steels are more difficult to magnetize but if once magnetized, it becomes difficult to demagnetize it.
3. The problem is greater at the root of weld (deeper and narrower V preparation), longitudinal welds and when DC is used for welding. Further, tendency for magnetic arc blow is more likely with lower voltage arcs, such as in case of TIG welding used for the root pass of multipass welds or manual metal arc welding using small diameter electrodes.
4. Magnetic particle inspection and use of magnetic clamp used for lifting can retain magnetism to cause the problems of arc blow.
5. In oil and gas production facilities hyperbaric welding with high ambient gas pressures the likelihood of arc blow is more compared to welding at atmospheric pressure.

7.4.2 Remedies for Magnetic Arc Blow

1. In general, the problem in welding and arc blow due to magnetism is expected above 20 gauss (2 mT) and 40 gauss (4 mT), respectively. The solution lies in bringing down the magnetic field in the joint preparation to below 10 gauss (1 mT).
2. When making circumferential welds instead of first making the outer joints the procedure should be to first carry out the central weld and then work towards the ends. If final closing weld is in centre arc blow can occur.
3. As far as possible, use an A.C. welding process. If this is not possible, use DC with the highest arc voltage possible.

The most practical method to overcome the problem is 'field nulling', where demagnetization is carried out by inducing reverse field during the welding process. Once the welding is completed, the reversing field is removed. Though this would lead to the return of magnetism it will have no adverse effect at least till next welding is performed on it. The process can be carried out manually or automatically using demagnetizers which ensures that the magnetic field in the joint preparation remains below 1 mT.

7.5 Welding of Austenitic Stainless Steels

Unlike ferritic stainless steels (except Fe–Cr alloys containing above 16%Cr), no phase transformation is involved in austenitic stainless steel and therefore no hard structure are formed in the HAZ during welding. However, to get a reliable and defect free weld, care is needed to avoid cracking, porosity, carbide precipitation (both in weld, HAZ and parent metal), sigma formation, etc. In general, in case of austenitic stainless steels, no PWHT is carried out in spite of the fact that weld residual stress in austenitic stainless steel is higher than ferritic steels, because of its higher coefficient of expansion. PWHT, if carried out, requires due consideration of deleterious effect of carbide precipitation in both the base metal and the weld in the sensitization range of temperature ($\sim$400–815 °C). In case where the stress relieving treatment is desired the welded component would have to be subjected to quench or solution anneal treatment. However, such a treatment is not possible in case of field welds or large size vessels.

7.5.1 Weld Defects in Austenitic Stainless Steels

The main problem in welding of austenitic stainless steel is hot cracking, i.e. cracking during weld solidification, both above the liquation temperature

(super-solidus cracking) and in the solid state, (sub-solidus cracking). Super-solidus cracking occurs due to presence of a liquid phase in the fusion zone [23]. Solidification cracking occurs particularly in fully austenitic and stabilized compositions, caused by formation of low-melting eutectics of impurities like sulphur and phosphorous. In stabilized stainless steels niobium and titanium also form low-melting CbC-austenite and TiC-austenite eutectic which cause cracking. In stabilized grades nitrogen picked up during welding significantly enhances cracking, which is reduced by minimizing the ratio of Ti or Nb to that of C and N present.

7.5.1.1 Role of Ferrite on Welding of Austenitic Stainless Steel

Being a ternary alloy, depending on temperature and composition at any particular temperature (based on ternary phase diagram), one or more phases of delta ferrite, alpha ferrite and austenite phases can be present singly or together. In the austenitic composition range at room temperature, the austenite can form directly or from delta ferrite which is first formed. In the latter case, the final austenite may contain some amounts of residual ferrite. 'Constitution diagrams' to demarcate the zones of austenite, ferrite and martensite in weld, singly or in combination, with respect to the chromium and nickel content were first made by Schaeffler in what is known as Schaeffler diagram (Fig. 7.15) [24]. Here instead of using actual %Cr and %Ni, equivalent values of these (incorporating the role of other elements in stabilizing ferrite and austenite) were used. This diagram is considered as most suitable for a

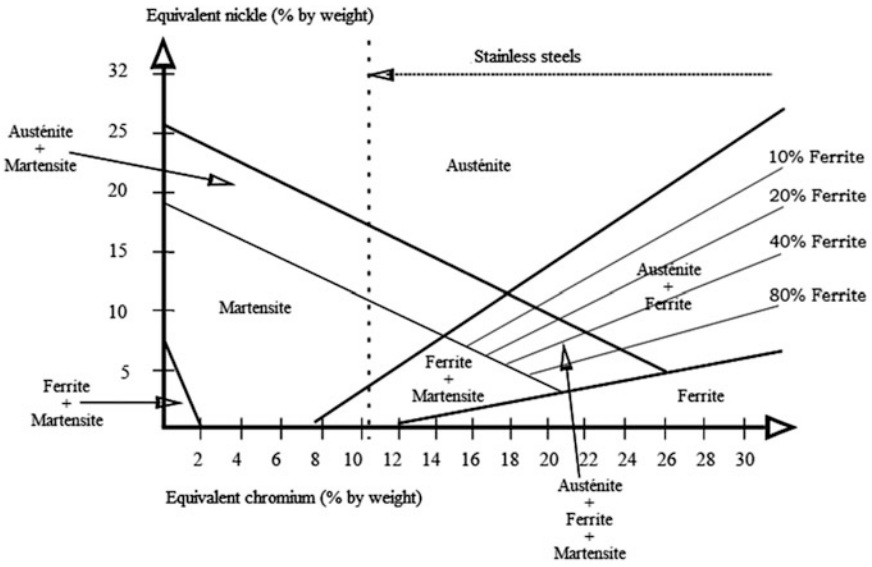


Fig. 7.15 Schaeffler diagram [24]

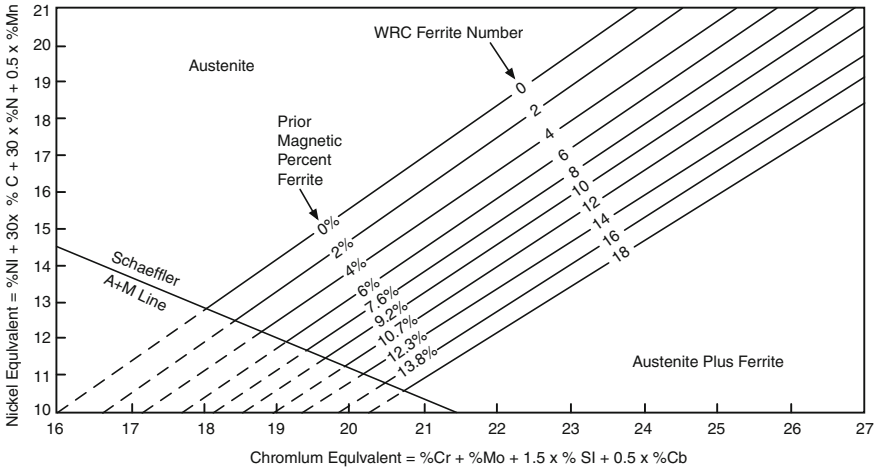


Fig. 7.16 DeLong diagram

general picture of weld metal structures for a wide range of compositions, but not accurate for ferrite containing austenitic weld metals. Schaeffler diagram was later modified by DeLong by incorporating additionally the strong austenite stabilizing tendency of nitrogen to calculate nickel equivalent. DeLong also introduced the concept of ferrite number instead of ferrite percentage to measure the delta-ferrite content in stainless steel. DeLong diagram (Fig. 7.16) shows the ferrite levels in bands, both as percentages, based on metallographic determinations and as a ferrite number 'FN', based on magnetic determination methods.

The Schaeffler and Delong diagrams are the original methods of predicting the phase balances in austenitic stainless steel welds and specially the latter had been used for welding of austenitic stainless steels like 304 or 316, etc. and ferrite/austenite differential metal welding (DMW) up to 1985. However, these diagrams do not adequately cover the modern stainless steel grades, including the duplex stainless steels, for which WRC in 1992 developed a new approach to prepare constitution diagram [25]. Figure 7.17 shows a typical WRC 1992 constitution diagram indicating ferrite content in stainless steel [26].

7.5.1.2 Ferrite Number

Due to inaccuracies in the measurement of ferrite content in austenitic stainless steel internationally accepted standardized method is to determine ferrite content or what is known as ferrite number (FN) based upon an arbitrarily defined relationship between a magnetic force and ferrite content of weld. The method consists of measuring the attractive force between a torsion balance and comparing with the values obtained from a carbon steel base plate with a non-magnetic copper coating of a specified thickness. The Ferrite Number is not equal to the volumetric ferrite

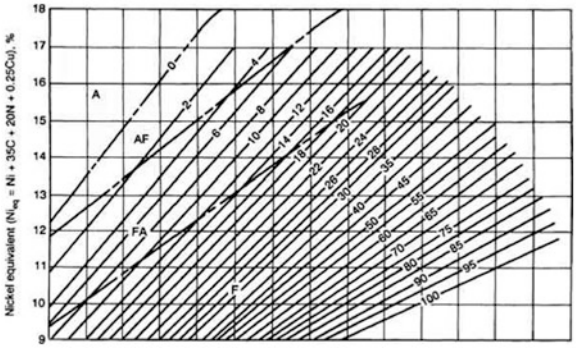


Fig. 7.17 WRC-1992 diagram predicting ferrite content in stainless steels [26]

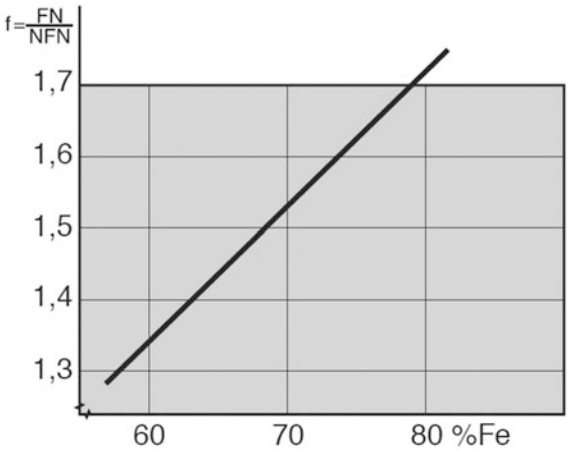


Fig. 7.18 Iron content versus factor f for relating % ferrite to FN

content (%) and a reasonable estimate of the ferrite content can be made by dividing the Ferrite Number by the factor f (% ferrite = FN/f) which is dependent on the iron content in the weld metal as shown in Fig. 7.18.

The calibration method provides the necessary linear relationship. The principles are accepted as the international standard ISO 8249 [27] and AWS A4.2-91 [28]. The Ferrite Number is not equal to the volumetric ferrite content (%). Although an absolute ferrite content cannot be measured accurately, a reasonable estimate of the ferrite content can be made by dividing the Ferrite Number by the factor f (% ferrite = FN/f) which is dependent of the iron content in the weld metal.

HAZ Cracking

In addition to the hot cracking of weld, micro-fissures are also observed in the HAZ (also termed Hazard HAZ) of reheated regions of weld metal deposits in both multipass welds and repair welds. This type of crack has been explained to occur

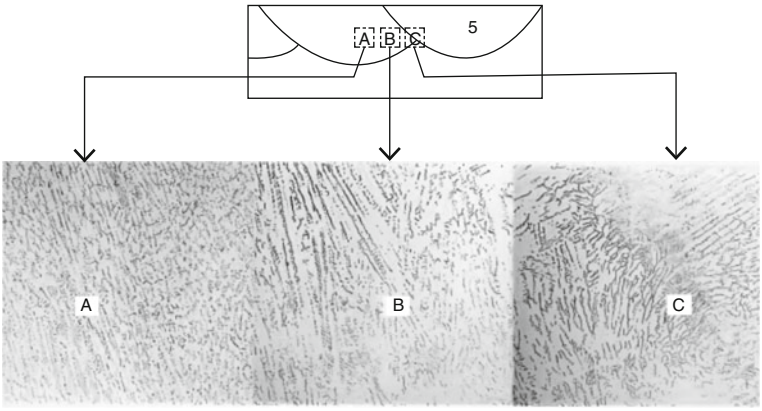


Fig. 7.19 Repeated heating reduces ferrite content of adjacent weld. Five cycles of welding reduced FN from 5 to 1 in B [29]

due to the development of low ductile area near the fusion zone of the subsequent weld bead. In this narrow zone the ferrite content is reduced below making it susceptible to cracking. Figure 7.19 shows the structure of a weld bead when the adjacent one was subjected to fusion five times. This resulted in the ferrite content to come down from 5 to 1% in HAZ zone of the weld bead [29]. On the other hand, in case of fully austenitic stainless steels such micro fissuring in HAZ has been explained on the basis of the grain boundary segregation of sulphur, phosphorous and silicon and grain growth during the thermal cycling.

Formation of low-melting NbC-austenite eutectic in Type 347 stainless steel, during rapid heating during welding, and its wetting of the grain boundaries is considered to be the cause of HAZ cracking in this alloy [30]. Unlike solidification cracking, which follows the interdendritic structure, micro fissuring proceeds intergranularly at temperatures close to the solidus. Similar eutectic is also formed in case of titanium but its melting point is higher and therefore this type of damage occurs more readily in case of Type 347 stainless steel.

7.5.2 Selection of Filler Metal for Welding of Austenitic Stainless Steels

Austenitic filler metals are used for both austenitic and ferritic stainless steels. For conventional stainless steels where presence of ferrite is essential to avoid solidification cracking, the amount and form of ferrite in the weld metal can be controlled by selecting a filler metal with the appropriate chromium and nickel equivalent using the DeLong or WRC-1992 diagrams (present day practice is for the latter which gives better approximation). Normally a high chromium-to-nickel ratio favours primary ferrite formation, whereas a low ratio promotes primary austenite.

Table 7.3 Suggested filler metals for some austenitic and ferritic stainless steels

Austenitic stainless steel, type	Condition under which weldment will be exposed in service	Electrode or filler rod type
Austenitic stainless steel		
304 308	As welded or fully annealed	308 (310 electrode can be used but pick up of Si can result in hot cracking)
304L	As welded or stress relieved	308L/347
321 347	As welded or after stabilizing and stress relieving heat treatment	347 (321 filler metal is not used because titanium gets easily oxidized and not recoverable)
309 309S 310	As welded	309
316	As welded or fully annealed	316
316L 316Cb	As welded or stress relieved	316Cb/316L
317	As welded or fully annealed	317
317L	As welded or stress relieved	317Cb
Ferritic stainless steels type		
405/410S	Annealed or As welded	405Cb/430; 309/310
446	Annealed or As welded	446, 309/310

An optimum condition can be attained for ferrite contents between 3 and 8 vol.% in the weld deposit. Ferrite contents above 3 vol.% usually guarantee primary ferrite formation and thus reduce hot cracking susceptibility. Table 7.3 gives suggested filler metals by Nickel Development Institute [31] though guidelines of reputed electrode manufacturers can also be used for selection.

7.6 Welding of Dissimilar Metals (DMW)

7.6.1 Considerations in DMW Welding

Quite often two dissimilar metals are to be welded. In such cases, the properties of three metals are to be considered, i.e. two metals being joined and the filler metal used to join them. Some of the important considerations in DMW are as follows.

7.6.1.1 Ferritic to Ferritic Steel

1. The weld metal should be equal to or stronger than the material being joined. Normally in case of welding low to medium alloy ferritic steels, the higher alloy is selected.

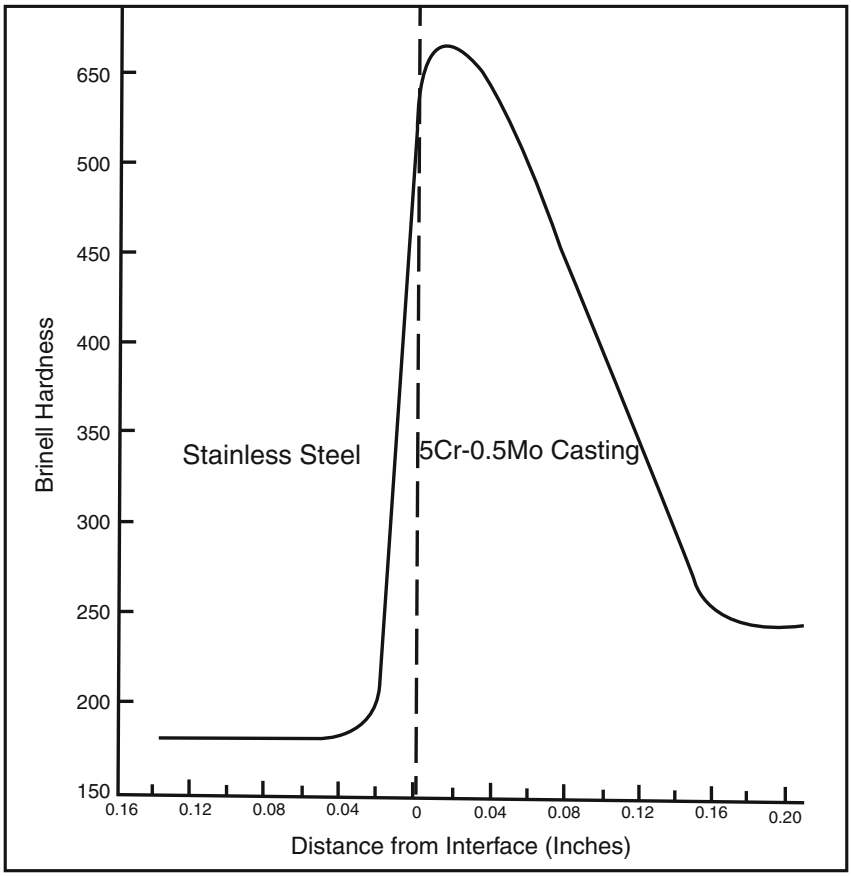


Fig. 7.20 Repair weld of P5 casting with stainless steel without pre or post weld heat treatment gives high hardness of P5 at DMW weld interface

2. Under corrosive conditions, the weld metal should be cathodic to the two base metals being joined to avoid accelerated corrosion of weld. Similarly, in case of oxidation or other high temperature attack, the resistance of weld metal should be equal to the least resistant base metal being joined.
3. In case of DMW of two ferritic alloys the parameters like preheat, interpass temperature, heat input, PWHT, etc. should meet the requirements of the higher alloy. For example, in welding 2.5Cr–1Mo to 9Cr–1Mo the procedure required for 9Cr–1Mo will be used.
4. It may be mentioned that to avoid PWHT, in welding of Cr–Mo steel, Type 309 electrode is quite often used for plant maintenance. This should be avoided or treated as temporary repair to be corrected later because the embrittled HAZ in Cr-Mo steel still exists. This is illustrated in Fig. 7.20 which gives change in hardness across a 5Cr–0.5Mo to stainless steel.

7.6.1.2 Austenitic Stainless Steel to Ferritic Steel

1. Weld metal dilution is an important aspect to be considered in case of welding ferritic to stainless steel, the extent of which depends on a number of factors. Though chemical analysis gives the most accurate results, normally a rough estimation can be made for major alloying constituents using the following base metal dilution percentages [32].

   * SMAW (covered electrode) 20–25%
   * GTAW 20–50%
   * SAW (submerged arc) 20–50%

   Dilution effect has a large role to play in selection of consumable for welding carbon steel or low and medium alloy steels to stainless steel. For example Type 308 electrode is normally used to weld Type 304 but while welding to carbon steel the dilution effect increases the amount of ferrite in the Type 308L weld beyond accepted level in the austenite + martensite zone. To counteract it higher alloy filler metal such as Type 309 and 312 are used which shifts the structure from austenite + martensite to austenite + ferrite.
2. Stainless steel to ferritic welds to be used in service over 425 °C would lead to cracking because of 40% higher coefficient of thermal expansion of former over the latter. Such welds should be made using Ni–Cr or NI–Cr–Fe (AWS A 5.14) type electrodes. This would avoid cracking because its coefficient of thermal expansion is in between both.
3. However, in case an equipment or component consists of ferritic and austenitic stainless steel parts and the ferritic portion require PWHT either because of its composition or thickness, any PWHT after fabrication shall adversely affect the corrosion resistance of austenitic stainless steel due to carbide precipitation. This may occur even if the austenitic stainless steel is of low carbon or stabilized grades, because long holding time in the temperature range of 620–670 °C is normally required. In such cases first V-grove for welding shall be made on both parts. The groove in the portion requiring PWHT will then be provided a buttered layer using 309 Cb electrode having FN over 10, and then subjected to the required PWHT cycle. Niobium containing stainless steel does not get easily sensitized and is, therefore, preferred. Buttered layer in such cases should be of sufficient width to keep the HAZ within itself and not affect the ferritic portion. After the heat treatment, final weld will be made using stainless steel electrode. No further PWHT is to be given to final closure weld. ASME Section IX QW-283 and related clauses give details of procedure to be used.

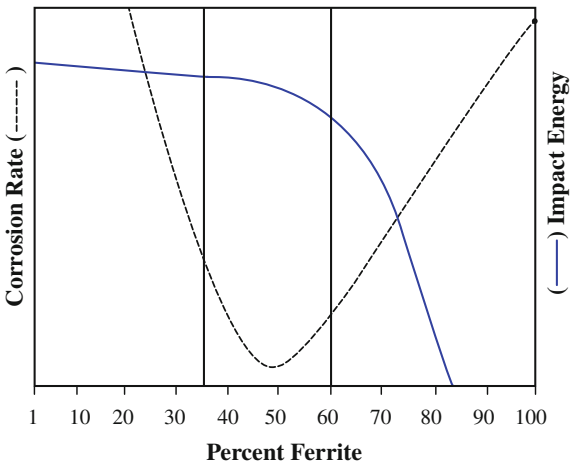


Fig. 7.21 Relationship between ferrite content and corrosion and impact properties

7.7 Welding of Duplex Stainless Steels

The weldability and welding characteristics of duplex stainless steels (DSS) are better than ferritic stainless steels, but not as good as those of austenitic stainless steels. As these contain about equal proportion of both ferrite and austenite, both hydrogen and solidification cracking are of concern. The problem is less serious in advanced grades of DSS because of the presence of Mo, Cu, W and especially, nitrogen. The formation of austenite in DSS is by solid state transformation from ferrite, which is time dependent. In the parent material phase balance is usually achieved by solution annealing in the two phase region followed by quenching to room temperature which is not possible in case of weld which cools at faster rate and cannot be subjected to required heat treatment after welding [33]. Thus if matching electrode is used it will not be possible to get required austenite/ferrite mixture and the weld deposit will be richer in ferrite and therefore shall not meet the requisite mechanical and corrosion resistant property. The relationship between ferrite content and corrosion and impact properties are shown in Fig. 7.21.

Some of the important considerations in welding of DSS are:

- Welding should be done using consumables, as autogenous welds will form excessively high ferrite.
- Consumables used should be over alloyed with respect to nickel (typically 7–9%) to achieve satisfactory phase balance. For example a good root run in 22Cr can be obtained by using super duplex consumable. Inconel and 309L have also been successfully used in number of cases where service conditions permit their use.

- Recommended shielding and backing gases for TIG welding are as follows [34].
  Shielding gas
  - Argon
  - Argon + 30% Helium to improve fluidity
  - TIG welds can benefit from 2 to 2.5% nitrogen addition to shielding gases
  - Helps maintain nitrogen level in weld
  - Too high a nitrogen is, however, deleterious

  Backing Gas
  - Argon
  - Argon + 5 to 10% Hydrogen
  - Nitrogen
- Heat input during welding is very important. Very low input combined with rapid cooling will result in high amount of ferrite in weldment. On the other hand excessive time in the 705–980 °C lead to formation of number of brittle intermetallic phases.
- For similar reasons while preheating is permitted, DSS should not be subjected to PWHT. Interpass temperature should not be more than 150 °C (100 °C for 2507 SDSS) [35]. However, for material in the range of 10–15 mm thick maximum interpass temperature of 225 and 150 °C has also been used for 22Cr and 25Cr DSS, respectively.

Welding procedure given by electrode supplier is important in carrying out welding. Where necessary, the procedure finally adopted should be discussed with manufacturer's technical personal.

7.8 Welding of Titanium

Titanium is highly reactive above 540 °C and easily picks up oxygen, nitrogen and hydrogen from the atmosphere. To avoid the deleterious effects of these impurities on quality of weld, only argon and helium are used as a shielding gas. Because of availability and cost factor, high purity argon (99.985% min) is widely used. The argon gas should have dew point of −60 °C or lower. Rubber hoses absorb air and should not be used. Hoses made of Tygon or vinyl plastic are preferred. To obtain a good weld, the joint and the surface of work pieces, at least two inches beyond the width of the gas shield, must be meticulously cleaned by degreasing and brushing followed immediately by pickling. Iron pick up is to be completely avoided.

For shop fabrication of components, welding is carried out in a completely sealed chamber under protective atmosphere. However, this is not possible in field or where the components are too large; a trailing shield is provided by using a special electrode holder so that the metal in the area of weld is protected until the temperature falls below 540 °C.

Table 7.4 Microprobe analysis of weld metal

Location	Composition %			
	316L		317L	
	Cr	Mo	Cr	Mo
Parent metal	16.3	2.6	18.4	3.2
Weld metal				
• Dendritic centre	14.3	1.8	14.2	2.0
• Interdendritic phase	20.1	5.7	24.0	6.6

7.9 Corrosion of Weld

7.9.1 Austenitic Welds

Corrosion of weld and HAZ is a serious problem in austenitic steels due to the precipitation of chromium carbide. This aspect has been discussed in detail in Chap. 8. Use of low carbon and stabilized grades of welding electrodes and base metal considerably reduces the changes of this type of attack. In spite of selection of the correct material preferential pitting attack of weld can be experienced in Mo containing high alloy steels because of Mo segregation that warrants the use of higher Mo consumables. The preferential attack of weld is sometimes experienced even in carbon steel in some specific environments, encountered in the oil, gas, refining and process industries, e.g. sea water injection system, oil and gas flow lines, organic acid systems, etc. Weld corrosion is primarily due to micro structural and compositional difference between the weld and the base metal. In case of the former, the solidification gives a cast dendritic structure where segregation of alloying elements and impurities like sulphur and phosphorous occur. While in most environments this difference is not significant, in other this may have a marked effect on preferential corrosion of weld. For example, in molybdenum containing austenitic stainless steels, micro segregation of chromium and molybdenum reduces the pitting resistance of welds. This has been confirmed by microprobe analysis of weld metal as shown in Table 7.4 [36].

In such welds, areas having lower Cr and Mo are susceptible to pitting in chloride environmental. The practical solution lies in using a filler metal of higher alloy content in cases where the preferential attack of weld is expected to be quite marked.

7.9.2 Carbon Steel

The instances of preferential weld corrosion (PWC) of carbon steel are more in handling of sea water injection system and some wet CO_2 containing systems in oil and gas industry. However, it is sometimes experienced in other systems also. The

mechanism of weld corrosion of C–Mn steel, unlike that of stainless steels, is not yet well understood The origin of preferential attack is usually a combination of a more active weld material (the weld would tend to be more susceptible to corrosion than the parent material if in isolation) together with galvanic coupling to the parent material. The influence of coupling is accentuated by the poor area ratio, i.e. a small anodic weld/large cathodic base material. Of the weld metals, the normal basic coated electrodes exhibit the more anodic potential and the acid types more cathodic, whilst the potentials for the weld metal from rutile electrodes are placed in an intermediate position. Some researchers have, however, disputed this. Addition of small amounts of nickel ($\sim 1\%$), copper, chromium or presence of low silicon in consumable is considered to have beneficial effect. For some applications preferential corrosion will be dependent on the rate of cooling and Mn level in the steel, which affect the grain size and the extent of martensite formation. The net effect is that the HAZ could be anodic to the parent plate.

Number of methods has been used in laboratory to test the corrosion properties of welds and their sensitivity to preferential weld corrosion and some of these have been used to determine the corrosion behaviour of weld with respect to the weld procedure. These are to be conducted in a laboratory on a sample weld to achieve confidence in the welding procedure. Recently, non-destructive field testing techniques for identifying a weld that is susceptible to preferential weld corrosion after fabrication have also been developed. The scanning reference electrode technique has been used to assess the preferential corrosion of weldments for use in offshore application when corroding freely and with applied potential. The technique has been found to be sensitive and reliable compared to other, immersion and potentiostatic anodic dissolution tests.

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Chapter 8
Material Degradation

Abstract Material degradation occurs by the process of corrosion and oxidation in wet and dry environments, respectively. In addition, the third form of damage is degradation of material due to metallurgical changes. Corrosion is an electrochemical process and there are many forms of damage, important amongst which are uniform corrosion, galvanic corrosion, stress corrosion cracking and pitting and crevice corrosion. These modes of damage affect the useful life of a component and various preventive measures are taken to minimize the effect. Corrosion preventive measures used are neutralization, addition of inhibitors, cathodic and anodic protection, painting and coating, etc. High temperature damage on the other hand occurs by reaction of oxygen, sulphur or other compounds present in environment. Oxidation produces solid layer and reaction takes place at metal oxide gas interface. Alloying primarily with chromium is used to impart resistance to oxidation of ferrous materials. The third type of damage, metallurgical degradation, involves primarily changes in morphology of phases present and precipitation of fresh phases, examples are graphitization, spheroidization, precipitation of secondary carbides and formation sigma, chi, π, G and other complex intermetallic phases. The damaging effects of these are either softening or, in most cases, embrittlement of the material. In this chapter details of various forms of material degradation along with preventive measures have described. Corrosion monitoring techniques and cost of corrosion to society have also been covered.

Keywords Electrochemical reactions · Passivation · Stress corrosion cracking · Pitting · Crevice corrosion · Cathodic protection · Corrosion monitoring · Oxidation resistant alloys · Metallurgical degradation

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8.1 Fundamentals of Aqueous Corrosion

8.1.1 Electrochemical Nature of Aqueous Corrosion

Corrosion in aqueous solutions is by far the most common of all corrosion processes. Aqueous medium is provided by water, seawater and various process streams in industry. The moisture in atmosphere and water in soil accounts for aqueous corrosion in these media. Rusting of steel is an example of aqueous corrosion. Iron reacts with water and oxygen present in the atmosphere to produce the corrosion product 'rust' according to the equation:

$$\mathrm{Fe} + \mathrm{O_2} + \mathrm{H_2O} = \mathrm{Fe(OH)_2} \rightarrow \mathrm{Fe(OH)_3} \tag{8.1.1}$$

The reaction involves two steps of electron transfer. Iron forms Fe^{2+} ion by losing two electrons that are consumed by oxygen and water to form hydroxyl ions:

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e} \tag{8.1.2}$$

$$\mathrm{O_2} + 2\mathrm{H_2O} + 4\mathrm{e} \rightarrow 4\,(\mathrm{OH})^- \tag{8.1.3}$$

Fe^{2+} ion subsequently reacts with hydroxyl ions to form hydroxide of iron. The electron liberating reaction, which represents oxidation, is termed anodic reaction. The electron consuming reaction, or the reduction reaction, is termed cathodic reaction.

For metals, the anodic reaction can be generally represented as:

$$\mathrm{M} \rightarrow \mathrm{M}^{n+} + n\mathrm{e} \tag{8.1.4}$$

where n is the valency of the metal. The cathodic reactions can vary depending on the nature of the corroding media and the reacting species available. The cathodic reaction in such a case can be any one of the following three reactions.

$$\text{Hydrogen evolution reaction in acid media:} \quad 2\mathrm{H}^+ + 2\mathrm{e} \rightarrow \mathrm{H_2} \tag{8.1.5}$$

$$\text{Oxygen consumption reaction in neutral media:} \quad \mathrm{O_2} + 4\mathrm{H}^+ + 4\mathrm{e} \rightarrow 2\mathrm{H_2O} \tag{8.1.6}$$

$$\text{Metal ion reduction:} \quad \mathrm{Fe}^{3+} + \mathrm{e} \rightarrow \mathrm{Fe}^{2+} \tag{8.1.7}$$

The anodic and cathodic reactions taking place on a metal surface is shown in Fig. 8.1.

The corroding system is analogous to an electrochemical cell (Fig. 8.2) consisting of an anode (zinc) at which the anodic or oxidation reaction occurs,

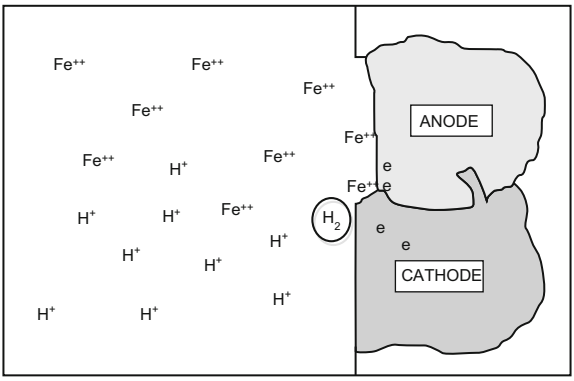


Fig. 8.1 Corrosion cell on metal surface

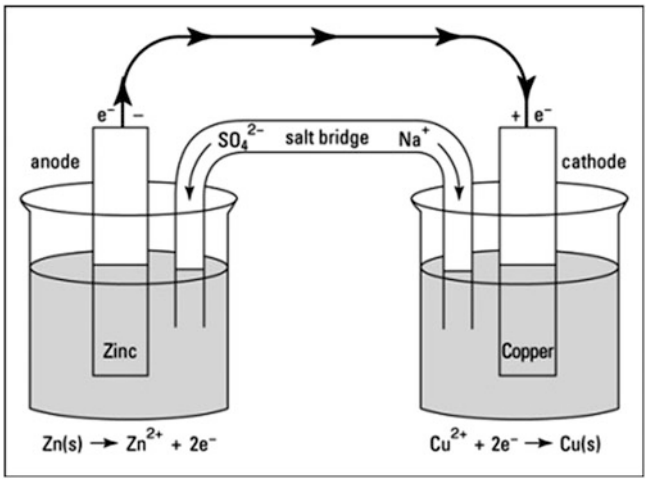


Fig. 8.2 A zinc/copper electrochemical cell

a cathode (copper), at which the cathodic or reduction takes place, an electrolyte, provided by the aqueous media, and an electronic conductor, which is provided by the corroding metal itself. Commonly used dry battery (Fig. 8.3) is another example of electrochemical nature of corrosion where corroding zinc releases electrons that are consumed at cathode (graphite).

In practice, the heterogeneities on metal surface, the concentration variation of oxygen or the reacting species, dissimilar metals, and differences in temperature, etc. can lead to local cell formation causing corrosion.

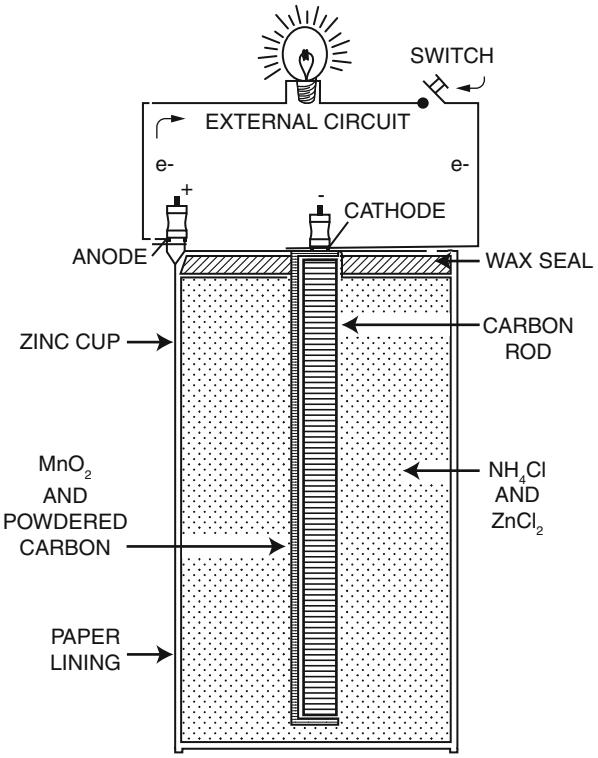


Fig. 8.3 Cross sectional view of a dry cell

8.1.2 Thermodynamics of Aqueous Corrosion

Like any chemical reaction, the corrosion reaction is also associated with Gibb's free energy change. The reaction is possible if the free energy change is negative:

$$\Delta G = -nFE \tag{8.1.8}$$

where

ΔG is the free energy change, in Joules,
N is the number of electrons involved in the reaction,
F is the Faraday constant, 943,600 coulombs,
E is the cell potential, in volts

A metal electrode immersed in an electrolyte develops a charged interface and a potential is developed at the electrode–electrolyte interface. This has been termed as *electrode potential or single-electrode potential.* Since the electrochemical cell consists of two electrodes, the cell potential is represented as:

$$E = E_1 + E_2 \tag{8.1.9}$$

where E_1 and E_2 are the single-electrode potentials of the constituent anode and cathode.

The single-electrode potential cannot be measured in absolute terms, for any measuring instrument dipped in the electrolyte develops a potential at the electrode–electrolyte interface. To get rid of this problem, a *standard hydrogen electrode* has been devised comprising a platinized platinum electrode immersed in a solution having unit activity of hydrogen through which hydrogen gas is bubbled under one atmospheric pressure at 25 °C. The potential of this electrode has been assigned a value of zero volts.

To measure the standard single-electrode potential, a standard hydrogen electrode is coupled up with another electrode kept in its standard state, i.e. a metal in equilibrium with its ions at unit activity at 25 °C. The measured potential is expressed with a zero superscript viz. E_1^0 or E_2^0. A listing of the standard single-electrode potentials constitutes the *electromotive force series* or EMF series. The standard EMF values of some metals are shown in Table 8.1. Metals at the top of the series give away electrons and function as reducing agents. The reducing ability of the metal increases as one goes up the series. On the other hand metal ions at the bottom of the series easily pick up electrons and therefore act as good oxidizing agent down the series. The potentials are referred to as *redox potential*, meaning that this potential is the equilibrium potential for reduction and oxidation reactions. An algebraic sum of the redox potentials of the two constituent electrodes gives the cell potential at the standard state, E^0. The potential of the Daniell cell (Fig. 8.2) consisting of copper and zinc electrodes is thus 1.1 V.

The change in electrode potential with change in concentration and temperature is calculated from the Nernst equation [1]

$$E_1 = E_1^0 + 2.3\,RT/nF \log a_{\text{oxid}}/a_{\text{red}} \tag{8.1.10}$$

Table 8.1 The EMF series

Equilibrium	E^0 (V)
$Li^+_{(aq)} + e^- \rightleftharpoons Li_{(s)}$	−3.03
$Na^+_{(aq)} + e^- \rightleftharpoons Na_{(s)}$	−2.71
$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)}$	−2.37
$Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)}$	−1.66
$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$	−0.76
$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)}$	−0.44
$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$	0
$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$	+0.34
$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$	+0.80
$Au^{3+}_{(aq)} + 3e^- \rightleftharpoons Au_{(s)}$	+1.50

where

E_1	is the single-electrode potential
E_1^0	is the standard single-electrode potential
R	is the gas constant (8.3145 J/mol K)
T	is absolute temperature
N	is the number of electrons transferred in the reaction
F	is the Faraday constant
a_{oxid} and a_{red}	are the activities of oxidized and reduced species, respectively.

8.1.3 Kinetics of Aqueous Corrosion

While thermodynamics deals with equilibrium conditions and predicts the possibility of a reaction to take place, the study of the rate of reactions comes under the purview of kinetics. Corrosion reactions are analogous to what happens in a *short-circuited cell*. The system is no longer in equilibrium, and the reaction proceeds either in the forward or backward direction at the electrodes generating a finite current flow in the circuit. The magnitude of current is a direct measure of the extent of corrosion, and the rate of current flow is a measure of the rate of reaction.

8.1.3.1 Polarization

As the current starts flowing in a short-circuited cell, as in case of corrosion, net oxidation and reduction reactions take place at the electrodes. The potentials of these electrodes start deviating from their equilibrium potential values. Such deviation from equilibrium potential is called *polarization* and the extent of deviation is termed *overvoltage*. The polarization diagrams of corroding metal, first developed by U.R. Evans and therefore also known as *Evans diagram*, are graphs of potential verses log current or log current density. There are two principal types of polarization: *activation polarization and concentration polarization.* Activation polarization arises out of a slow step in the electrode reaction for which activation energy in the form of an increment in potential is required for the reaction to proceed. The overvoltage increases linearly with increase in the rate of reaction as is graphically represented by in Fig. 8.4 [2, 3]. The point of intersection of the anodic and cathodic polarization lines represents the situation where the rate of oxidation reaction equalizes the rate of reduction reaction. This corresponds to the rate of corrosion (i_{corr}) and the linear region gives us the Tafel slopes. A sharp polarization leads to a decrease in corrosion rate, whereas a flat polarization curve increases the rate of corrosion.

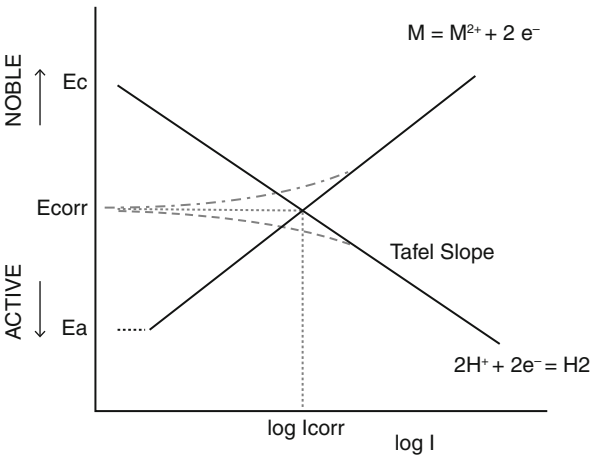


Fig. 8.4 Schematic polarization curve (Evans diagram) showing corrosion rate and Tafel slope

Concentration polarization arises as a result of build up or depletion of ions at the electrode surface as the reaction proceeds. A change in the ratio of a_{oxid}/a_{red} in the Nernst equation brings about a change in the value of the electrode potential, *E*. The diffusion of the reacting species to the electrode–electrolyte interface controls the reaction rate. Accordingly, for the metal dissolution reaction (anodic reaction), concentration polarization is not encountered as there is an abundant supply of metal atoms. For cathodic reactions, concentration polarization is the controlling factor in electrolytes of dilute concentration of the reacting species, e.g. H^+ or O_2.

8.1.3.2 Passivation

Another important phenomenon, *Passivity,* is a controlling factor in determining the rate of corrosion. Passivity refers to the phenomenon of loss of chemical reactivity of a metal or alloy in an environment where thermodynamically the reaction ought to have occurred. Most of the metals when anodically polarized would show continuous increase in corrosion but in some cases like aluminium, stainless steels and titanium, a sharp drop in corrosion rate beyond a certain potential (Fig. 8.5) is observed. It results from the formation of a thin, oxidized or chemisorbed protective film on the surface of a metal, on being polarized anodically. However, beyond a certain potential there is again a sharp increase in corrosion rate and this region is known as trans passive region. Many other metals active in the EMF series, like iron, nickel, titanium can be passivated simply by exposure to strong oxidizing media.

For a more in-depth understanding of the fundamental of corrosion processes, the standard text books on corrosion, e.g. by Fontana [1], Uhlig [4], Jones [5] may be consulted.

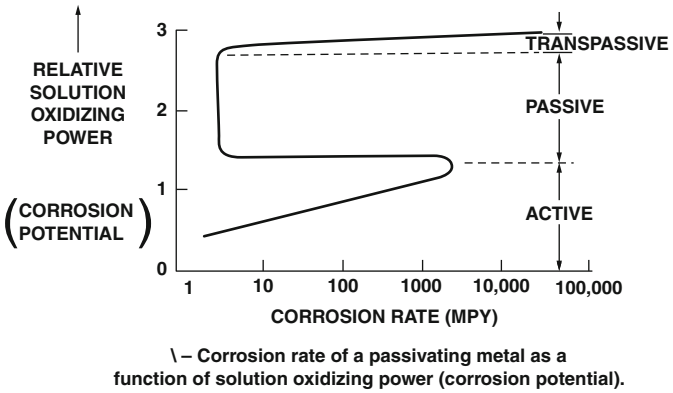


Fig. 8.5 Passivation characteristics

8.2 Forms of Corrosion

The damage due to corrosion, which is of practical importance, is manifested in various forms. These have been classified into eight forms and some of the important ones are as under.

8.2.1 Uniform or General Corrosion

This is the most common form of corrosion resulting in general thinning when exposed to a corrosive environment. The corroded surface may be either smooth or rough, which is mainly controlled by solubility of the corrosion product. This is the most common form of corrosion experienced in atmospheric corrosion, general process side corrosion and acid corrosion. Except acid attack which leaves more or less uniform surface, mostly the corroded surface is rough and the variations are not much, the average corrosion rates can be easily determined as shown in Fig. 8.6. On the basis of the above, the corrosion rate is calculated (expressed generally as mm/year or mils/year where 1 mil = 1/1000 in.) and the value added as corrosion allowance (CA) in a particular medium and included as additional thickness where necessary. As a result of corrosion, the load carrying capacity of a corroded component is reduced. In case of corrosion resistant and nonferrous alloys the rate of attack depends on the resistance of a material in the concerned environment. In the case of stainless steel and nickel-based alloys, general corrosion is experienced only in highly corrosive solutions. Depending on the type, concentration and temperature, metals and alloys have different rates of corrosion in different environments. Alloy selection guides for almost all chemicals have been compiled by NACE and other organizations [6–9]. Information is also available in tabular form or, in some cases, as corrosion curves or alloy selection guide by alloy

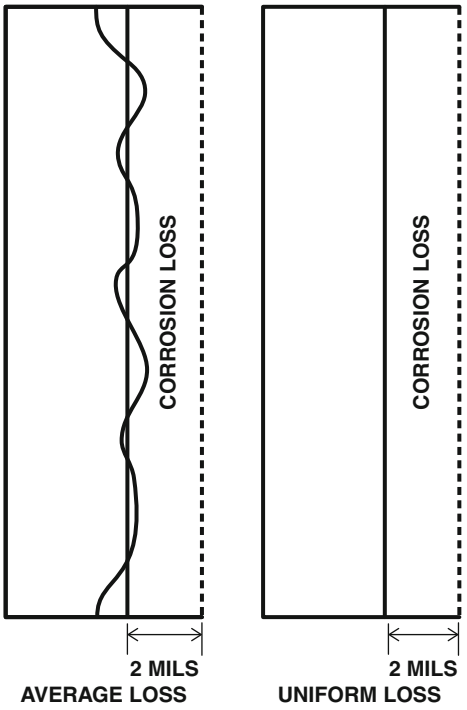


Fig. 8.6 Showing uniform corrosion of carbon steel which has some degree of roughness

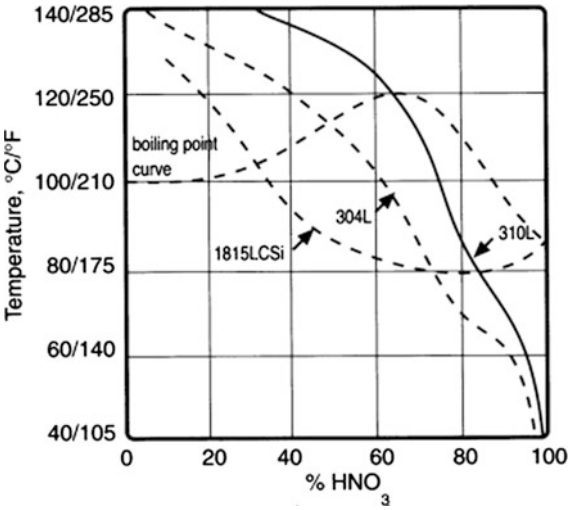


Fig. 8.7 Isocorrosion in nitric acid for Alloy 304, 304L, 310 and 1815LCSi at a corrosion rate of 0.1 mm/year (4 mpy) [10]

manufacturers like Sandvik, Outokumpu, Special Metals, etc. As an example alloy selection guide for nitric acid is given in Fig. 8.7 [10]. One has to keep in mind that these information are only guidelines and not applicable for all types of combinations of chemicals and contaminants encountered in industry.

8.2.2 Galvanic Corrosion

Wherever dissimilar metal are used in contact with each other in the same environment, the more anodic metal will corrode at a faster rate while the less anodic metal will be protected. This is termed as *galvanic corrosion* or *two-metal corrosion.* The intensity of attack depends on the following factors:

8.2.2.1 Potential Difference

In general, higher the potential difference greater will be the attack. For example, iron will corrode at a higher rate when in contact with cupronickel compared to that with naval brass. It is possible to measure and tabulate galvanic series according to the corrosion potentials of various metal and alloys exposed to a specific environment. Heat exchangers in sea water service have multi-metal components and, therefore, galvanic series in sea water has been extensively studied. Table 8.2 [11] gives the galvanic series of various metals and alloys in sea water. The unshaded symbols in case of stainless steel show its active state in acidic water which may exist in crevices or low velocity or poorly aerated condition. The shaded areas show the potentials in passive state. The table shows considerable variations in potential which sometimes makes the prediction more difficult, especially for those metal and alloys which are closer to each other in the series.

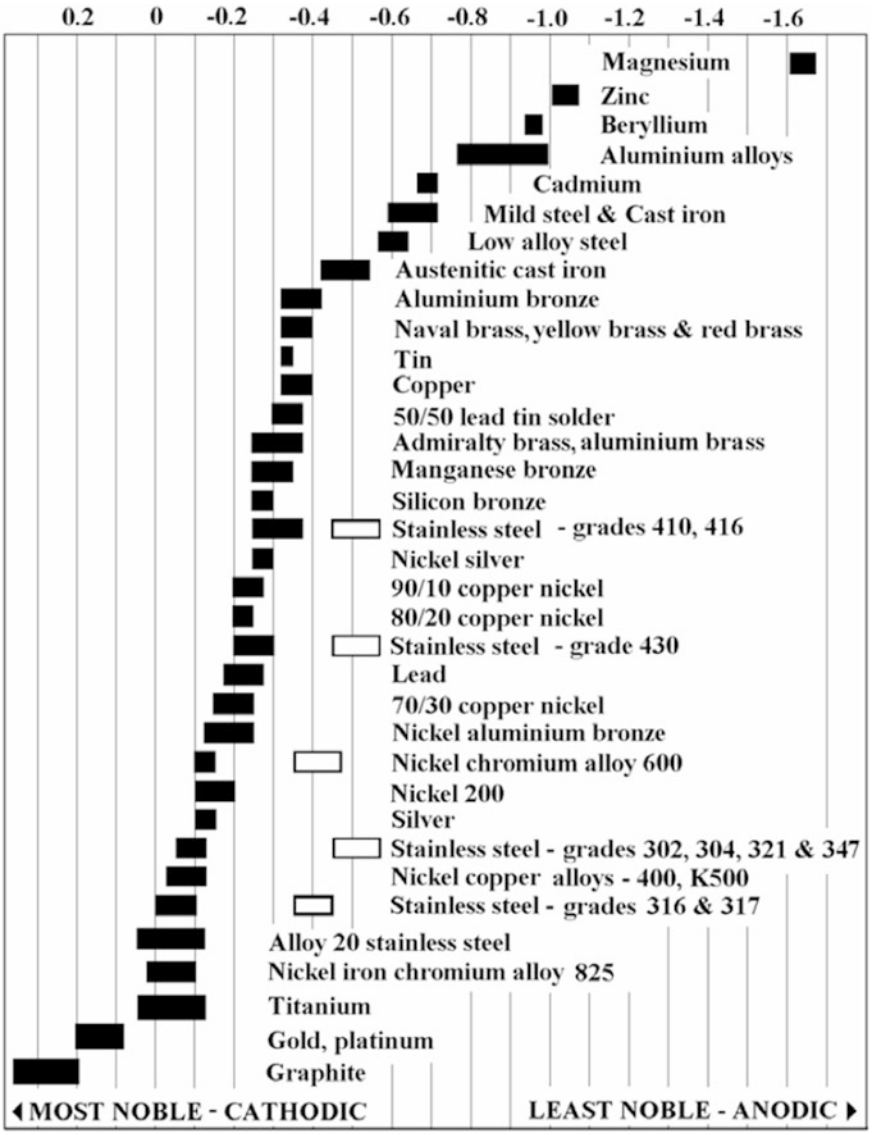
Resistivity of Medium

Resistivity of the medium determines the distance to which the galvanic effect will affect corrosion or not. As the resistance increases, the distance till which the galvanic effect will be operative would decrease. In seawater service, a large area will be affected but in case of low conductive media like fresh water, the attack will be localized at and near the junction between the two metals. It can be assumed that the local corrosion rate near the interface is approximately three times higher than the average corrosion rate, decreasing exponentially away from the interface within a length of ten pipe diameters [12]. The extent of corrosion would, however, also depend on the nature of water, that is, fresh brackish or sea water. Figure 8.8 shows the nature of attack expected where carbon steel partition plate is used with stainless steel tube sheet in fresh water service (high resistance), where stainless steel acts as noble metal with respect to carbon steel as base metal.

8.2.2.2 Area Effect

In corrosion process electrical balance of the anode and cathode system is restored and there is no net accumulation of charges on a corroding surface. However, what is important is that the current densities on anode and cathode are not necessarily

Table 8.2 Galvanic series of metals and alloys in flowing seawater



equal as these depend on the relative anode and cathode areas. Figure 8.9a illustrates two such different conditions. The importance of this relationship is that anodic current (corrosion rate) increases when the anode to cathode ratio is less than 1(small anode and large cathode) and decreases when it is more than 1 (large anode and small cathode) as shown in Fig. 8.9b.

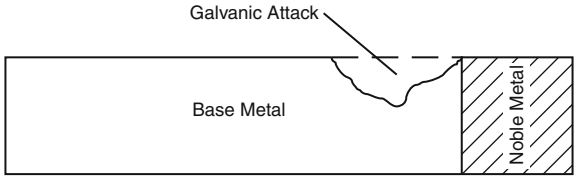


Fig. 8.8 Low conductivity of media restricts spread of galvanic corrosion

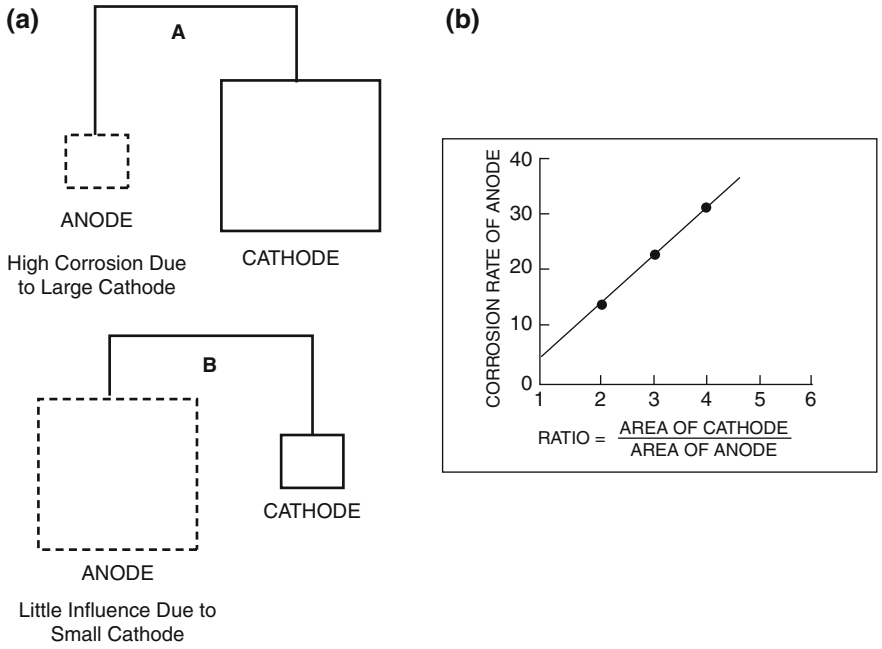


Fig. 8.9 **a** Anode:Cathode ratio; *A* Small anode large cathode; *B* Large anode small cathode. **b** Area effect during galvanic corrosion

8.2.2.3 Cathodic Polarization Characteristics

In case of a multi-metal component, the galvanic effect will also be intensified by depolarization of cathode due to the presence of oxygen or any other oxidizing agents in the aqueous environment and polarization characteristics of metals or the surface in question.

Polarization Characteristics of Metal

As stated earlier, in case of exchangers ten times the diameter of the tube can be considered to be acting as cathode. However, this is not found to be the case where the tubes are made of titanium or stainless steels, especially high performance stainless steel like 254 SMO, DSS, etc. because these are easily polarized. For a considerable time copper alloys were in use for exchangers in sea water service. When better materials were developed, the existing copper alloy tube sheets were re-tubed with titanium or 6Mo austenitic steel, but this resulted in highly accelerated galvanic corrosion of copper alloy tube sheets. After detailed study it was established that the high corrosion rate was due to large increase in cathode to anode ratio. The reason is that these alloys get so easily polarized that instead of small length of the tube at inlet, a large length of the tube acts as cathode thus increasing the effective cathode to anode ratio manifold compared to that in all copper alloy tube bundle [13]. This increased area ratio, which in many cases may be as high as 1000:1, is likely to result in large increase in the corrosion rates even in cases where normal potential difference between the two is too small to have a substantial galvanic effect. The author has investigated a case where 3 mm Monel™ cladding of exchanger cover in seawater service got corroded where tubes were of 254 SMO.

Polarization Effect of Biofilm

In mid-seventies it was observed that biofilm formed on inert surface of stainless steel in natural seawater has a catalytic effect on the cathodic reaction in the corrosion process [14]. The resulting noble potential of the order of 300–350 mV SCE increases the risk of pitting and crevice corrosion. This can also have an effect in increasing galvanic corrosion. The biofilm is active at lower temperatures; once the temperature rises where biofilm is killed, the catalytic ability stops. It has been observed that the critical temperature at which this occurs is 30 and 40 °C in northern Atlantic and Mediterranean, respectively [14].

8.2.2.4 Prevention of Galvanic Corrosion

1. Avoid use of different metals in combination, where possible, such as, copper alloy or stainless steel tube with carbon steel tube sheet and cover; copper alloys valves in carbon steel line;
2. Quite often fasteners, that is, nuts, bolts, screws, are not given the due importance as in many cases they are not directly exposed to the process medium. However, under atmospheric condition also galvanic corrosion occurs, especially inside plant areas where polluted atmosphere exists. Example is carbon steel nuts or bolts with stainless steel flange. The impact on fasteners is more

because their surface area is much smaller than the component fastened. This results in large cathode to anode ratio. Table 8.3 gives recommended combination of fasteners for different materials [15].

3. In case of coating more anodic material against corrosion, be sure that noble metal part is also coated. In case of exchanger cover (carbon steel) along with copper alloy tube sheet and tubes (about 10D lengths from inlet end) should also be coated.
4. Install galvanic cathodic protection system.

Table 8.3 Guide for the selection of fasteners based on galvanic action

Base metal	Fastener metal					
	Zinc and galvanized steel	Aluminium and aluminium alloys	Steel and cast iron	Brasses, copper, bronzes, monel	Martensitic stainless steel (Type 410)	Austenitic stainless steel (Type 302 304, 303, 305)
Zinc and galvanized steel	A	B	B	C	C	C
Aluminium and aluminium Alloys	A	A	B	C	Not recommended	B
Steel and cast iron	AD	A	A	C	C	B
Terne (Lead Tin) plated steel sheets	ADE	AE	AE	C	C	B
Brasses, copper, bronzes, monel	ADE	AE	AE	A	A	B
Ferritic stainless steel (Type 430)	ADE	AE	AE	A	A	A
Austenitic stainless steel (Type 302/304)	ADE	AE	AE	AE	A	A

Key
A Corrosion of the base metal is not increased by the fastener
B Corrosion of the base metal is marginally increased by the fastener
C Corrosion of the base metal may be markedly increased by the fastener material
D Plating of the fasteners is rapidly consumed, leaving the bare fastener metal
E Corrosion of the fastener is increase by the base metal

5. NORSOK M-001 [12] recommends the following steps to control galvanic corrosion for handling of sea water or corrosive produced water.

   - Select material, wherever possible having potential difference of not more than 50 mV, especially where anode to cathode area is expected to be considerably on the lower side. Apply electrical insulation of dissimilar metals.
   - Install a distance spool (of most noble one) between the dissimilar metals, separated by at least 10 pipe diameters from each other. The distance spool may be non-conducting material like GRP or of a metal that is coated internally with non-conducting material like rubber.
   - Apply a non-conducting coating on the most noble of the dissimilar metals, extended to at least 10 pipe diameters into the less noble pipe material.
   - Apply corrosion allowance on the less noble metal.
   - Install, if possible, internal resistor controlled sacrificial anodes through access fittings near the interface.

8.2.3 *Pitting Corrosion*

Pitting is one of the most common modes of corrosion, resulting in localized failures. Pitting corrosion of carbon steel is common in soil, fresh water and brackish water and corrosion resistant materials like aluminium and stainless steels in chloride environment. In pitting corrosion, the attack penetrates at much faster rate compared to the lateral corrosion. Pitting occurs, depending on type of material and environment, due to:

- Whenever a deposit is formed on metal surface under neutral pH, corrosion occurs below it by cathodic reaction involving oxygen (Fig. 8.10) that gets consumed after some time. Because of continuing presence of oxygen in the bulk flowing water, an oxygen concentration cell is formed leading to corrosion and migration of negatively charged ions, especially chloride, under the deposit. The resultant acidic condition compared to bulk solution further enhances

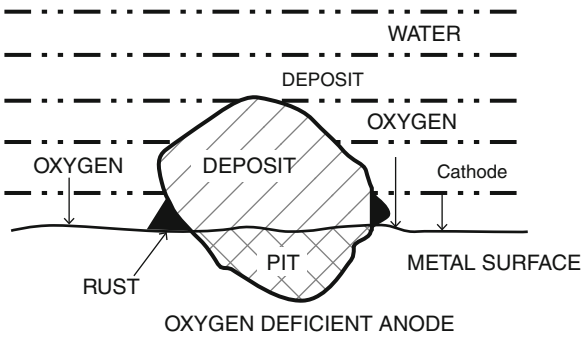


Fig. 8.10 Under deposit corrosion

corrosion leading to pitting. As a matter of fact, Under Deposit Corrosion (UDC) accounts for a large number of failures in piping systems like cooling and fire water lines and in coolers and condensers where low velocities result in deposition of suspended solids. In the latter case, the problem is comparatively more serious when water is on the shell side where flow is not linear but up and down (Fig. 8.11) resulting in the deposits to settle down causing UDC of tube OD surface. Thus, the life of carbon steel tube bundle in water service is less when water is on shell side of a fixed tube sheet construction, as adequate cleaning to remove deposit is not possible. Table 8.4 compares performance of carbon steel cooler tube bundles with water on tube and shell side in two trains of the same plant using cooling water of same quality. Improved performance of the former system is evident from the data given in the table.

- Pits develop at breaks in the protective film of corrosion products, e.g. in cases of sulphide attack or of atmospheric corrosion in marine environments at points of breaks in mill scale or in paints or coating on steel.

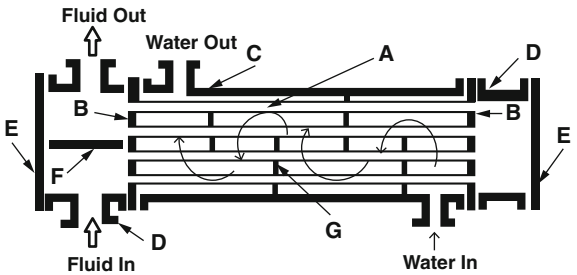


Fig. 8.11 UDC in case of water on shell side

Table 8.4 Failure history of carbon steel coolers with water on tube and shell side

TRAIN A—water on shell side	
Exchanger material	Carbon steel
Commissioned	1st July 1968
1st failure	June 1970 (6 tubes plugged)
2nd failure	January 1971 (40 tubes plugged}
Bundle replaced in May 1971	
1st failure	Dec. 1972 (10 tubes plugged]
2nd failure	Dec. 1973 [80 tubes plugged)
Bundle replaced in May 1974	
[Material changed to SS 304]	
TRAIN B—Water on tube side	
Exchanger material	Carbon steel
Commissioned	1st June 1970
1st failure	30th January 1974 (2 tubes plugged}
2nd failure	14th June 1976 (8 tubes plugged)
3rd failure	9th October 1978 (20 tubes plugged}
Bundle replaced	10th June 1979

- Tubercles formed due to water corrosion of iron result in pitting. In the presence of sulphate reducing bacteria (SRB), the intensity of attack increases as SRB is active under anaerobic condition.
- Carbon film formed on copper during annealing has also been reported to cause pitting type of attack in potable water, where the carbon film acts as an active cathode surface.
- The basic mechanism discussed earlier in case of carbon steel is also operative in case of stainless steel. The resultant pits formed on carbon steel is comparatively broader and shallower than that in stainless steel. Localized breakdown of protective oxide or passivation film on aluminium and stainless steels results in high rate of pitting.

8.2.3.1 Pitting of Stainless Steel

All grades of stainless steels and aluminium and its alloys have an active/passive state and high chloride, high temperature and low pH environments are likely to cause severe pitting in many of the common grades of stainless steels. In process plants, 15% of corrosion failures of stainless steels have been estimated to be due to pitting. Chlorides have the most damaging effect. Because of its small size and high mobility, chloride ions migrate inside the pit under the potential gradient formed between anode (at breaks in the film) and the surrounding cathode. Metal chloride formed inside pit is acidic salt and hydrolyses to produce hydrochloric acid resulting in the lowering of pH inside the pit:

$$M^+Cl^- + H_2O = MOH + H^+Cl^- \tag{8.2.1}$$

The passivity is broken and attack progresses along the pit bottom. This autocatalytic reaction is shown in Fig. 8.12. In stagnant conditions pits tend to grow downwards on horizontal surfaces and rarely grow upwards. Further, pits are less frequent on vertical surfaces.

8.2.4 Crevice Corrosion

Intense localized corrosion frequently occurs within the crevice between overlapping components having gaps of micron dimension. Some important instances are gasket faces of flange, tube to tube sheet joint, lap joints, fasteners, etc. Even deposits/biofilm can act as crevice. While most metals and alloys are subjected to this type of attack, those having active/passive stages, e.g. stainless steels and aluminium are affected the most. Tighter gaps, larger crevice depth and larger surface area help in increasing the rate of crevice corrosion of stainless steels in chloride environments.

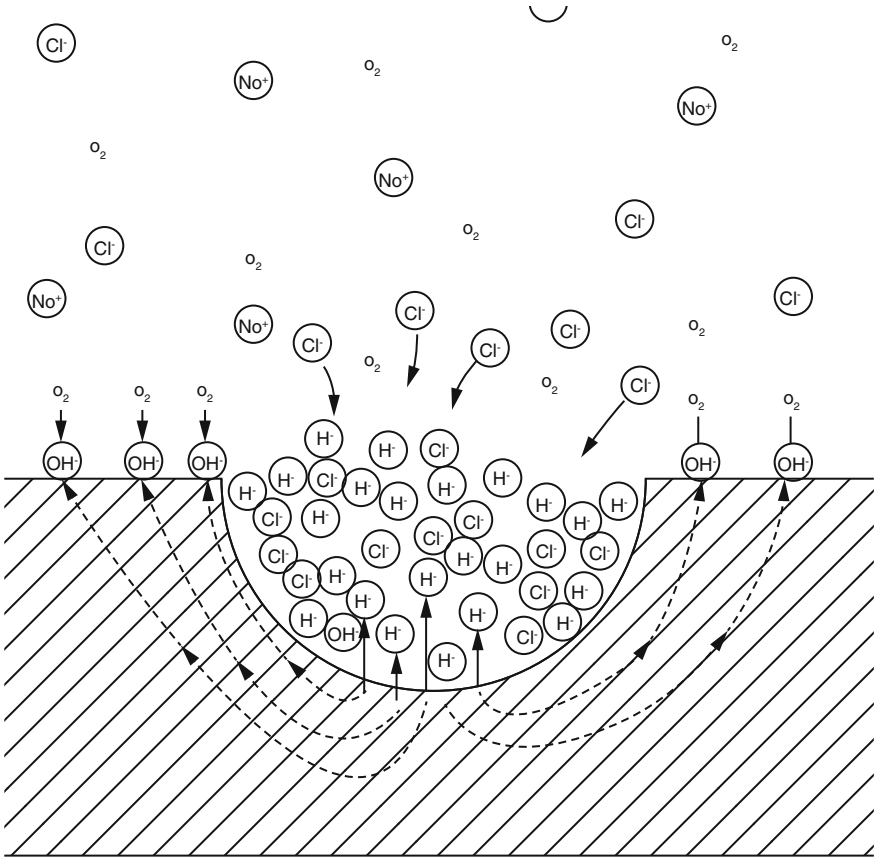


Fig. 8.12 Pit formation involves autocatalytic reaction

The major cause of crevice corrosion is entrapment of water in very fine gap between two mating surfaces. The overall reaction involves creation of metal ion and reduction of oxygen within and outside the crevice, respectively. Initially this is uniform over the entire surface but after a short interval, the oxygen within the crevice is depleted. Corrosion continues within the crevice, producing an excess of positive charge in the solution, which is balanced by migration of negatively charges chloride/sulphate within the crevice. An autocatalytic situation, as in case of pitting, develops resulting in rapid attack. The mechanism is illustrated in Fig. 8.13. There is a long incubation period, but once initiated the attack progresses rapidly. Optimum crevice resistance is achieved with an active–passive metal possessing:

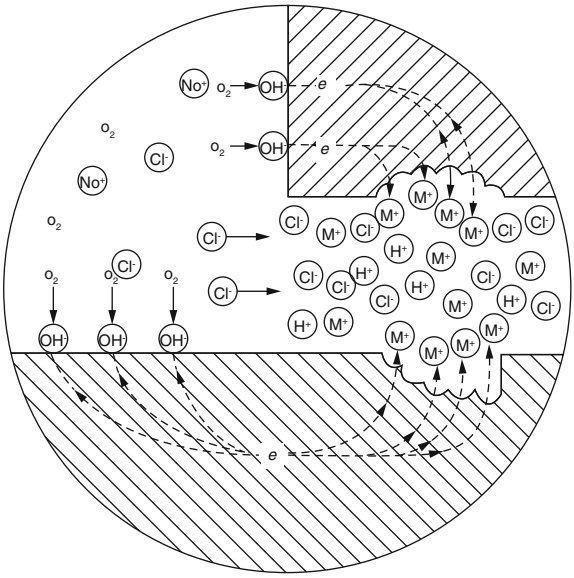


Fig. 8.13 Crevice corrosion due to fine gap at flange joint

1. A narrow active–passive transition
2. A small critical current density
3. An extended passive region

Crevice corrosion of stainless steels is more commonly observed with the following combinations:

- Gasket and O ring to flange
- Bolt connection consisting of head to washer, washer to base plate and bolt thread to nut
- Pads to vessel wall in case the former is partially (not fully all around) seal welded to the vessel
- Barnacles or microbiological film attached to surface
- Sleeve to pump shaft in sea water service
- Plastic tape to metal

8.2.4.1 Controlling Pitting and Crevice Corrosion in Stainless Steels

The fact that resistance to corrosion of stainless steel is due to the formation of stable film of chromium oxide on the alloy surface it is the defect free nature of the film which has a large role to play. Further, the film should not only be defect free but should also have the ability to repair any damage to the film during service. Thus both crevice and pitting corrosion can be considered concurrently though they may not be fully identical. Increasing chromium content is the first step that can be

taken to improve pitting and crevice resistance but there is a limit to it because chromium content beyond 25–27% makes the steel brittle. Based on studies carried out, just as in case of carbon equivalent, the effect of individual alloying elements on pitting resistance has been converted to equivalent effect of chromium and the sum total of these added to the actual chromium content. Thus the relative resistance of various stainless steel to pitting is represented using empirical formulas, known as Pitting Index or Pitting Resistance Equivalent Number (PREN), which for various types of stainless steels are represented as

$$\begin{aligned} \text{Ferritic} \quad & \text{PRE} = \%\ \text{Cr} + (3.3 \times \%\ \text{Mo}) \\ \text{Austenitic} \quad & \text{PRE} = \%\ \text{Cr} + (3.3 \times \%\ \text{Mo}) + (30 \times \%\text{N}) \\ \text{Duplex} \quad & \text{PRE} = \%\ \text{Cr} + (3.3 \times \%\ \text{Mo}) + (16 \times \%\text{N}) \end{aligned}$$

It may be noted that 16 × %N is presently used for all grades of stainless steels. Nickel has no role in changing the passivation characteristics (PREN). However, increase in nickel content does have an effect in decreasing the rate of pitting attack [16]. The PRE values, based on the above for the nitrogen alloyed grades are shown in Table 8.5 [17].

Figure 8.14 [18] ranks various alloys as regards their pitting resistance. For seawater (20,000 ppm chloride) of pH 7.8, alloys with an index of above 32 have adequate resistance to pitting, but those with an index of 40 and above are highly resistance to pitting corrosion at ambient temperatures. Pitting tendency is very

Table 8.5 Typical PRE values for various stainless steels

Grade	304L	316L	SAF 2304	317L	2205	904L	SAF 2507	254 SMO	654 SMO
$PRE_{16\times N}$	19	26	26	30	35	36	43	43	56
$PRE_{30\times N}$	20	26		30		37		46	63

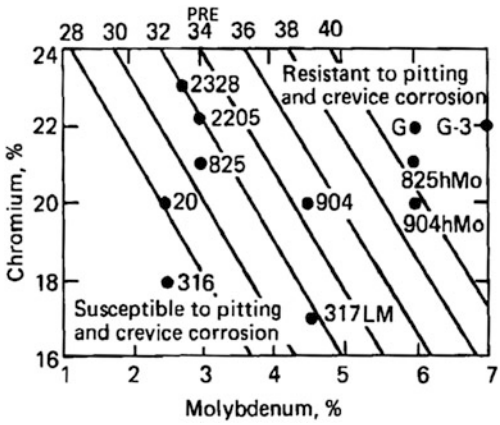


Fig. 8.14 PRE versus resistant to pitting [18]

much related to the environment (pH, chloride concentration, presence of oxygen and temperature), and where the ranking in a specific system is not available, the PRE index can be used as a broad guideline in the selection of alloys. Pitting susceptibility is also dependent on the presence of oxygen in the system; the susceptibility drastically decreasing in the absence of oxygen.

Pitting and crevice corrosion susceptibility increases with temperature. For example, alloy suitable at 40 °C may fail at higher temperatures. From practical point, therefore, it is also necessary to rank various alloys on the basis of their Critical Pitting Temperature (CPT) which is normally determined by highly corrosive 10% ferric chloride solution [ASTM G48 method]. Gradation as obtained from test carried out in chloride containing water of neutral pH would, however, be closer to the conditions encountered in many industries than that in highly acidic ferric chloride solution. Figure 8.15 [19] shows CPT versus PRE of austenitic and duplex stainless steels based on test carried out as per ASTM G48. Crevice corrosion is more severe of the two and therefore CCT values are lower than the CPT. To ensure freedom from crevice corrosion, design temperatures should in general be at least 15–25 °C below the temperatures given by the CPT values, although the critical temperature strongly depends on the crevice geometry.

Other than material selection, certain additional precautions are taken for metals and alloys in environment likely to cause pitting and crevice attack. Some of the important ones are as follows:

– Wherever possible, heat tint film formed on stainless steel or titanium after welding should be removed by pickling. These thicker films are less protective than air formed film and have higher susceptibility to pitting.
– Formation of deposit on surface should be avoided. Where this is not possible, the surface should be cleaned during plant shutdown.

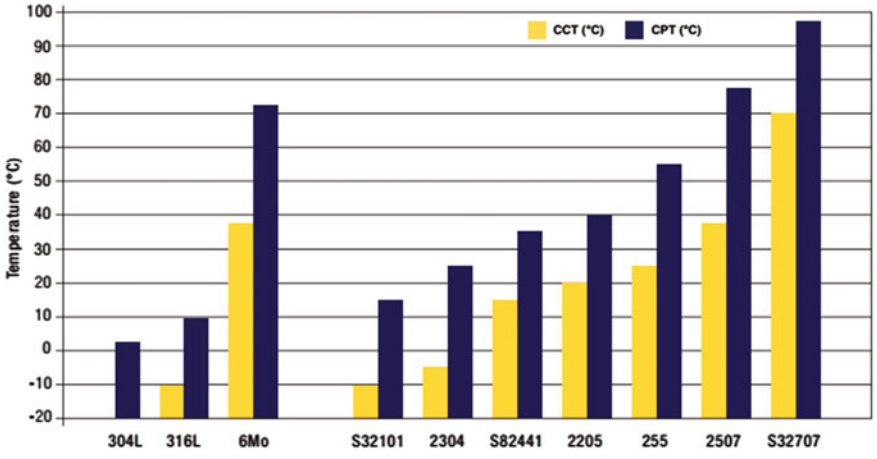


Fig. 8.15 Critical pitting and crevice temperatures of austenitic and duplex stainless steels [19]

- In case of cooling water systems, stagnation of water for long periods should be avoided. UDC can occur even in low flow circulating fresh water system. This is especially important in sea or brackish water for Cu–Ni or stainless steels. Even potable waters containing considerable amount of suspended solids have caused serious pitting corrosion. During plant shutdown of long duration, the exchangers must preferably be drained. Where sea water is used, exchanger should be flushed with fresh potable water having low chloride content (50 ppm max) or preferably DM water. Alternately, water circulation should be maintained to avoid settling of solids.
- For hydro testing or washing of stainless steel equipment and piping DM water or fresh water with 50 ppm max chloride (only if DM water is not available) should be used.
- Gaskets, washers, etc. having mating surfaces should be properly matching and tightened to minimize chances of crevice formation.

8.2.5 Stress Corrosion Cracking (SCC)

This is one of the most common modes of failure and account for over 25% of all corrosion failures in the process industry. All alloys fail by SCC in some specific environment. For SCC to occur, for a particular alloy the following two conditions need to be fulfilled:

(i) Presence of an environment, specific for the particular alloy, and
(ii) Presence of tensile stress, applied or residual.

In other words, in the absence of any of the two, SCC will not occur. Table 8.6 lists the specific environments in which some of the commonly used alloys are susceptible to SCC. This list is not complete and is continuously growing with identification of new cases in industries.

Important characteristics of SCC are as follows:

(1) Pure metals are normally immune from SCC.
(2) Each alloy/environment combination has a definite mode of cracking. For example, copper alloys generally alloys fail in ammonia environment intergranularly (Fig. 8.16a) [20], but the mode of failure of 300 series of stainless steels in chloride environment is highly branched transgranular (Fig. 8.16b) [21] cracks. In sensitized condition and at temperatures below 50 °C cracks are generally intergranular.
(3) In some copper alloys like Cu–Zn, Cu–Al, Cu–Mn, etc. change in mode of cracking from inter to transgranular occur beyond certain concentration of alloying element. In the composition range in between the two the mode of cracking is inter + transgranular.

Table 8.6 Alloy-environmental systems susceptible to stress corrosion cracking

Alloy	Environment
Carbon steel	Carbonate and bicarbonates Caustic Nitrate Cyanide Anhydrous ammonia $CO/CO_2/H_2O$ mixture
Austenitic stainless steel	Organic and inorganic chlorides Acidic hydrogen sulphide Caustic Sulphurous and polythionic acids Nitrates Hydroxide Chlorides
Nickel-based alloys	Caustic above 315 °C (Alloy 200, 400 and 600) Mercurous nitrate (Alloy 400) Mercury (Alloy 400) Hydrofluoric acid + Oxygen (Alloy 400) Fluosilicic acid (Alloy 400)
Copper-based alloys	Amines (can break down to ammonia) Dilute ammonia Ammonium hydroxide Mercury Sulphur dioxide
Aluminium	Chlorides Marine atmosphere
Titanium Alloys	Organic chlorides above 285 °C Hydrogen embrittlement Methanol Seawater (Sodium chloride) Nitrogen–Tetroxide
Tantalum	Hydrogen embrittlement

(4) SCC in polythionic acid occurs when the stainless steel is in sensitized condition and the mode of cracking is intergranular.
(5) SCC does not occur in presence of compressive stress.
(6) In many cases, the cracking time versus stress shows an endurance limit, i.e. the cracking susceptibility decreases with decrease in stress. Here the tensile stress is a combination of residual, operating, welding, fabrication and other stresses induced.
(7) Welding stresses may be as high as the yield stress of the material and, therefore, cracks develop more readily at welds and HAZ. In equipment and piping where possibilities of SCC exist the inspection is in most cases is first carried out on welds.

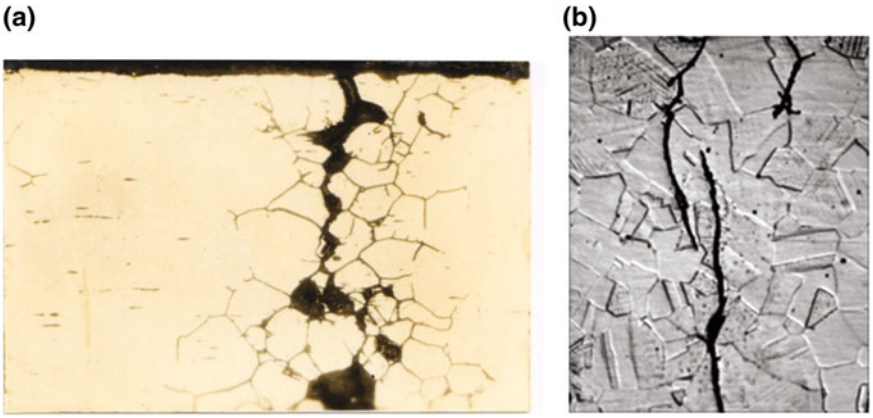


Fig. 8.16 **a** Intergranular cracking of 70Cu–5.8Mn alloy [20]. **b** Transgranular cracking of stainless steel [21]

(8) SCC susceptibility also depends on composition of the alloy. For example Cu–Zn alloys become susceptible to SCC only above 10%Zn; Cu–Al and Cu–Ni alloys are less susceptible than Cu–Zn alloys. Similarly nickel content has a large influence on SCC of austenitic stainless steels. The susceptibility first increases and then decreases with increase in nickel content, the minimum time of cracking being around 10–15%Ni. Effect of nickel in improving the resistance to SCC of Fe–Cr–Ni and high nickel alloys is shown in Fig. 8.17 [22]. As a practical guideline, alloys with a minimum nickel content of 22%, such as, alloy grades 904, 28 and 20, seldom experience SCC. Alloys with high nickel of $\geq 42\%$, e.g. Types 825, G, 625 and C276 are fully resistant to SCC. Ferritic and duplex stainless steels are also highly resistant to SCC. For practicing engineer Fig. 8.17 can be used as a guideline for alloy selection.

8.2.5.1 Prevention of Stress Corrosion Cracking

Stress corrosion cracking may be reduced or prevented by application of one or more of the following methods:

1. Lowering the stress below the threshold value by annealing or PWHT in the case of residual stresses of by reducing the operating load or pressure. It should be kept in view that no PWHT is carried on austenitic stainless as it renders the material prone to intergranular corrosion.
2. Eliminating the critical environment species by, degasification, demineralization or distillation.

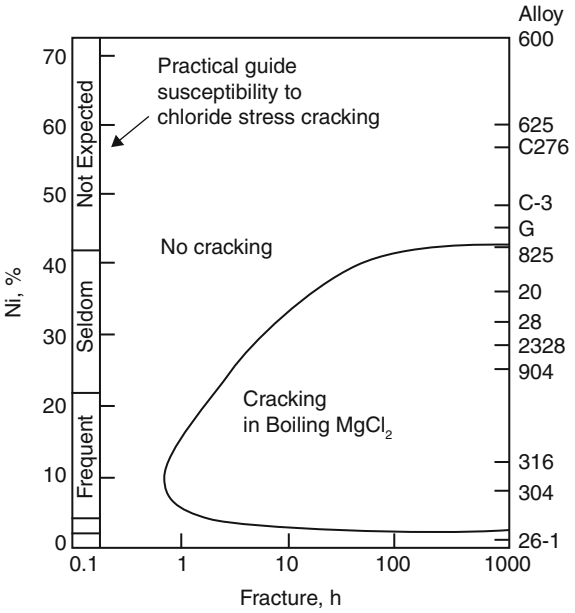


Fig. 8.17 CSCC of different stainless steels [22]

3. Changing the alloy is another possible recourse where neither the environment nor stress can be changed. For example, it is a common practice to use high nickel or duplex stainless steels where austenitic stainless steels are liable to fail due to SCC.
4. Application of cathodic protection.
5. Adding inhibitors to the system, if feasible. Phosphate and other inorganic and organic corrosion inhibitors have been used successfully to reduce stress corrosion cracking effect in mildly corrosive mediums.
6. Substantial improvement in resistance to SCC as a result of shot peening has been obtained in practice. This is because peening produces residual compressive stresses on the surface of the metal.
7. Cladding of the susceptible alloy with pure metal or an alloy which is immune to cracking.

8.2.5.2 Some Practical Considerations in Use of Stainless Steels

In process industry stainless steel, normally 304 or 316 grades are extensively used for both equipment and coolers and condensers. It is also quite common to consider up gradation of carbon steel or copper alloy tubes to stainless steel if the performance of the cooler is not found satisfactory. However, before making a decision due attention should be given to the possible failures due to pitting, crevice attack

and stress corrosion cracking. There have been number of instances where the expected improvement has not been achieved because all aspects of the problem were not taken into consideration.

Chloride Concentration and Temperature Limits

Chloride Limit

In a number of instances water from various sources like river, lake, underground, and estuaries come in contact with stainless steels. In such cases normally conventional stainless steels like 304L or 316L are used. Question arises as to what is the safe level of chloride which can be specified in such cases? Various values of chloride have been suggested specially for potable water; but temperature, presence of crevice, surface conditions and the grade of steel play a large role in performance. Table 8.7 gives the chloride limits of various grades of stainless steels in different waters recommended by the Nickel Institute [23].

Temperature Limit

As regards CSCC it is difficult to suggest the minimum limits of chloride and temperature. It is well known that the CSCC susceptibility increases with increase in temperature and chloride concentration. However, generally accepted temperature limit for CSCC for stainless steels (Types 304, 316, etc.) varies from 60 [12, 24] to 50 °C minimum, though cracking at lower temperatures has also been reported [25, 26]. Collapse of roof of swimming pools due to failure of stainless steel rods supporting it have also been reported [27, 28]. Based on the investigation, collaborative guidelines for architects, designers, builders and pool managers were published in 1995 [29]. Temperature limits for other grades of stainless steels are:

Duplex stainless steel	100 °C
Super duplex stainless steel	110 °C
Super austenitic stainless steel	120 °C

Table 8.7 Suitability of stainless steels in waters

Chloride level, ppm	Stainless steel grades
<200	304L, 316L
200–1000	316L, Duplex alloy 2205
1000–3600	Duplex alloy 2205 6%Mo super austenitic Super duplex
>3600 to	6%Mo super austenitic Super duplex
15,000–26,000	6%Mo super austenitic Super duplex

Cooling Water System

Failure of stainless steel in water service is quite common. In this connection detail survey was carried out in Japan [30]. Seven hundred fifty five cases of failure of exchangers were analyzed on the basis of structure, orientation, tube material and years of service. The data was analyzed in four different ways and final conclusions were arrived at based on chloride versus skin temperature of the tube. The limitation of such study is that one has to depend on bulk chloride level and skin temperature and local conditions ignored as the same were not identified. The location of cracking was also not available in all cases. Thus the data had lot of scatter but still it was possible to establish the trend. Without going into details of different variations, the main conclusions are shown in Fig. 8.18 (Redrawn from Fig. 14 of Ref. [30]) and listed below. In conclusion, it can be stated that:

- Possibilities of cracking, independent of the orientation, are higher in cases where water is on shell side.
- The chloride and skin temperature for cracking to occur in case of water on shell side are 10–20 ppm and 20–25 °C, respectively, in case of both the orientations.
- The chloride and skin temperature for cracking in case of horizontal orientation with water on tube side are 30 ppm and 90 °C, respectively.
- In case of vertical orientation and water on tube side, the chloride level and skin temperature for cracking will be about 100 ppm and 30 °C, respectively.

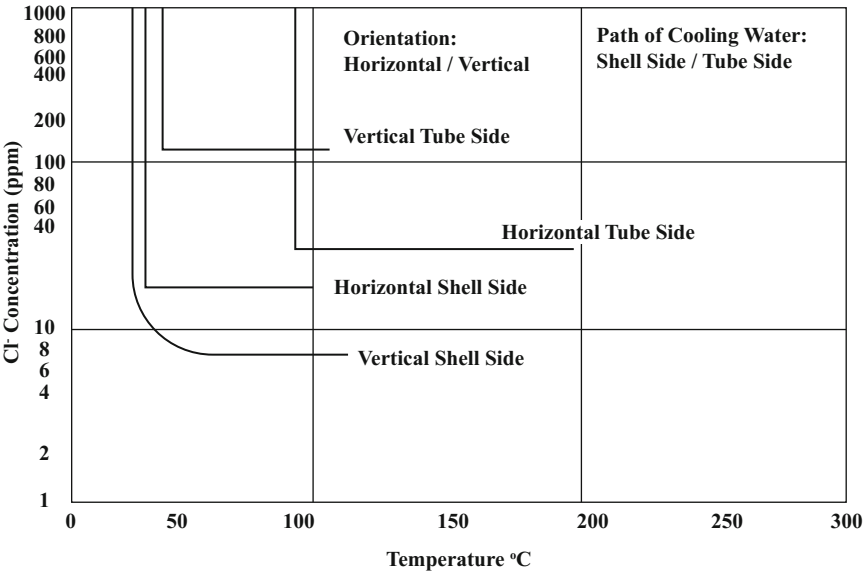


Fig. 8.18 Summary of the survey on performance of stainless steel exchangers with respect to orientation and path of cooling water

- The survey also found that there was not much difference between performance of Types 304 and 316 in horizontal exchangers with water on shell side. However, the performance of 316 was much better in horizontal exchangers with water on tube side, especially with respect to chloride level (300 ppm against 10 ppm for vertical).

MTI survey [31] also predicts possibilities of CSCC in the presence of minimum 10 ppm chloride. It may be mentioned that as per API 581, in case chloride is <1 ppm and pH $\geq$ 10, the possibilities of CSSC should be examined.

Process Plant Equipment

In another survey undertaken by the Society of Chemical Engineers and The Japan Petroleum Institute [32] performance of different grades of stainless steels, including known resistant grades, in petrochemical and refinery industries were surveyed. As far as damaged units are concerned 44 cases were related to exchangers and 23 to towers and vessels. Though most used initially selected alloy belonged to 300 series (304, 34 cases; 304L, 4 cases; 316, 10 cases and 316L, 13 cases), in 35 cases CSCC resistant alloys (DSS 15 cases; SS 444 (19Cr–2Mo); others 7 cases) were selected initially itself. Table 8.8 summarizes the result of the survey which shows that most of the failures were in heat exchanger and minimum chloride level and temperature, except a few cases, were 1–10 ppm and 50–100 °C, respectively. In case of coolers and condensers the most susceptible locations are both ends of the tube to tube sheet joint (Fig. 8.19) [33], depending on which side is the water. Chloride can concentrate at these locations. Such failures can also occur in case the process medium contains chloride. A good practice is to seal weld the tube to tube sheet joint.

Table 8.8 Salient features of survey results

Unit type subjected to CSCC	Number of cases	°C at CSCC location	Number of cases	Cl (ppm) at CSCC location	Number of cases
Heat exchanger	44	0–50	6	ppm level	51
Tower/vessel	23	50–100	49	1–10	8
Piping	15	100–150	23	10–100	11
Reactor	6	150–200	17	100–1000	9
Pump	2	200-250	4	>1000	7
Others	6	250–300	2	%level	7
		300-350	0	0–10%	5
		350–400	1	>10	1

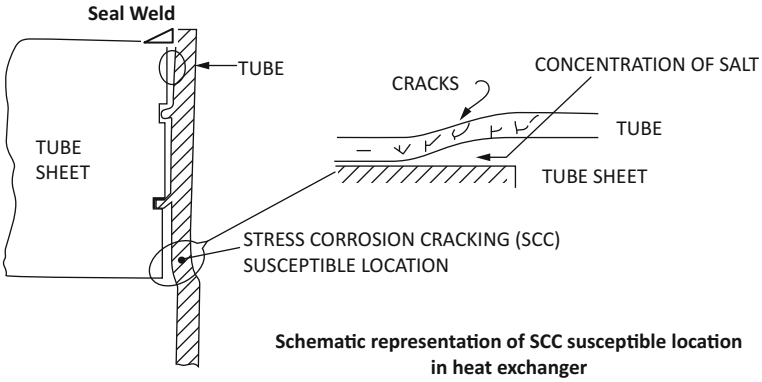


Fig. 8.19 Locations where CSCC of stainless steel is likely to occur [33]

8.2.5.3 External Stress Corrosion Cracking (ESCC) of Insulated Stainless Steel

In case of austenitic stainless steels, the problem of corrosion under insulation (CUI) is of greater concern in spite of its being a corrosion resistant alloy. The problem is primarily related to its high susceptibility to chloride stress corrosion cracking, known as External Stress Corrosion Cracking (ESCC). Cracking occurs when under the insulation there is presence of both water and chloride on the metal surface. The source of chloride is (i) environment (coastal plants and offshore installations), (ii) insulation, (iii) process stream and (iv) condensate or cooling water. Most CSCC failures occur in the temperature range of 49 and 150 °C. When insulation is properly installed and maintained, it prevents the ingress of moisture at the surface of the insulated item. So long as the insulation is water tight there is no problem. A properly insulated stainless steel can operate at 90 °C in a high chloride, ambient environment for many years without an SCC failure. The problem arises when the insulation system deteriorates.

Depending on the geographic location, rain can contain from 75 to 375 ppm chlorides [34]. In coastal environments, the atmosphere can be a source of both chloride and water. Thus maximum ESCC of stainless steel is experienced near coastal areas. The other source of chloride can be the insulation itself. Many of the commercially used insulations contain some amounts of leachable chloride. In such a case the water passing through the insulation would dissolve the chloride present in the insulation. It has been reported that with continual migration of moisture containing the chlorides the level of chloride accumulation on metal surface can vary from 1000 to 20,000 ppm to initiate CSCC [34]. Today most insulation is manufactured with low chloride or with inhibitors (silicate) that help retard SCC. Inspite of this, precaution against ESCC is taken during design of plant. Third

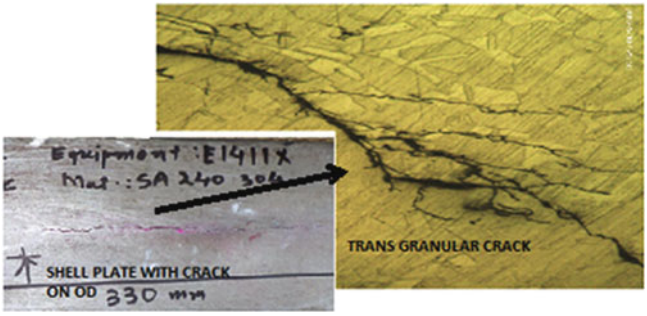


Fig. 8.20 CUI of SS 304 exchanger shell in an inland plant

source is cooling water or process medium containing chloride or condensate from leaky steam trap falling on insulated equipment and reaching the metal surface. Figure 8.20 [35] shows a case of CUI of the shell of a 304 stainless steel exchanger.

Prevention Against (ESCC) of Stainless

Prevention against External Stress Corrosion Cracking

Followings are the preventive methods taken against ESCC:

1. Make the jacketing system watertight; including where re-insulated after some years of service (life of a well maintained system is 15 years) [34]. In case the insulation is removed for some maintenance jobs, the same should be redone to the same degree of quality as for a new job, which quite often is neglected. The use of galvanized steel as jacket material is prohibited in case of stainless steel to avoid its cracking by liquid zinc, in case of fire.
2. Various types of insulating materials like glass wool, rock wool, magnesia, cellular glass, etc. have been used in the industry but the present trend is to use mainly glass wool and cellular glass (with a chloride free adhesive) for stainless steel. Sodium silicate is also added to insulation as inhibitor.
3. The following guidelines for the selection of insulation for 300 series stainless steel have been issued by US Atomic Energy Commission [36]:

Each type of insulating material should be qualified by the manufacturer or supplier for use by:

– An appropriate test to reasonably assure that the insulation formulation does not induce stress corrosion. Two acceptable tests are (i) ASTM C692-71 “Standard Method for Evaluating Stress Corrosion Effect of Wicking-Type Thermal Insulations on Stainless Steel” (Dana test) and (ii) RDT M12-IT, “Test Requirements for Thermal Insulating Materials for Use on Austenitic Stainless Steel”, Sect. 8.5 (Knolls Atomic Power Laboratory (KAPL) test).

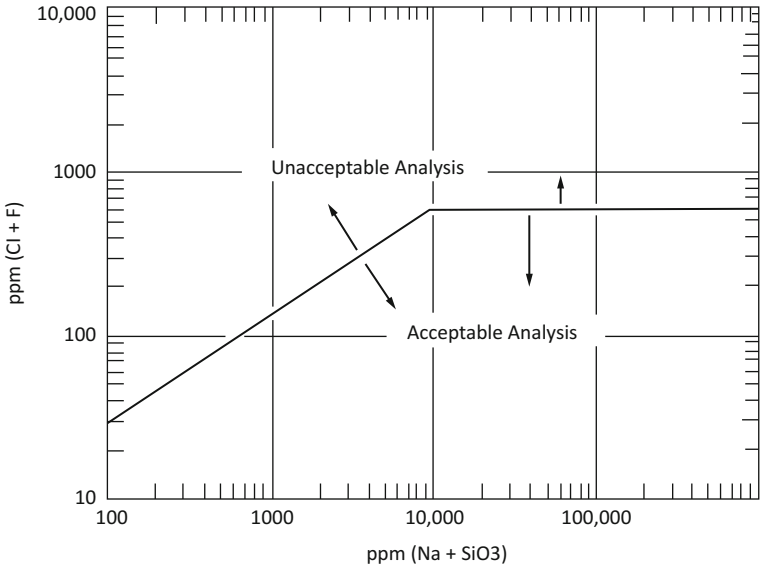


Fig. 8.21 Role of leachable silicate and Cl + F content of insulation on ESCC of stainless steel [36]

– Chemical analysis of the insulation would be done as per ASTM standards to determine the ion concentrations of leachable chloride, fluoride, sodium and silicate. Insulating material that is not demonstrated by the analysis to be within the acceptable region of Fig. 8.21 of this guideline should be rejected. This requirement is also covered under ASTM C795 "Standard Specification for Thermal Insulation for Use in Contact with Austenitic Stainless Steel".

Production Test: Users should ask for submitting production test for chemical analysis (as above) in case of large supply during the project stage to ensure that it is in the acceptable region and that sum of Cl + F and Na + Silicate does not deviate by more than 50% from the values used for qualifying the insulation.

It may be mentioned that in case of process plants, except for critical items, qualification test (ASTM C692-71 or RDT M12-IT) for the evaluation of cracking susceptibility under insulation is not necessary. Also, adhesive used for fixing cellular glass insulation should be free from chloride and fluoride.

4. Provide a barrier layer of about 1 mm thick aluminium foil (wrapped tightly) or apply suitable zinc and chloride free paint on the stainless steel before placing the insulation.
5. Ensure leaking water or chemicals do not fall on insulated equipment.

8.2.5.4 ESCC of Non-Insulated Stainless Steel

There have been a number of instances of failure of non-insulated stainless steels at temperatures below 50 °C and even at room temperature. The failures have occurred in service and also during transport and storage. The cracks are normally intergranular and have been seen both at weld and on base metal. In case of low temperature cracking, the role of sulphur and fluoride also need to be considered. Laboratory tests carried out have established the role of fluoride along with chloride in causing stress corrosion cracking [37]. In addition to its presence in insulation, the main source of fluoride is suspected to be the weld rod coatings consisting of fluorspar (CaF) and cryolite (3NaF.AlF3).

8.2.6 Intergranular Corrosion (IGC)

Another form of localized corrosion, more commonly encountered in stainless steels and nickel alloys containing chromium, is the attack along grain boundaries when heated in the critical temperature range known as sensitisation temperature.

8.2.6.1 Austenitic Stainless Steel

In austenitic stainless steels IGC is of serious concern when the alloys are exposed to the temperature range of 400–815 °C either during welding or high temperature service. As these occur more commonly in the HAZ of welded components, this type of corrosion is also known as *weld decay*. The main cause is the depletion of chromium at grain boundaries. Chromium has high affinity for carbon and when heated or cooled through the critical temperature range of 400–815 °C, chromium carbide is precipitated at grain boundaries. Carbon atoms being small in size diffuse faster than chromium and, therefore, the base metal in a narrow band on both sides of the grain boundary gets highly depleted of chromium. Chromium which is combined with the carbon is no longer available to provide resistance to corrosion as only dissolved chromium forms the protective oxide film. The corrosion resistance of chromium depleted area therefore is reduced and the attack progresses along the grain boundaries. The degree of sensitization depends on number of factors, such as, grade and carbon content of alloy and time for which it is retained or exposed at a particular temperature. Thus normal or H grade of alloy will get more easily sensitized than low carbon or stabilized grades. Figure 8.22 shows a case where welded SS 304 pipe in corrosive service failed in the HAZ of both longitudinal and circumferential welds. Attempts at weld repair shifted the attack to HAZ of repair weld. In this particular case alloy 304 pipe was used by mistake in place of specified SS 316L pipe. ASTM A 262 [38] gives the various tests to determine the susceptibility to IGC which is summarized in Table 8.9.

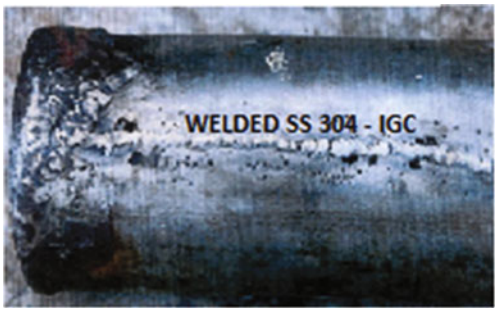


Fig. 8.22 Intergranular corrosion of welded pipe. Repeated welding did not prevent further cracking

Table 8.9 Summary of intergranular corrosion test (IGC) as per ASTM A-262

Test type	Test purpose	Remarks
Oxalic acid test, ASTM A262, Practice A (Oxalic acid etch)	A rapid method of screening stainless steel grades which are essentially not susceptible to IGC associated with chromium carbide participates	The test is used as acceptance test and not for rejection
Ferric sulphate–Sulphuric acid, ASTM A262, Practice B (Streicher test)	Provides a quantitative measure (weight loss) of the relative performance by testing in boiling ferric sulphate—50% sulphuric acid solution for 24–120 h	Measures the susceptibility of stainless steels and nickel alloys to IGC associated with the precipitation of chromium carbides at grain boundaries. Also detects sigma phase in stabilized alloys and cast molybdenum-bearing stainless alloys
Nitric acid, ASTM A262, Practice C (Huey test)	The specimens are boiled for five periods, each of 48 h, in a 65% solution of nitric acid. The customer specifies the maximum permissible corrosion rate and data on sensitizing heat treatment	Used to check whether the material has been correctly heat treated and effectiveness of stabilizing elements and reduction in carbon content. The test also detects intermetallic precipitations, like sigma phase
Copper–Copper Sulphate–16% Sulphuric acid, ASTM A262, Practice E (Strauss test)	Specimens after test are viewed for appearance of cracks after bending through 180° over a diameter equal to the thickness of the specimen	This test determines the susceptibility of austenitic stainless steel to IGC associated with the precipitation of chromium-rich carbides
Copper–Copper Sulphate–50% sulphuric acid, ASTM A262, Practice F	Weight loss after test provides a quantitative measure of the relative performance of the material evaluated	The test measures the susceptibility of "as received" stainless steels to IGC

8.2.6.2 Knife Line Attack

While IGC covers sufficiently large width of the HAZ, sometimes a narrow band of attack is observed in stabilized grades of stainless steels 321 and 347, which has been named as *knife line attack*. During welding, the base metal immediately adjacent to the fusion line is heated to temperatures high enough to re-dissolve the carbides of Ti and Nb. However, the rapid cooling rate prevents re-precipitation of carbides and both chromium and stabilizing elements remain in solution. During post-weld stress relieving heat treatment, this narrow area is reheated to the temperature range where chromium carbide forms. Precipitation of chromium carbide results in the susceptible of the narrow band to IGC. Knife line corrosion can be avoided by heating the weldment above the solutionizing temperature at around 1000 °C and cool at normal rates.

8.2.6.3 Remedial Measures

Intergranular corrosion can be prevented or minimized by controlling the formation of chromium carbides. The following measures used are as follows:

- Solution annealing or quench annealing, where the fabricated components are heated to the temperature range of 1050–1100 °C and then rapidly cooled.
- Small amounts of titanium or niobium are added to the steel. These elements have higher affinity for carbon than chromium and therefore Ti or Nb carbides are formed in preference to Cr-carbide. Type 304 grades of steel containing titanium and niobium are designated as 321 and 347, respectively.
- Carbon content in steel is reduced from normal 0.08% max to 0.03% max. Low carbon grades are designated with suffix L, e.g. 304L, 316L, 317L, etc. Normally for highly corrosive service 0.025%C is preferred for good performance. For most of the stainless steels and high performance steels the carbon is limited between 0.02 and 0.03%.

In addition to control over composition, some additional steps should be taken to minimize chances of intergranular corrosion in known corrosive environments:

- All materials should be procured in solution-annealed condition.
- The welding procedure followed should avoid high heat input or long holding time. Use of low heat input welding techniques minimizes the time for carbide precipitation, and therefore the amount of chromium transfer to the carbides is reduced.
- Surfaces to be welded should be clean and free from carbonaceous material to avoid carbon pick up during welding. This is especially important for maintenance welding.
- Carbon steel clamp or external items should be welded to a stainless steel pad and not directly on the stainless steel equipment.

To ensure the quality of the material procured it is common practice to get from supplier test certificate as per the ASTM A262. The standard gives different types of tests as per the end use and whether welding is involved or not. The stabilized and low carbon grades do not make the steel completely immune to IGC. If held for long period in service within the susceptible range, the base metal becomes susceptible to IGC.

8.2.6.4 Ferritic Stainless Steel

Ferritic stainless steels are also susceptible intergranular corrosion but attack is more common in alloys containing above 15% chromium like Type 430 and Type 446. Sensitisation in ferritic stainless steel takes place during cooling from higher temperatures (>925 °C) due to precipitation of both chromium carbides ($Cr_{23}C_6$) and chromium nitrides (Cr_2N). Susceptibility to intergranular attack in ferritic stainless steels is prevented by

- PWHT at 600–650 °C for several hours
- Lowering of carbon and nitrogen contents to extremely low level ($\sim$0.003%)
- Addition of titanium, niobium and tantalum as stabilizing elements.

Susceptibility to intergranular corrosion of ferritic stainless steels can be detected using ASTM A763 [39]. Nickel alloys (Inconel 600 and 601 and Incoloy 800, Hastelloy B and C) are similarly susceptible to IGC because of the precipitation of chromium carbide at grain boundaries. Many aluminium base alloys are also susceptible to intergranular corrosion. The attack in these cases occurs due to the presence of a precipitated phase at grain boundaries, which are anodic to base metal. In case of Al–4%Cu alloy (Duralumin™) due to depleted zones of copper adjacent to grain boundaries in Al–Cu alloys

8.2.7 Erosion–Corrosion

Performance of many materials is adversely affected when erosive action of moving fluid is superimposed over corrosion. Various types of corrosion damage like impingement attack, cavitation damage fall under the category of erosion–corrosion. The situation arises because of the relative movement between a corrosive fluid and the metal surface. Generally this movement is quite rapid, when mechanical wear effects or abrasion are involved. The protective film on the metal surface is mechanically removed from the metal surface. Continuous exposure of fresh metal does not allow the natural stifling of corrosion rate with time. As the phenomenon involves a localized action, erosion corrosion is characterized in appearance by grooves, gullies, waves, rounded holes and valleys and usually exhibits a directional pattern. Most metals and alloys are susceptible to

erosion-corrosion damage. Many types of corrosive medium could cause erosion corrosion. These include gases, solutions and suspended solids in liquids (slurries). Equipment exposed to moving fluids having turbulent flow, change in direction, flashing of vapours, two phase flow and slurries are subjected to erosion corrosion. Some of these are piping systems, particularly bends, elbows and tees where sudden change in direction takes place as shown in Fig. 8.23. Valves, pumps, impellers, agitators, heat-exchanger tubing, orifice and nozzles are subjected to erosion corrosion.

8.2.7.1 Prevention of Erosion Corrosion

Five methods for the prevention or minimizing damage due to erosion corrosion are used. In order of importance, or extent of use, these are: (1) materials with better resistance to erosion corrosion, (2) design, (3) alteration of the environment, (4) coatings and (5) cathodic protection.

Better Materials: The reasons for using better materials that give improved performance are obvious. This represents an economical solution to most erosion–corrosion problems. For example, in many cases it is common to replace carbon steel bends with stainless steel where impingement damage is experienced or upgrade the metallurgy of pump impellers, without changing that of the casing.

Proper Design: This is an important means by which life can be extended or the attack practically eliminated. Design here involves changes in shape, or geometry, increasing pipe diameter and using large radius bends, increasing the thickness of material in vulnerable areas; providing easily replaceable or corrosion resistant impingement plates, ferrules, etc. Over and under penetration of welds which can form local turbulence should be avoided in case of materials which are velocity-sensitive in the medium being handled.

Alteration of the Environment: Deaeration is an effective method, but in many cases it is not sufficiently economical for minimizing erosion-corrosion damage. Further, such a solution is applicable only in a closed system.

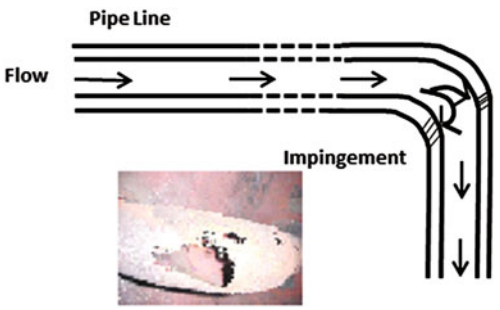


Fig. 8.23 Erosion corrosion downstream at bend due to change in flow direction

Surface Modification: Coating of various kinds that produce a resilient barrier between the metal and its environment are sometimes used, but are not always feasible for solving erosion-corrosion problems. Hard facings, or weld overlays with corrosion resistance material is sometimes helpful in specific situations.

Cathodic protection: This has been found effective in some cases. For example sacrificial anodes on condenser heads protect the inlet ends of tubes against impingement attach. Similarly zinc plugs in water pumps help to protect steel impeller.

8.2.8 Cavitation Damage

Cavitation damage is a special form of erosion corrosion. It is caused by the formation and collapse of vapour bubbles on a metal surface. In a moving liquid, low pressure areas are sometimes formed locally, e.g. vortex, oscillating surface, sudden depressurization of liquid, etc. This low pressure area is immediately filled with vapour and gets stabilized as a bubble and carried along with the stream. When high pressure area is reached, the vapour condenses and bubbles collapse on the metal surface with a great force, the level of which may reach as high as 60 ksi. The high stresses in many cases results in mechanical damage when repeatedly hit with collapsing bubble. The protective film is also removed and corrosion rate increases. In short, the component is affected with closely spaced pits leading to complete dislodging of the material in the affected area.

8.2.8.1 Prevention of Cavitation Damage

Various steps can be taken to minimize damage due to cavitation. Some of the important ones are as follows:

- Reduce hydrodynamic pressure difference of fluid
- Use material with higher hardness having higher resistance to cavitation
- Provide smoother surface finish to minimize repeated bubble collapse on same point.
- Apply well bonded resilient coatings on surface.
- Provide cathodic protection.

8.2.9 Fretting Corrosion

Fretting corrosion occurs at contact areas between materials under load and subjected to vibration and slip. The relative motion necessary to produce fretting corrosion is extremely small; displacements as little as 10^{-8} nm can cause fretting

damage. It appears as pits or grooves in the metal surrounded by corrosion products. Fretting is also called friction oxidation, wear oxidation and chafing. It is observed in engine components, automotive parts, bolted parts, pumps and other machinery. Essentially, fretting is a special case of erosion corrosion that occurs in the air without the presence of any water.

8.2.9.1 Prevention of Fretting Corrosion

Fretting corrosion can be minimized or practically eliminated in many cases by applying one or more of the following preventive measures:

1. Lubricate with low-viscosity, high-tenacity oils and greases as lubrication reduces friction between bearing surfaces and tends to exclude oxygen.
2. Increase the hardness of one or both of the contacting materials. This can be accomplished by choosing a combination of hard materials or hard alloys.
3. To minimize relative motion increase friction between the mating parts by roughening of surface.
4. Use gaskets to absorb vibration and to exclude oxygen at bearing surfaces.
5. Increase load to reduce slip between mating surfaces.

8.2.10 Corrosion Fatigue

Corrosion fatigue is defined as the reduction of fatigue limit resistance in the presence of a corrosive medium. Unlike normal fatigue failure there is usually a large area covered with corrosion products and a smaller roughened area resulting from the final brittle ductile fracture. Figure 8.24 shows array of cracks formed in economizer tube because of corrosion fatigue. In corrosion fatigue no endurance limit is observed. Renewed attention has been given to corrosion fatigue because of potential catastrophic failures in aerospace, nuclear and marine (offshore platforms, submarines) structures.

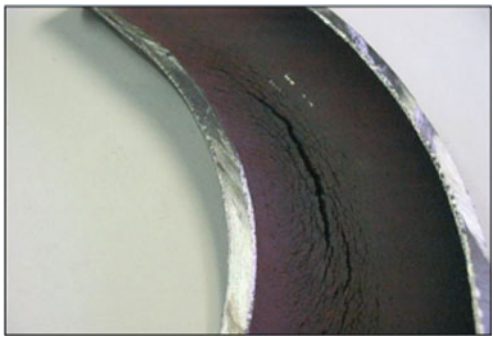


Fig. 8.24 Corrosion fatigue crack in an economizer tube

8.2.10.1 Prevention of Corrosion Fatigue

1. Upgrading the metallurgy
2. Providing cathodic protection
4. Using inhibitor
5. Shot peening the surface to induce compressive stresses.
6. Using coatings, such as, electrodeposited zinc, chromium and nitride coatings.

8.2.11 Dealloying Corrosion

In some alloy systems, preferential removal of one of the alloying constituent takes place under certain environmental conditions. This type of corrosion is known as *dealloying* or *selective leaching*. Copper, zinc and aluminium alloys, e.g. brasses, bronzes, etc. are more susceptible to this type of attack. The phenomenon is known as dezincification and de-aluminification. From the point of view of operation these are important as localized attack can lead to an early failure of exchanger tubes. In case of brass (more than 15%Zn) and Admiralty brass tubes, dezincification occurs where zinc is preferentially leached out. This type of attack occurs more commonly in waters containing high oxygen and carbon dioxide, seawater and where the water velocities are low. The attacked area is coppery red in colour and the cross section of the attacked area shows bright yellow coloured brass under a red porous layer of copper. This type of attack is also experienced in Cu-Al (de-aluminification) and Cu-Ni (de-nickelification) alloys.

Gray cast iron sometimes shows the effects of selective leaching particularly in relatively mild environments. The affected cast iron has the appearance of graphite and is quite soft to be easily cut with a penknife. This phenomenon is known as *graphitic corrosion* which occurs due to selective leaching of the iron matrix leaving the graphite network embedded in corrosion product. The graphite is cathodic to iron, forming a galvanic cell whereby the iron is dissolved, leaving a porous mass consisting of graphite, voids and rust. The cast iron loses strength and its metallic properties. Dimensional changes do not occur, and dangerous situations may develop without detection. Graphitic corrosion does not occur in nodular or malleable cast iron because the graphite network is not present to hold together the residue. White cast iron has essentially no free carbon and therefore not subjected to graphitic corrosion.

8.2.12 Microbiologically Influenced Corrosion (MIC)

Corrosion in metals, especially steels, by microorganisms has been recognized since long in different industries. The problem is more serious in water and soil

environments. Various dominating microbial species have been identified to affect corrosion process of which sulphate reducing and sulphur oxidizing bacteria and iron/ manganese utilizing bacteria cause the greatest damage. Cooling and fire water lines, heat exchanges, etc. are affected. Almost in all cases, the waters involved are either raw (untreated) or inadequately treated to prevent MIC. Biological organisms affect corrosion processes of metals by directly influencing the anodic/cathodic reactions, damaging protective film on metal surface and by producing corrosive substance. Depending on the nature of the microorganisms, the bacteria thrive either under aerobic or anaerobic conditions and form mound type deposits with localized attack. For MIC it is necessary for the microorganisms to lodge and grow at any point. Thus in case of water, stagnant and low flow conditions help in attachment followed by colonization of microorganisms. The corrosion is localized and occurs under bio mound formed. MIC related corrosion is also experienced in upstream and downstream of oil and gas operation where integrity of production tubing, pipelines, vessels, storage and transmission lines and other equipment are affected. Microorganisms also have a major role in making the gas sour. The problems in these cases arise because many microorganisms use hydrocarbons as source of energy. As the source of microorganisms is primarily the reservoir, biocides are regularly injected in the production wells. Microorganisms have also a major role in making the gas sour,

8.3 Corrosion Control

While corrosion is the most common form of material deterioration, there are methods available to prevent or minimize it. The various approaches can be categorized as

- Use of corrosion resistant materials
- Alteration of environment
- Electrochemical protection
- Providing barrier coatings
- Improve design

The type of preventive methods to be used depends on a number of factors, i.e. environment, damage mechanism, desired life, safety considerations and, finally, the cost or economics. More often than not, optimum solution is to be obtained, by combination of the various methods. Any preventive method is directly related to the specific environment under consideration. These are discussed in detail while considering the corrosion and corrosion control in the chemical process industries. In the present section a board outline of the basic approaches to corrosion preventive methods has been given.

8.3.1 Corrosion Resistant Materials

8.3.1.1 Metals and Alloys

The most common method of preventing corrosion is the selection of suitable material of construction (MOC) for a particular service. While elemental metals have inherent tendency to corrosion, these properties can be modified by alloying with one or more metals and non-metals. In most of the cases, the alloying not only improves corrosion resistance but also mechanical and physical properties which are essential for these to be used as an engineering material. Use of various corrosion resistant metals and alloys has been discussed in relation to different processes in this book in respective chapters.

8.3.1.2 Non-metals

This category involves integral or solid non-metallic construction (mainly self-supporting) and also sheet linings or coverings of substantial thickness (to differentiate from paint coating). The five general classes of non-metallic are (1) natural and synthetic rubbers; (2) plastics (3) ceramics (4) carbon and graphite; and (5) wood. In general, rubbers and plastics, as compared to metals and alloys, have low strength and are soft. However, they are more resistant to many chemicals, including hydrochloric acid, but less resistant to oxidizing acids like strong sulphuric and nitric acids. They normally have less resistance to solvents, and most of them can be used at relatively low temperatures (75–90 °C). Some of the plastics like fluorocarbons can, however, be used at high temperatures (up to 300 °C) and also in highly aggressive environments. Ceramics possess excellent corrosion resistance, low electric and heat conductivity, but they are fragile. Wood is attacked by aggressive environments. In subsequent chapters, the application of non-metallic has been referred to under specific situations of dealing with corrosion problems.

8.3.2 Alteration of Environment

There are various methods by which corrosivity of an environment can be modified to decrease the extent of corrosion damage. The applicability of one or more of such methods depends on the process requirements, design and economics and these aspects should be given due consideration. Altering the environment provides versatile means for reducing corrosion. Typical changes are (1) lowering temperature, (2) decreasing velocity, (3) removing oxygen or oxidizers, and (4) changing concentration of corroding chemicals. In many cases, depending on the particular system, these changes can significantly reduce corrosion and allowing the use of cheaper material.

8.3.2.1 Lowering Temperature

Temperature has a large influence on corrosion rate. Normally, corrosion increases with increase in temperature, quite often exponentially. In cases where the corrosion rate is controlled by film formation this increase is less or negligible initially but increases rapidly beyond a certain temperature as in the case of iron in concentrated sulphuric acid or type 304 stainless steel in nitric acid. There is another situation, especially where corrosion is controlled by dissolved oxygen, the corrosion rate first increases with temperature. As the temperature rises, the solubility of oxygen decreases and beyond a certain temperature oxygen level comes down drastically. Otherwise in most situations, if the conditions permit, corrosion can be minimized by lowering the temperature.

8.3.2.2 Decreasing Velocity

Though there are some important exceptions, lowering of velocity reduces corrosion rate where the corrosion process is under cathodic diffusion control or where the stability of protective film is lost beyond a certain velocity. The examples are the presence of dissolved oxygen in natural and seawater and corrosion in film forming systems, respectively. However, this method of corrosion protection requires consideration of the material and environment as the effect of velocity on corrosion rate is complex. Copper alloys used in sea water service have limits on maximum velocity beyond which accelerated corrosion occurs as shown in Table 8.10 [40] and, therefore, these are designed to be used below the limiting velocities. It is also to be remembered that too low a velocity or a stagnant condition is not advisable in many cases because it promotes deposition of suspended solids including corrosion products. The deposited solids cause under deposit corrosion (UDC) and, therefore, a minimum velocity of 0.9 m/s (3 feet/s) is recommended specially in case of copper alloys and stainless steels. In process industry there are numerous examples of corrosion failures due to low velocity conditions, such as, failure of fire water mains in 4–8 O'clock position, which for most of the time remain idle (no flow condition); shorter life of carbon steel exchanger bundle with water on shell side compared to that with water on tube side; short life of ejector condenser carbon steel tubes situated at higher elevations, nearer to column top, etc.

Table 8.10 Velocity limits of various copper alloys used in exchangers handling seawater

Maximum velocity—feet per second (fps)/metre per second (m/s) average				
No of passes	Cu–2%Sn (C68700)	Cu–10%Ni (C70600)	Cu–30%Ni (C71500)	Cu–16Ni–0.5%Cr (C72200)
Once through	6.5 (2.0)	7.5 (2.3)	9.5 (2.9)	10.0 (3.1)
Two pass	5.5 (1.7)	6.5 (2.0)	8.0 (2.4)	10.0 (3.1)

8.3.2.3 Removing Oxygen or Oxidizing Agent

Oxygen has a large role to play in the corrosion process in many environments. Except for the passivating type of metals and alloys, removal of oxygen is one of the important corrosion control techniques. Examples are the treatment of boiler feed water, deaeration of seawater used for desalination plant and seawater injection in oil fields, avoiding ingress of air in an acid system, etc. In passivating metals or alloys, on the other hand, the presence of oxygen is essential for retaining the passivity in highly corrosive situations. For example, in urea reactor air injection is done to protect stainless steel and even titanium (to some extent) to get optimum performance from these metal and alloys against carbamate corrosion.

8.3.2.4 Changing Concentration

There are generally two types of effect of concentration on corrosion rate in a corrosive solution. In many cases corrosion rate increases with concentration, but this is not always true. Many materials exhibiting passivity are marginally affected by the change in concentration of the corrosive species till it reaches a limit after which there is a sudden increase. There are others which show sudden drop in corrosion rate at high concentrations. Sulphuric acid is an example where the solubility of iron sulphate suddenly decreases in concentrated sulphuric acid. This results in the formation of a protective layer of iron sulphate. Thus, depending on the material/corrosive combination, corrosion rate can be controlled in some cases by changing the concentration, in case process requirements are met.

8.3.2.5 Neutralization

Small quantities of acidic constituents are produced during the manufacturing process in a number of cases, e.g. HCl in the overhead of crude distillation unit, CO_2 in steam produced in fired and waste heat boilers (WHB), thermally degraded products in amine treating unit, HCl in platforming or hydro treating units. Where the amount of acid is low, corrosion associated with condensed acidic water can be controlled by neutralizing the acidity. This is a very cost-effective preventive method. The neutralizing agents normally used are caustic, sodium carbonate, ammonia and various types of amines. While using caustic, care should be taken as both carbon steel and stainless steels are susceptible to caustic cracking. Failures in boiler or steam circuit due to caustic are not uncommon.

8.3.2.6 Inhibition

An inhibitor is a substance that, when added in small concentrations to an environment, decreases the corrosion rate. There are numerous inhibitor types and

compositions, both organic and inorganic. Most inhibitors have been developed by empirical experimentation, and many inhibitors are proprietary in nature and their compositions are not disclosed. Inhibition is not completely understood because of these reasons, but it is possible to classify inhibitors according to their mechanism and composition.

Adsorption-Type Inhibitors

These represent the largest class of inhibiting substances used for process and cooling water related corrosion control. In general, these are organic compounds which adsorb on the metal surface and suppress metal dissolution and reduction reactions. The inhibitors may be anodic, cathodic or mixed (general) depending on whether, they get adsorbed on anode, cathode (Fig. 8.25) or on the whole surface. The anodic and cathodic inhibitors increase the polarization of the respective reactions, affecting a decrease in i_{corr}, as would be evident from the polarization diagram in Fig. 8.4. Inhibitors that get absorbed at anodic sites are very effective provided the amount added is above the critical level. This is because any anodic area remaining free of inhibitor film would locally corrode at high rate, resulting in pitting because of small anode and large cathode (*area effect*). In most cases, it appears that adsorption inhibitors affect both the anodic and cathodic processes, although in many cases effect in unequal.

Inhibitor is also used in industry for chemical cleaning of boilers, exchangers, etc. Some of the organic chemicals like thio-compounds have very good inhibitive properties and have been used as pickling inhibitor. As these contain sulphur as one of the elements in the organic chain, any H_2S produced during pickling process can

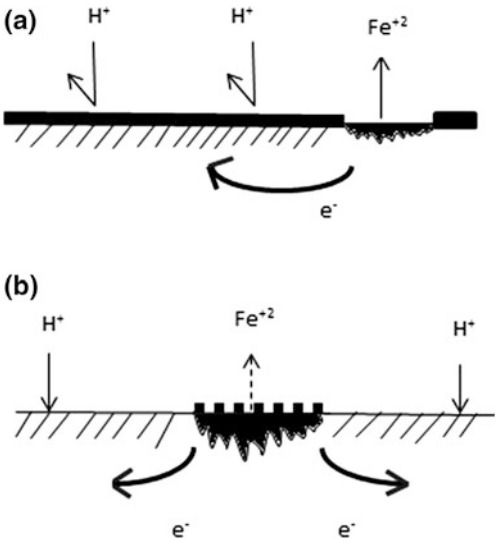


Fig. 8.25 Inhibitor adsorbed on *A* Cathodic and *B* Anodic areas

result in the absorption of hydrogen by steel causing hydrogen related damage like blistering and cracking. Studies carried out have shown that some of the thio-compounds enhance hydrogen absorption and cause cracking of high steel strength. [41].

Passivators

Most of the inorganic inhibitors, e.g. chromate, nitrite, molybdates, etc. passivate steel by forming a protective film of iron oxide. These are very effective as inhibitor, and especially chromates were the most popular inhibiting agent for cooling water system for a number of years. However, chromium being a carcinogenic element its use was phased out since 1970s and today its use is prohibited in many countries. Use of molybdates is preferred in close circuit cooling water systems using combination of fresh and sea water where the latter is used to cool the return circulating water. These inhibitors fall under the category of anodic inhibitor and, therefore, can cause pitting type attack, if adequate amount is not added.

Vapour-Phase Inhibitors

These are very similar to the organic adsorption-type inhibitors and possess a very high vapour pressure. As a consequence, these materials can be used to inhibit atmospheric corrosion of metals without being placed in direct contact with the metal surface. In use, such inhibitors are placed in a closed space in the vicinity of an article to be protected and the inhibitors are transferred by sublimation and condensation on the metal surface. The vapour-phase inhibitors (VPI) are only effective if used in closed spaces and therefore are used against corrosion during transport and storage of articles inside packages or on the interior of machinery during shipment. These are also used for protection of sealed instruments.

Oxygen Scavengers

These substances act by removing oxygen form the solution which promotes corrosion by controlling cathodic reaction. Examples of this type of inhibitor are sodium sulphite and hydrazine which remove dissolved oxygen from aqueous solutions according to the reactions:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \tag{8.3.1}$$

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \tag{8.3.2}$$

It is apparent that such inhibitors will work very effectively in solutions where oxygen reduction is the controlling cathodic reaction but will not be effective in

strong acid solutions. These inhibitors are extensively used in boiler water treatment, idle time preservation of boilers, and seawater injection in oil and gas production.

8.3.3 Electrochemical Protection

8.3.3.1 Cathodic Protection

"*Use a thief of catch of thief*" is a famous saying which has been successfully used in practice. Cathodic and Anodic Protection (CP and AP) fall under similar category where the electrochemical nature of a corroding metal or alloy in a particular environment is utilized to prevent corrosion. Electrochemical reactions occurring on a corroding surface are the anodic (dissolution of metal) and cathodic reactions, e.g.

$$\mathrm{M} \rightarrow \mathrm{M}^{n+} + n\mathrm{e}^{-} \tag{8.3.3}$$

$$2\mathrm{H}^{+} + 2\mathrm{e} \rightarrow \mathrm{H}_2 \tag{8.3.4}$$

The principle of cathodic protection (CP) may be explained in simple terms as supplying electrons to the metal structure to be protected from an external source; thus suppressing the metal dissolution. This will be clear if we examine the polarization diagram of a corroding metal (Fig. 8.26). On a corroding surface some areas are anodic and other cathodic. The flow of current between the two results in

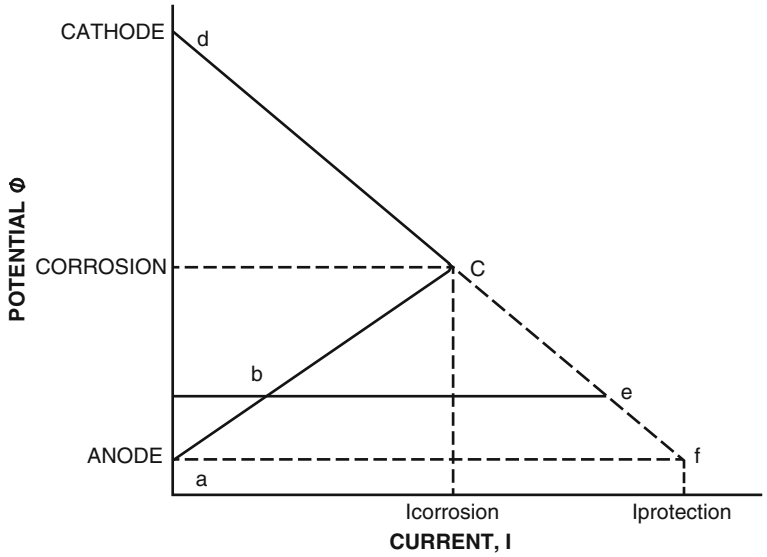


Fig. 8.26 Polarization curve for cathodic potential

their polarization in which the potentials of anode and cathode approach each other till the quasi-equilibrium condition (equal to *I*corrosion) is reached. Now, if additional current from an external source is applied with corroding metal as cathode, the polarization potential of cathode will further shift towards the anode. With increasing current the potential of cathode will continue to shift till it becomes equal to anode potential and at this stage the flow of current between anode and cathode (corrosion) will become zero and the structure will be protected. The principle of cathodic protection is simple but in actual practice, designing of a system requires considerable inputs depending on the individual situation. CP can be provided in all types of aqueous media and soils. Some common examples are underground pipeline and tanks, subsea lines, ships, offshore structure, heat exchangers, storage tanks, etc.

Methods of Applying Protective Current

The application of external current for protection can be done by using either a galvanic anode system or an impressed current system. In a galvanic system the metallic structure is coupled with a more electronegative metal which corrodes and the electron released in the process is discharged on the structure being protected, which acts as cathode of the system. Thus the anode sacrifices itself for supplying the protective current and therefore known as sacrificial/galvanic anode system. Impressed current system, on the other hand, consists of supplying the current to the structure from an external source, usually a rectifier, connecting the negative terminal to the structure and positive terminal to an auxiliary anode. In both the cases, electrons enter the metal through the metallic conductor. The two systems are schematically shown in Fig. 8.27a, b and their advantages and disadvantages in Table 8.11.

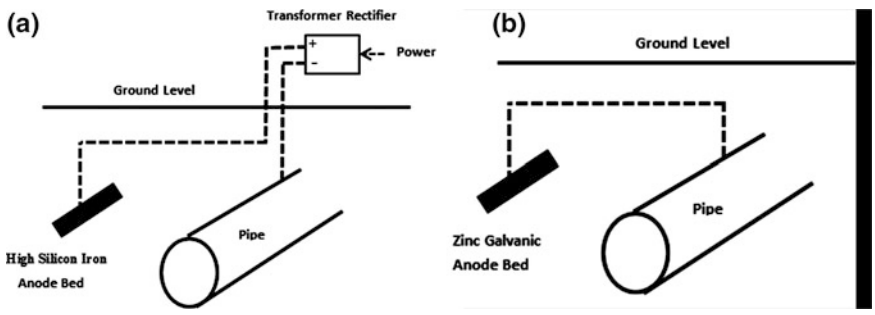


Fig. 8.27 **a** Impressed current cathodic protection system. **b** Galvanic current cathodic protection system

Table 8.11 Advantages and disadvantages of galvanic and impressed current systems

Galvanic	Impressed current
No external power required	External stable supply of power required
Fixed current	Adjustable current
Limited current output	High current output
Effective only in low resistivity medium	Can be used in environment of almost any resistivity
Effective only for smaller and well coated structures	Can be used for very large structure and also ones with poor quality coating
Does not cause stray current corrosion	Stray DC currents can be generated

Anodes Used for Cathodic Protection (Added This Portion)

Impressed Current

- High Silicon Iron (Fe–14%Si) anodes used for underground structures.
- Mixed Metal Oxide Anodes (MMO) consists of very thin layers of metal oxides over titanium. These are used where there are possibilities of chlorine evolution or oxygen evolution in sea water and soil or fresh water, respectively.
- Graphite though it is difficult to handle because of its brittleness.
- Lead alloy of various compositions used in seawater.
- Platinised titanium.

Galvanic Anode

- Magnesium Alloy generally used in soil environment.
- Zinc Alloy used in soil environment.
- Aluminium Alloys used mainly in sea water.

Protective Potential

The protection of a metal or an alloy can be said to be achieved when a minimum potential is attained in a particular environment measured against a reference electrode. For iron, steel and stainless steel the protective potential is minimum—850 mV, against $Cu/CuSO_4$ reference electrode when exposed to soil and water (both fresh and seawater). There are other criteria which have been discussed in NACE Standard RP 0169 [42], but the—850 mV criterion is more commonly used. However, in addition to $Cu/CuSO_4$, other reference electrodes like Ag/AgCl, pure zinc, etc. are used. The protective potential in case of using a reference electrode other than $Cu/CuSO_4$ varies and these variations with respect to the $Cu/CuSO_4$ are given in Table 8.12, which should be used as correction factor.

Table 8.12 Different reference electrodes compared to $Cu/CuSO_4$ electrode

Electrode	Electrolyte	Potential compared to $Cu/CuSO_4$	Comments
$Cu/CuSO_4$	Saturated $Cu/CuSO_4$	0	Robust suitable for field use
Calomel	Saturated KCl	−60	Very stable. Used in laboratory
Ag/AgCl in sea water	Sea water	−60	For field use
Ag/AgCl	Saturated KCl	−100	For high temperature
Pure zinc in sea water	Sea water	−1000	Simple for coarse measurement

One important point in designing of CP is to keep the maximum potential at any location to be not more than 1.1 V against $Cu/CuSO_4$ electrode. Above this potential hydrogen evolution and softening of the coating are aggravated and must be avoided.

Magnitude of Applied Current

The current requirement for complete protection depends on the nature of the environment and on the metal to be protected. But in all cases, the applied current density must exceed the value required to produce the minimum protective potential. The amount of current needed for protection increases with increase in the severity of corrosion and the area to be protected. On economic grounds, therefore, cathodic protection is seldom applied in highly corrosive media or on bare structures. In most cases a coating is supplemented by cathodic protection. On a good quality coated structure protection is needed only at the breaks and weak points in the coating which may comprise about 2–4% of the total surface of the structure. Although the current density for the protection of the metal exposed at the voids will be the same as required for bare steel, the total current requirement would be dramatically reduced because the area needed protection will be very small. In some instances, especially in the case of seawater and hard water, calcareous deposits formed on the metal surface also act as an effective barrier to the environment and lower the magnitude of the protective current with time. On the other hand, with time, coatings tend to deteriorate which results in increase in the current requirement. The design of CP system, therefore, must take into account this extra current demand over the life time of the component being protected.

That exact current density needed for complete protection can be determined in several ways. In case there are existing cathodically protected lines, an idea of current requirement can be obtained. However, in areas where no pipelines are being cathodically protected, a rough guide at design stage can be obtained from the orders of magnitude of current density required for protecting the steel structure in

Table 8.13 Current requirements for cathodic protection of bare steel

Environment	MA/m^2
Soil with resistivity < 1000 Ω-cm	66–275.0
Soil with resistivity 1000–10,000 Ω-cm	33–66
Soil with resistivity 10,000–30,000 Ω-cm	22–33
Soil with resistivity >30,000 Ω-cm	11–22
Highly aggressive soil with anaerobic bacteria	165.0–440.0
Still fresh water	22–44
Moving fresh water	44–66
Turbulent fresh water	55–165.0
Hot fresh water	55–165.0
Still seawater	11–33
Moving seawater	33–275.0
Concrete	0.55–1.65

different environments as given in Table 8.13. In areas where an unprotected pipeline already exists, the best practice is to carry out trial runs on it by what is known as '*current drainage survey*'.

Checking Effectiveness of Cathodic Protection

The effectiveness of cathodic protection can be checked in several ways. The most common method is to check periodically the environment to structure potential at predetermined locations (test points), which in case of underground pipelines, are provided at a distance of every 1–2 km. These measurements can be periodically taken manually or with the use of fixed reference electrodes. In case of the latter, data are collated and automatically transferred to a central control station through SCADA (Supervisory Control and Data Acquisition) system. In the case of buried pipelines which were provided with CP reduction of number of leaks per year also gives an idea of the effectiveness of cathodic protection achieved. Periodic checks on surface conditions of protected structure visually or by weight loss measurements on coupons coupled with the structure being protected are also some of the methods which are used to have an idea of the efficiency of CP system.

Because the test points are provided at considerable distances, local areas where complete protection is missed cannot be detected. For such a situation, close interval potential survey (CIPS) has been developed. During CIPS a team of two persons walks over the pipeline with two sticks to which the reference electrode is attached. Measurements of soil to pipe potential are made at distances of every 0.4–0.75 m along the pipeline. The data are recorded in a computer carried as a backpack. Wherever the potential is found to be below the minimum protective potential, necessary steps are to be taken to correct the situation. If the deviation is

not large, current output is adjusted to increase the potential to the required level. If large areas are affected or drop in potential is large then it indicates considerable deterioration in the coating efficiency. In such a case, first a Pearson survey is carried out. The Pearson survey is being used since a number of years to locate damage or deterioration of coating in buried pipeline. The technique employs an AC signal injected onto the pipeline and compares the potential gradient along the pipeline between two mobile earth contacts. At coating defects increase in voltage gradient occurs which is noted and recorded. To conduct the survey the operator with step probe and the receiver walks along the pipe route, putting the probe every 2 m in the soil. To ensure that the operator walks over the pipe route, the route is first located and marked prior to start of the survey. Once the damage portions are located, these are compared with potential survey. The identified portions of the line are then dug up for inspection and necessary repair.

Typical Applications of Cathodic Protection

Cathodic protection has been used successfully on practically every type of structure in contact with liquids or soil saturated with liquids. The following list demonstrates the applications in which CP can significantly reduce corrosion:

Buried Structures

(a) Pipelines and utilities
(b) Underground tanks for storage of petroleum products and bullets for LPG
(c) Bottoms of above ground storage tanks

Tanks and Vessels

(a) Effluent and sewage disposal plants
(b) Hot water and storage water tanks
(c) Coolers and condensers

Submerged Structures

(a) Ship and barge hulls
(b) Piers, pilings and offshore platforms.
(c) Bridges (reinforcement steel)
(d) Offshore pipelines

As CP requires a bulk electrolyte to facilitate placement of anodes, the system cannot be used to protect structure exposed to moist air or gases as in the case of atmospheric exposure. However, galvanizing or aluminizing is also a case of cathodic protection wherein the protection is afforded by zinc or aluminium to the iron substrate in small areas exposed to the atmosphere adjacent to coating breaks.

8.3.3.2 Anodic Protection

Whenever a metal or an alloy is made the anode and forced to discharge current to a cathode by impressing current from an external source, the anode surface potential shifts towards cathode, a phenomenon known as *polarization*. For most of the metals and alloys a continuous shift in potential is observed with increase in current, the current being the measure of corrosion rate. However, under some conditions stainless steels, titanium, nickel and their alloys show a large decrease in current (i.e. corrosion rate) once the potential reaches a certain value, specific to the alloy and the environment (Fig. 8.5). This phenomenon is known as *passivation* and occurs as a result of formation of a thin protective film on the surface. If the potential of a corroding metal is maintained within the passivating range, a marked decrease in corrosion can be achieved. Thus, by using a special instrument known as potentiostat, which varies the potential instead of current, it is possible to anodically protect stainless steels or any other metals and alloys which show good passivation characteristics. Normal austenitic stainless steels derive their corrosion resistance by naturally formed chromium oxide film on the surface. Under corrosive conditions, the film breaks down and does not re-form easily, resulting in high corrosion rate. This state is known as active state of stainless steel. Under highly oxidizing conditions, the potential may on other hand reach trans passive region resulting in very rapid corrosion, with chromium going in solution as hexavalent chromium. However, by anodic protection the protective film can be re-formed and maintained, if the potential is maintained within the passivation range. In manufacturing of sulphuric acid, the principle of anodic protection has been successfully used and since early 1980s anodically protected 316L is being used to protect acid coolers and associated piping (Fig. 8.28) [43]. The decrease in corrosion rate (mils/year) of 316L in concentrated H_2SO_4 as a result of AP is illustrated below:

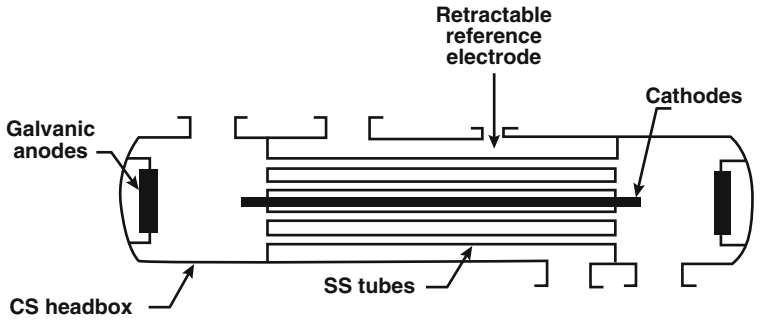


Fig. 8.28 Anodic protection of 316L stainless steel hot 95%H_2SO_4 cooler [43]

	$93\%H_2SO_4$		$95\%H_2SO_4$	
	Temperature (°C)		Unprotected	Protected
	Unprotected		Protected	
70	29	<2	–	
100	495	25	41	<2

Anodic protection requires careful design of location of cathode and reference electrodes and equipment is therefore supplied with the anodic protection system installed. Especially for piping, where geometry is non-uniform and diameters are small (with limited throwing power of the current), the cathodes and reference electrodes are to be dispersed throughout the piping system. The entire system is balanced so that all surfaces of the piping are maintained within the safe range. Automatically controlled anodic protection system reacts to any change in operating conditions and adjusts the current supplied to any part of the system to maintain the desired potential. Anodic protection permits use of smaller diameter pipes by use of higher velocities (up to about 3 m/s). In such a system, normally the cooler is of shell and tube type. The entire system is balanced so that all surfaces coming in contact with acid are maintained within the safe range of potential as any positive or negative shift beyond the limits shall lead to accelerated corrosion. Anodic protection system reacts automatically to any change in operating conditions and adjusts the current supplied to any part of the system to maintain the desired potential.

8.3.4 Coatings

Coatings are the most commonly used protective measure used against corrosion damage, especially for steels. These provide the most economical method and are applicable for varieties of exposure conditions from mild to high corrosive conditions. The types of coatings used are metallic, inorganic and organic.

8.3.4.1 Metallic and Other Inorganic Coatings

Relatively thin coatings of metallic and inorganic materials can provide a satisfactory barrier between the metal and its environment. The chief function of such coatings is (aside from sacrificial coatings such as zinc) to provide an effective barrier. Metallic coatings are applied by electrodeposition, flame spraying, cladding, hot dipping and vapour deposition. Inorganics are applied or formed by spraying, diffusion or chemical conversion. In both cases a complete barrier must be provided because porosity or other defects can result in accelerated localized attack on the base metal.

Electrodeposited Coating

The coating is produced by electroplating, where the character of the deposit depends on many factors including temperature, current density, time and composition of the bath. By adjusting these variables it is possible to produce coating that are thick (say 20 mils) or thin (thousand of a mil), dull or bright, soft (lead) or hard (chromium), and ductile or brittle. Hard chromium plating is utilized to coat bearing surface of a shaft against wear. The electroplating can be of a single metal or layers of several metals. Zinc, nickel, tin and cadmium, in that order, are plated on the largest tonnage basis. While zinc protects the exposed steel in damaged areas, nickel, copper, tin, chromium, etc. accelerate the attack because these are, unlike zinc, are cathodic. The latter are, therefore, used primarily for decorative purposes. In case of zinc and tin there are two important differences. In case of zinc there is a reversal from anodic to cathodic nature above 70 °C. On the other hand, cathodic tin becomes anodic in the absence of oxygen. Tin, therefore, protects the steel base of a can used in the preservation of tinned items. Electroless plating has also been developed where the plating is achieved by simple immersion of the part in an appropriate solution without the passage of electricity. Electroless nickel has good resistance to corrosion.

Flame-Sprayed Coating

This process, also called *metallizing*, consists of feeding a metal wire or powder through a melting flame so that the metal, in finely divided liquid particles, is blown onto the surface to be protected. The coatings are usually porous and are not protective under severe wet corrosive conditions. Generally the porosity decreases with the melting point of the metal; zinc and aluminium are better from this standpoint than steel or stainless steel. The surface to be sprayed must be roughened (sandblasted) to obtain a mechanical bond. Sometimes a paint coating is applied over the sprayed metal to fill the voids that provides a better barrier. The porous metal acts as a proper base for the paint to achieve a good anchorage. Flame spraying is also an economical way of building up worn surfaces on parts such as shaft. High melting metals may also be deposited by plasma-jet spraying. Flame-sprayed applications include tank cars and vessels of all kinds, bridges, ship hulls and superstructures of offshore platforms.

Hot Dipped Coating

Hot-dip coatings are applied to metals by immersing them in a molten metal bath of low melting point metals, chiefly zinc, tin, lead and aluminium. Hot dipping is one of the oldest methods of metal coating. Galvanized steel is a popular example. Thickness of the coating is greater than electroplates because very thin dip coatings are difficult to achieve. As the process is carried out with molten metal, a metallurgical bond is formed at the interface.

Vapour Deposited Coating

This is accomplished in a high-vacuum chamber. The metal to be coated is vapourized by heating electrically, and the vapour is deposited on the parts to be coated. This method is more expensive than others and is generally limited to 'critical' parts, for example, high-strength parts for missiles and rockets.

Diffusion Coating

Diffusion coating involves heat treatment to ensure alloy formation by diffusion of one metal into the other. For this reason the process is also termed *surface alloying*. Parts to be coated are packed in sold materials or exposed to gaseous environments containing the metal that forms the coating. Sherardizing (zinc), chromizing (chromium) and calorizing or alonizing (aluminium) are examples of diffusion coating processes. Carbon steel, low-alloy steels and stainless steels are given aluminium coating (Alonized™) for use under specific conditions. For example Alonized™ steel has good resistance to hot sulphurous gases and are used for SO_2/SO_3 heat exchanger tubing in manufacturing of sulphuric acid. Alonized™ Cr–Mo and stainless steels are reported to have been successfully used as heater tubes of cracker and in processing of naphthenic acid containing crude for its resistance against carburization and naphthenic acid corrosion, respectively. This process is not generally recommended for aqueous environments.

Chemical Conversion Coating

Coating by chemical conversion is produced by 'corroding' the metal surface to form an adherent and protective corrosion product. Examples are Bonderizing and Parkerizing (phosphatising in phosphoric acid bath), Chromatizing (exposure to chromic acid and dichromates) and Bluing (oxidizing in hot potassium nitrate). The treatments provide a good base for the paint and also short-term protection to base metal before the paint is applied. For temporary protection during storage, oil-based protectives perform well on phosphated surface. Chromate treatments are applied to magnesium and zinc parts and offer some measure of corrosion resistance, although the parts are normally painted after the treatment. Bluing of steel is mainly done on firearms. These coatings are used for indoor/sheltered exposure and are generally applied with a petroleum product (like oil or grease) to avoid rusting at breaks in coatings.

8.3.4.2 Non-Metallic Coatings

In addition there are some old and well-tried lining techniques, still being used. Glass-lined steel is an important material of construction for the process industries

and also in the home appliances. Glass-lined steel is widely used in the drug industry, wine, brewery and many others where severe corrosives or contamination of product are involved. Cement as lining against corrosion is utilized for many applications. Examples are encasing of structural steel (also for fireproofing), lining of bottom 3–9 O'clock section of overhead receiver of crude distillation columns with acid resistant cement, internal lining of pipeline in sea water service with sulphate resistant cement, etc. Other examples are acid resistant brick lining for storage tank of hot sulphuric acid and carbon brick lining for hydrochloric acid.

8.3.4.3 Organic Paint Coatings

A paint coating provides a relatively thin barrier between the substrate material and the environment and is used to protect more metals on a tonnage basis than any other method for combating corrosion. Exterior surfaces are most familiar, but internal coatings or linings are also widely utilized. Aside from proper application, the three main factors to be considered for organic coatings, listed in order of importance, are (1) surface preparation, (2) selection of primer or priming coat, and (3) selection of top coat or coats. Thus a paint system can be compared with construction of a house as shown in Fig. 8.29 [44].

Surface Preparation

If the metal surface is not properly prepared, the paint will peel off because of poor bonding and, therefore, surface preparation can be compared to the foundation of a house. Surface preparation involves surface roughening to obtain mechanical bonding ('teeth') as well as removal of dirt, rust, mill scale, oil, grease, welding flux, crayon marks, wax and other impurities from the surface. In other words, a clean, rough surface is needed. The best method is to grit-blast the steel surface. Blasted surface profile provides good anchorage to the applied coating. Other methods of surface preparation used are pickling and other types of chemical treatments like phosphatizing. Mechanical methods, such as, scraping, wire-brushing, chiselling and chipping are also used but are not as effective as grit blasting in giving a long life. Various surface preparation methods are graded according to their effectiveness in various standards related to painting. Table 8.14 gives the various standards/guidelines normally used for painting.

Selection of Paint System

As the primary function of a paint is to protect the base metal against corrosion, local climatic and pollution conditions play an important role in selection of a paint system. As a guideline, therefore, the environment is classified into different grades according to their aggressiveness, such as, very low (inside heated/air conditioned

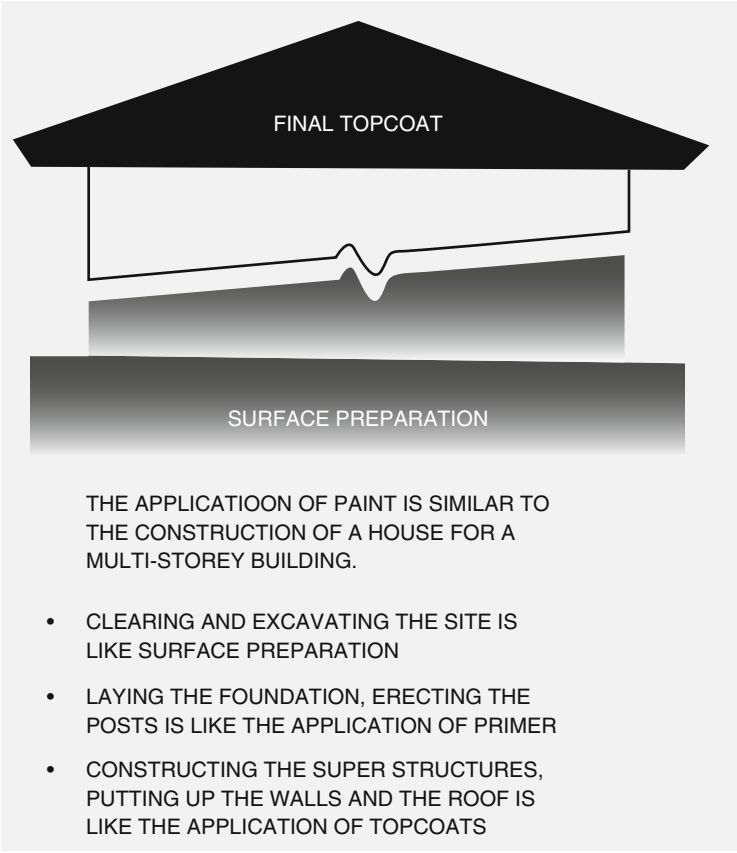


Fig. 8.29 Analogy of painting with construction of a house [44]

building), low (dry or rural areas remote from pollution), medium (coastal with low salinity, urban and non-polluting industrial areas), high (coastal areas from 300 m up to 1 km from shore, inside damp closed space like swimming pool) and very high (off shore, beach front and highly polluted industrial area). In selection of paint for a process plant another important consideration is the microclimatic effects of acidic or alkaline fallout, airborne chemicals, which may accelerate the deterioration of protective coating in limited area of a plant what will be value which is otherwise located in rural or medium environmental zone. One such example in most of the plant is cooling tower and water treatment plant situated near each other. These areas not only require a better quality paint system but any repainting is also not easy to undertake because of the continuous presence of water film on structures deposited from windborne mist from the cooling tower.

Paints used are acrylic, alkyd, chlorinated rubber, epoxy or polyurethane-based and applied in 2–3 coats. Of these, alkyd paints are not suitable for highly

Table 8.14 Standards for the surface preparation prior to fresh and maintenance painting

Nature of surface preparation	Finish No. SSPC[a]/ NACE[b]	Description	ISO 8501-1:1988[c]
Loose and peeling paint		Remove loose material by scraping, wire brush or power-washing (for repainting)	
Dirt, grease, oil		Remove by washing with a detergent solution (e.g. Trisodium phosphate—(TSP)	
White metal blast cleaning	SSPC-SP5 NACE No. 1	A blasted surface with a grey-white, uniform metallic colour, slightly roughened to form a suitable anchor	Sa 3
Near-white blast cleaning	SSPC-SP10 NACE No. 2	A surface free from oil, dirt, mill scale, or, paint with at least 95% of any given square inch being 'White Metal', and 5% with slight discolorations	Sa 2.5
Commercial blast cleaning	SSPC-SP6 NACE No. 3	An oil and dirt free surface except for slight discoloration caused by rust stain or mill scale. At least two-thirds of any square inch shall be free of all visible residues	Sa 2
Brush-off blast cleaning	SSPC-SP7 NACE No. 4	An oil and dirt free surface with tightly adhering mill scale, rust, paint acceptable if they have been exposed to the abrasive blast pattern	Sa 1
Water blasting	NACE No. RP-01-72	Removal of oil, loose rust, loose mill scale and loose paint by water at pressures of 2000–5000 psi at a flow of 4–14 gallons per minute	
Hand tool cleaning	SSPC-SP2	Gives methods of preparing metal surfaces by removing loose mill scale, loose rust and loose paint by wire-brushing, sanding, scraping or chipping with hand	
Power tool cleaning	SSPC-SP3	Same as above but with the help of power tools	
Pickling	SSPC-SP8	Gives methods of preparing metal surfaces acid pickling	

[a]Society for Protective Coatings (originally Steel Structures Painting Council—SSPC)
[b]NACE International (National Association of Corrosion Engineers—NACE)
[c]Originally Swedish Standard SIS 055900–1967

aggressive environments. The first coat is the primer and for industrial paints zinc rich/zinc silicate paints are preferred. Dry film thickness (DFT) of primer coat in micron may vary from 40 to 75, except in case of epoxy and polyurethane coatings where the second and third coats are thicker. The total thickness in such cases may be in the range of 250–350 microns. Selection of a paint system in a particular environment is quite difficult and the best procedure is to take the advice of a paint specialist. Further, the details of the various ingredients that go in a particular paint are not well specified in the product technical document. The first step in the selection should, therefore, be taken jointly with the specialist and the paint

manufacturers. If authentic feedback about the performance under similar conditions is available, selection becomes easier. Otherwise, a list of possible paints should be identified and their comparative performance evaluated by laboratory testing and field trials. Various standards are available for such evaluation [45, 46].

Maintenance Painting

Any painting system has limited life as the coating deteriorates with time. Once the deterioration reaches a certain level it becomes necessary to repair/repaint the affected area. To assist in taking a decision to repaint, various standards have been developed where degree of rusting is classified based on % area and distribution of rusting. Table below gives degree of rusting classified in three standards based on % area of rusting [47].

ISO[a]	European Scale[b]	ASTM[c]	% area rusted
Ri0	Re0	10	0 ($\leq$0.01)
Ri1	Re1	9	0.05 (>0.01 up to 0.03)
Ri2	Re2	7	0.5 (>0.10 up to 0.3)
Ri3	Re3	6	1.0 (>0.30 up to 1.0)
Ri4	Re5	4	8.0 (>3.0 up to 10)
Ri5	Re6	2	40/50 (>16 up to 33)
		1	– (>33 up to 50)
		0	– (>50)

[a]ISO 4628-3 paints and varnishes—Evaluation of degradation of coatings—Designation of quantity and size of defects, and of intensity of uniform changes in appearance—Part 3: Assessment of degree of rusting

[b]European rust scale published by the European confederation of paint, printing ink and artists 'Colours Manufacturers' Associations (CEPE), Brussels

[c]ASTM D 610–01 Evaluating degree of rusting on painted steel surfaces1

Degree of rusting, as would be apparent from the above Table, has been classified into scales of 0–5 in ISO and 0–6 in European Scale in the increasing order of % rusted area covered. Here 0 means no rusting and 5 and 6 means % of area covered is 40–50%. On the other hand ASTM classification numbers 0–10 (given in bracket in the Table) are in reverse order where 10 means less than $\leq$0.01 rusted areas and 0 means >50 rusted area. In addition to knowing the area affected it is also important to know how the rusted area is distributed. Distribution of rusting is classified in grades of spot, general, pinpoint and hybrid. The ratings are given in tabulated form and distribution also in pictorial form.

The importance of these standards is in taking decision as to whether the paint system should be locally or totally replaced. It is generally recognized and also specified (ISO 12944-5) that repainting should be carried out once the extent of damage reaches 1%, corresponding to grade Ri3 [47]. In practice, unless decision is taken at correct time and large area of the surface is allowed to be affected,

repainting as per the original painting schedule becomes necessary. If the damage to paint is localized or in small areas the repainting becomes easier and good quality of painting can be maintained.

The area to be repainted shall not only cover the affected area but also some of the surrounding areas. One of the suggested procedures is [47]:

1. The area to be repaired will be 10 times rusted area of large and twice of localized area.
2. In case affected area is beyond grade Ri4 the whole area would require repainting. On the other hand local repair can be carried out if damaged is within grade Ri4.

The major problem in maintenance painting is related to good surface preparation by shot blasting, which in an operating plant is most of the time not possible. Any substandard job done drastically reduces the life of the repainted area resulting in repeated paining, in some cases almost every year. Developments have taken place in the formulation of what are known as maintenance paints. The major advantage claimed is in the ability of these paints to have good bonding with old paint in the absence of grit blasted surface. Thus the paints can be applied on a surface well cleaned by wire-brushing and have a reasonably good life.

8.3.4.4 Coating and Wrapping of Pipeline

Underground and underwater pipes are protected against corrosion by use of wrapping and coatings. This forms the first line of defence. Under severe corrosive conditions (low resistivity or chemical contaminated soil and under water) cathodic protection is provided additionally to get long life. Pipelines carrying crude, petroleum products and gas are compulsorily required to have both coating and warping along with cathodic protection. Coating and wrapping requires the same steps of surface preparation as in case of painting. However, here it is more critical as once laid, recoating is very difficult. External coatings must be properly selected and applied. Shop-applied coating gives better life because of cleaner atmosphere and good working conditions. In such cases the pipes are coated at a permanent or temporary central location and then transported to the site by road, rail or any other means. However, sometimes during construction of a process plant the coating is done at work site because various sizes of pipes are required to be coated. For better application of the coating, mechanical wrapping and coating machines must be provided along with greater supervision.

The material used for coating pipes has varied over the years as technology evolved. In the 1940s and 50s coal tar, wax, and vinyl tape were more popular. In the 1960s asphalts were used; and in the 1970s fusion bonded epoxy was introduced. Polyethylene tape and extruded polyethylene jacket material was also used from the early 1950s. At present the following types of coatings are more commonly used for high pressure cross-country underground or under sea pipelines and also in case of plant piping in areas of high corrosivity:

(a) 3-Layer polyethylene,
(b) Fusion bonded epoxy,
(c) Polypropylene.

Coal tar enamel/epoxy are cheaper and are being used as general purpose coating under many conditions. One important requirement of a coating for catholically protected pipeline is its resistance to debonding which cause localized attack at debonded spots.

8.3.5 Precautions During Design and Construction

During process and engineering design and project execution some important points are to be considered, which will affect the performance in long run. The following sections demonstrate some of the design aspects that may accelerate corrosion:

- Both stagnation and high flow rates have an adverse effect. Common examples of stagnation include non-draining structures, dead ends, badly located components, and poor assembly. Consideration should be given to the velocity effect taking into consideration the nature of the fluid and the type of material. Replaceable baffle plates or deflectors are beneficial, where circumstances permit their use.
- Equipment, piping and common engineering structural steelwork require regular painting and if good accessibility is not taken care of during the design stage, serious consequences may result.
- Designs that introduce local stress concentrations directly or as a consequence of fabrication should be carefully considered. Of particular importance are alternating stresses; vibration or shock loading; service temperatures (thermal stresses; fatigue; and wear). Profiles and shapes contribute to stress-related corrosion if materials are susceptible to failure by SCC or fatigue.
- Design tanks and other containers for easy draining and easy cleaning. Tank bottoms should be sloped towards drain holes so that liquids cannot collect after the tank is emptied. For example, concentrated sulphuric acid is stored in steel tanks but if the acid tank is incompletely drained and the remaining liquid is exposed to the air, the acid will absorb moisture, resulting in dilution and rapid attack at liquid line.
- List complete specifications for all materials of construction and provide instructions to be sure that the specifications are followed all the way through to final inspection. Specify quality control procedures during construction. A situation may arise when the specified material is not available and an alternate material is required to be used to maintain project schedule. This change should be got approved and properly recorded on drawing with instructions to replace it at the earliest opportunity.

- Specify procedures for testing and storage of parts and equipment. For example: (i) steel plates and pipes should not be placed on ground, (ii) the tube ends should be plugged to avoid ingress of water inside pipe, (iii) after hydraulic testing do not let the equipment sit full or partially full of water, specially the latter, for any extended period of time. This could result in microbial corrosion and pitting. The above corrective measures are of greater importance for stainless steel equipment and piping which should preferably be transported by sea in completely sealed condition to avoid contamination with chloride bearing air and water.

8.4 Corrosion Monitoring

Basic maintenance approach in industrial and process units is to consider all aspects of materials deterioration. Corrosion control forms an important part of this exercise. Considering the economic aspect, selection of corrosion resistant material and appropriate corrosion control measures are introduced. In spite of all care, some corrosion of damage occurs during the lifetime of equipment. Periodic damage assessment and also its progress, efficiency of corrosion protection measures (periodic or ongoing) are to be resorted to prevent breakdowns and accidents and get maximum life. To achieve this, corrosion monitoring forms an important part of plant operation. Various methods are used, direct and indirect, to assess whether a system is operating within the set limits of corrosion damage and its rate. For example, one would like to know not only whether there is general corrosion, pitting, stress corrosion cracking, hydrogen attack, but also the rate at which the damage is progressing. Depending on the nature of the operation, the degree of corrosion damage is determined by periodic inspection over the lifetime of a component during shutdown. However, with increasing period of continuous run, it is also necessary to observe how far the corrosion control measures are functioning. This is achieved by monitoring the corrosion controlling parameters which can be correlated to the extent of corrosion. There are many monitoring methods, but some of the important ones, broadly classified into the followings have been outlined:

1. Analysis of process stream
2. Coupon exposure
3. Electrical/Electrochemical methods

8.4.1 Analysis of Process Stream

This method of corrosion monitoring is extensively followed because it becomes a part of the operation. Some important examples are:

1. Overhead corrosion in crude distillation unit in refining is monitored by analyzing overhead water for iron, chloride and pH. Here chloride is the corroding agent, pH is the corrosion controlling agent and iron gives indirect measure of corrosion rate. The relationship between the parameters is shown in Fig. 8.30 [48].
2. In CO_2 removal, corrosion is controlled by addition of V_2O_5. To ensure that proper protection is being provided the amount of V^{5+} (vanadium pentoxide) is regularly measured.
3. In boiler operation corrosion is controlled by continuous monitoring of pH, oxygen content and water. Monitoring of hydrogen in steam also gives a good indication of corrosion taking place because the reaction product of steam with iron is hydrogen. The condensate corrosivity is ascertained from pH.
4. Corrosion control of cooling water system requires regular monitoring of various parameters related to water quality and inhibitors added.

8.4.2 *Coupon Test*

One of the important methods of testing consists of exposing weighed and dimensionally measured rectangular or disc specimens of steel or any other alloy in the medium and directly determining corrosion rate from metal loss after a known period. These tests give better idea about the behaviour of a material as the coupons become an integral part of the process. The main aim of carrying out these tests is to confirm original material selection, efficiency of inhibitor system and to evaluate alternate materials. After proper specimen preparation to provide a uniform surface, coupons are mounted on appropriate racks, electrically isolated from the mounting

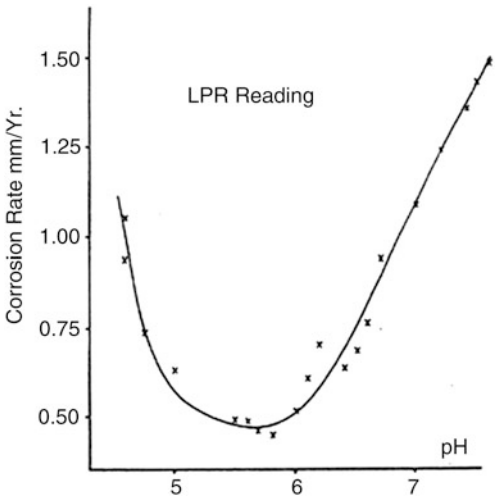


Fig. 8.30 pH versus corrosion rate in crude distillation overhead [48]

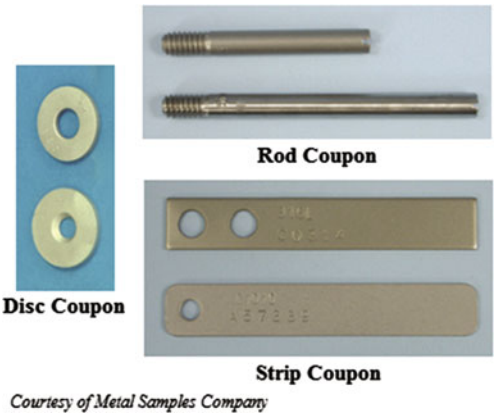


Fig. 8.31 Rectangular, rod and disc coupons [49]

hardware and from each other, to prevent galvanic effects, and installed in piping and equipment. Exposure racks for coupons are designed to fit any particular exposure condition, e.g. pipe flange, vessel nozzle, agitator bracket, piping, etc. After specific exposure periods, which may vary from a few days to months, depending on the corrosive conditions, the samples are removed to evaluate the nature and extend of attack. Figure 8.31 shows coupons of various types [49].

One advantage of this method is that the effect of fabrication techniques, e.g. welding, stressing, galvanic contact, etc. can be evaluated pertaining to actual operating conditions. For example, to study the weld decay and stress corrosion cracking, welded and U-bend specimens, respectively, may be exposed. Further, these tests are suitable for evaluating uniform and pitting corrosion, especially the latter, which is difficult to evaluate by other methods of field monitoring except NDT.

8.4.3 Electrochemical Techniques

In spite of the advantage of coupon test to evaluate the corrosion resistant properties more fully under actual operating conditions, search for other methods of measurements has continued. The disadvantages of the coupon test are: (a) longer test period and greater number of samples required and (b) the necessity of shutdown to remove the specimens for examination. Use of electrical method dispenses with these two as the change in corrosion rate can be made continuously for any desired period. Two methods, i.e. electrical resistance and linear polarization resistance methods have been developed in this connection. Electrical noise measurement is another technique.

8.4.3.1 Electrical Resistance Technique (ER)

The method is based on measurements of changes on electrical resistance. A wire, tube or strip element of the metal to be tested is mounted on a probe and exposed to the corrosive environment. As corrosion occurs, the cross-sectional area of the measuring elements is reduced increasing the element's resistance, which is calculated from the formula;

$$R = r \times L/A \tag{8.4.1}$$

where L = element length; A = cross-sectional area; r = specific resistance.

A suitable electric circuit is used to measure the element's resistance and a 'reference' element sealed within the probe body. Measurement of the resistance ratio of the exposed to protected element is used to measure the corrosion rate. The instrument reading is converted to metal loss and readings compared so as to determine the average corrosion rate occurring during the time the reading were made. Since both corroding and protected samples are affected by change in temperature equally, measuring the resistance ratio minimizes the influence of changes in the ambient temperature. When measuring, the instrument produces a linearized signal (S), proportional to the exposed element's total metal loss (M). Taking the standard probe's (wire, strip, cylindrical, etc.) geometric and dimensional factors incorporated into the 'probe life' (P), the corrosion rate (C) in mils per year is derived by:

$$C = \frac{P \times 365(S_2 - S_1)}{\Delta T \times 1000} \tag{8.4.2}$$

T being the lapse time in days between two readings S_1 and S_2.

Measurements using this technique can be made in conductive liquids, mixed-phase systems and also in soil and concrete. Figure 8.32 gives the general arrangement [49].

8.4.3.2 Linear Polarization Resistance Technique (LPR)

The flow of electron from anode to cathode is measure of corrosion (Icorr) and therefore corrosion rate can be determined using the following formula:

$$C = \frac{I\text{corr} \times E}{A \times D} r \times 128.67 \tag{8.4.3}$$

where,

C Corrosion rate in 'mils per year' (mpy)
E Equivalent weight of the corroding metal (g)
A Area of corroding electrode (cm^2)
D Density of corroding metal (g/cm^3)

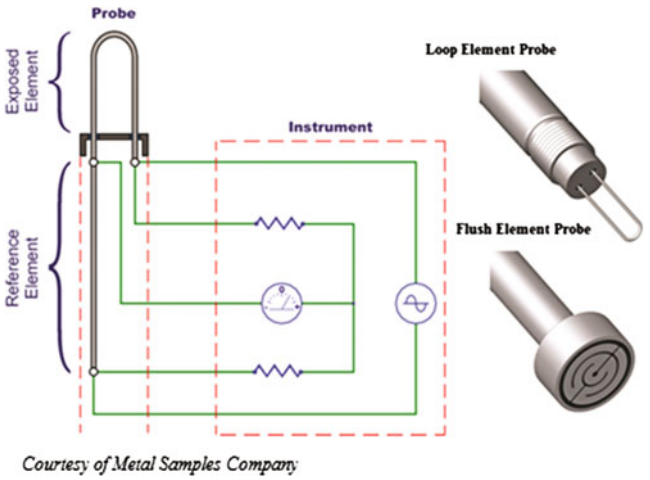


Fig. 8.32 Electric resistance system for corrosion monitoring [49]

Direct measurement of *I*corr is not possible. However, with small externally superimposed potential (polarization), a shift in potential (ΔE) will produce measurable current flow (ΔI). Based on theoretically derived Stern–Geary equation, [52], it is found that at small values of ΔE, ΔI is directly proportional to *I*corr.

$$\frac{\Delta E}{\Delta I} = (\beta_a + \beta_c)/(2.3I\text{corr}(\beta_a + \beta_c) \tag{8.4.4}$$

The β_a and β_c being the Tafel constants, the relationship can be expressed as

$$I\text{corr} = \frac{\Delta I}{\Delta E} \times \text{constant} \tag{8.4.5}$$

The value $\Delta E/\Delta I$ is known as the *Polarization Resistance* and from this method the corrosion rate can be measured if the polarization is maintained within ± 10 to 20 mV of the open circuit potential (that is in both the noble and active directions).

The original instruments used modified technique with two electrodes with each electrode being made of the same alloy. However, in this case solution resistance led to overestimation of corrosion rate. The 3-electrode system, PAIR™ technique (Fig. 8.33), uses separate circuits to measure ΔI and ΔE. A potential of 20 mV is applied across the substantially identical electrodes and the resulting current, which is proportional to I, is converted to instantaneous corrosion rate is MPY. This technique has been used successfully for number of years, in almost all types of corrosive environments. Some of the more common applications are as follows:

- Cooling water systems
- Secondary recovery system
- Potable water treatment and distribution systems

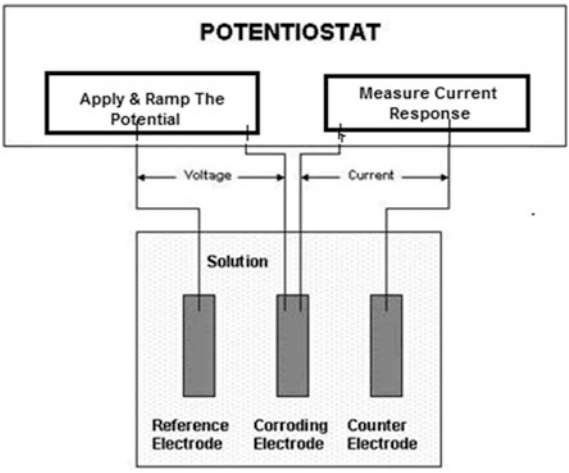


Fig. 8.33 LPR systems for corrosion monitoring

- Amine sweetening
- Waste water treatment systems
- Pickling and mineral extraction processes
- Pulp and paper manufacturing
- Hydrocarbon production with free water

8.4.4 Hydrogen Probe

In certain process, the hydrogen atoms formed as a result of corrosion get first adsorbed on the metal surface, a part of which is then absorbed by the metal. Thus quite soon the surface coming in content with the solution gets saturated with dissolved hydrogen and a concentration gradient across the wall thickness (between external and internal surfaces) is established. This results in hydrogen to diffuse towards the outer wall and get released to atmosphere. The hydrogen entering the metal cause different types of damage, especially in carbon and alloy steels. Hydrogen damage is also experienced in high pressure high temperature systems. The hydrogen flux intensity, which is an indication of hydrogen activity and possibilities of hydrogen damage, need to be monitored. There are two types of probe, one based on electrochemical principle and the other on pressure build up due to accumulated hydrogen, which are being used.

8.4.4.1 Electrochemical Hydrogen Patch Probe

The hydrogen probe cell is fitted on the outer surface of the vessel or piping. The atomic hydrogen, arriving on OD, permeates through a Pd–foil cell, kept in close contact with the metal surface. The cell contains an electrolyte through which

current is supplied to oxidize the hydrogen. The current used is directly proportional to the hydrogen reaching the OD and therefore an indication of the hydrogen activity. Another development in this direction has been the use of nickel plated film, changed to nickel oxy-dioxide (NiOOH) in an alkaline solution, instead of Pd. This gives much more reliable results.

8.4.4.2 Hydrogen Pressure Probe

For high temperature hydrogen damage, one has to use a pressure probe where the probe assembly consists of three subassemblies: the gauge assembly, the insertion rod sensing element assembly, and the packing gland assembly. The gauge assembly consists of a body, a pressure gauge (0–40 psi), a temperature gauge, and a bleed valve. Hydrogen permeating through the rod is collected and the pressure build up with time is measured. This system can also be used to measure the hydrogen activity in sour and HF service. One disadvantage of this method is that the hydrogen permeation characteristics of pipe and vessel are not reflected in the data as in the case of the electrochemical patch which is directly fixed on the equipment wall. Patch probe based on pressure is also being marketed. Different types of Corrosion Monitoring Hydrogen Probes are shown in Fig. 8.34.

8.4.5 Field Signature Method (FSM)

In the film signature measurement (FSM) corrosion monitoring is done by creating a pattern by induced electric current around any location where corrosion is likely to occure. For this purpose sensing pins are attached in the area being monitored [50]. A large area of several metres can be covered by this technique which is non-intrusive. By this method general and localized corrosion like pitting and erosion can be evaluated and because of this there are many areas where this technique can be used.

1. Provides high level of accuracy and sensitivity.
2. Detects changes in corrosion rates much earlier than ordinary methods, allowing corrective action to be taken before damage occurs.
3. Monitors changes in the actual pipe wall.
4. Detects general corrosion as well as localized attacks and differentiates between the two.
5. Detects corrosion and other deterioration over an extended area of the pipe wall.
6. High data collection frequency.
7. Remote and wireless data communication to operator's office.

Figure 8.35 shows FSM set up for specially determining the corrosion rate of welds.

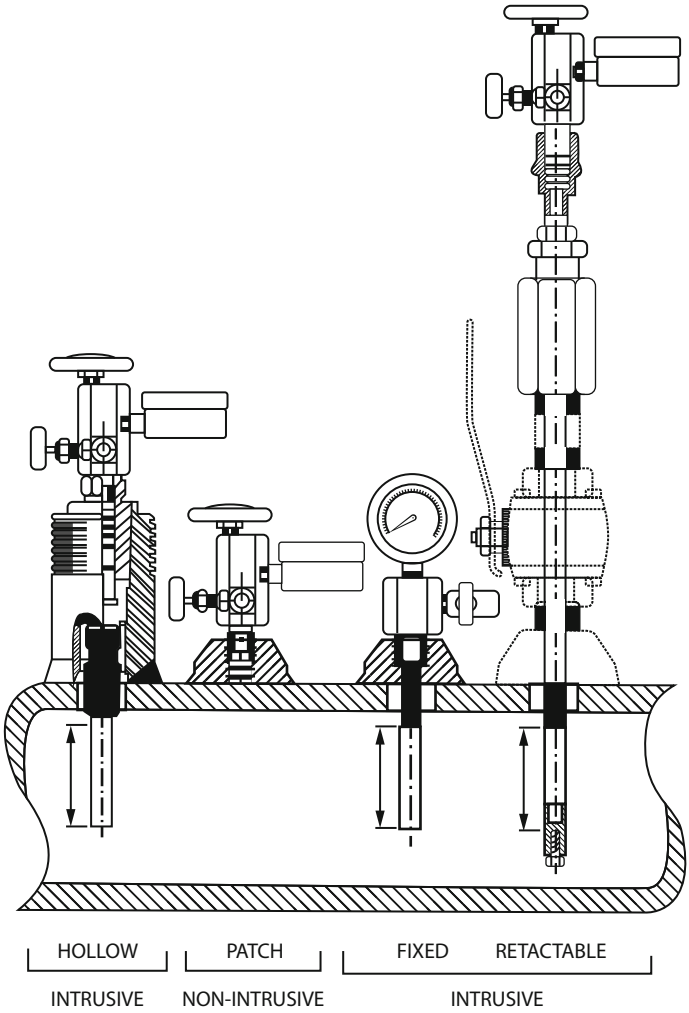


Fig. 8.34 Hydrogen pressure probe

8.4.6 Sand Probe

Many oil and gas wells are entrained with sand particles which cause erosion of pipeline and valves. Continuous monitoring of the effects of an abrasive material in a fluid is possible with the use of the sand probe. The technique (Fig. 8.36) consists of placing a sacrificial tube having a predetermined thickness in the line. When the probe wall is holed through, the sacrificial tube element allows pipeline pressure to flow through the nipple to the pressure gauge. Pressure gauge assembly then signals

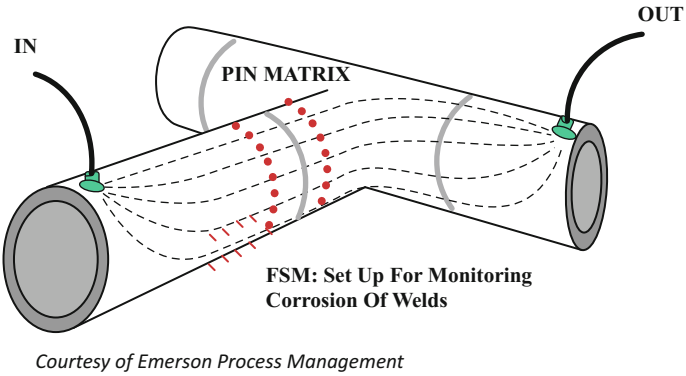


Fig. 8.35 FSM set up for specially monitoring the corrosion of welds [50]

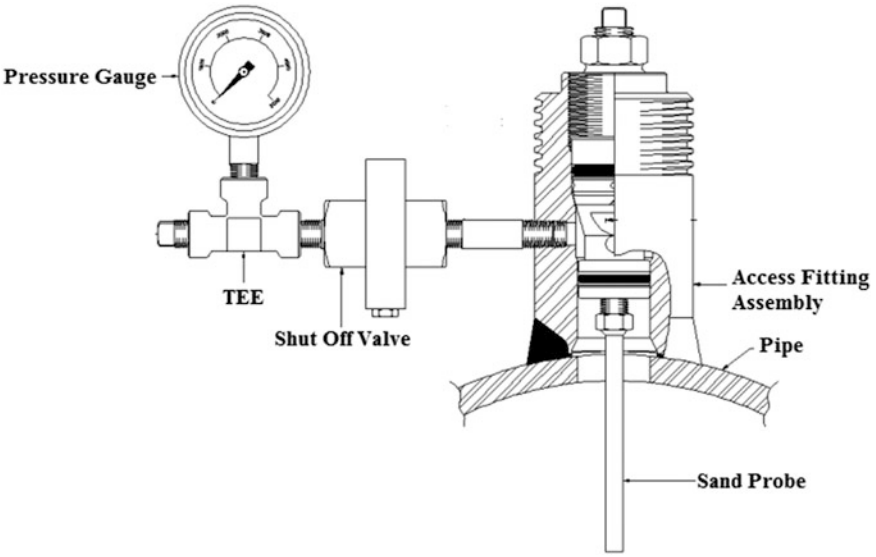


Fig. 8.36 Sand/erosion probe

the effect of erosion on the sacrificial tube. There are various types of intrusive and non-intrusive probe assemblies.

8.4.7 Bio-Probe

Bio-probe is used to collect samples of bacteria in gas and oil producing systems. As only surface or sessile bacteria cause corrosion, the bacterial population on a

system's metal surface is more relevant to corrosion than the total combined bacterial population in the system's fluids. The same bacteria that cause problems in gas pipelines, tanks, vessels, oil wells and water handling systems attach themselves to the bio-probe's sample element. The bio-probe is designed for use under oil field condition and, therefore, economical for sampling corrosion-causing biological activity.

8.5 Metallurgical Degradation

As discussed earlier, alloys having different chemical composition and heat treatment are produced to meet certain required specific properties of strength, toughness, ductility, hardness and resistance to corrosion and oxidation. Most of the metallurgical characteristics are retained if the service temperature remains below a certain value. However, at higher temperatures metallurgical degradation takes place and especially for ferrous materials this plays an important role in retaining their desired performance. Interaction of environment with material at high temperatures also leads to metallurgical degradation, as already discussed.

Carbon and alloy steels generally contain more than one phase, with different structure and phase morphology. Any change either during fabrication or in service, in the formation, precipitation or distribution of phases can adversely affect the properties of the material. Some of the important types of metallurgical degradation experienced in process industries are:

(i) Spheroidization (ii) Graphitization (iii) Phase Change/Phase Precipitation (iv) Temper Embrittlement (v) Carburization/Decarburization (vi) Hydrogen Damage (vii) Nitriding.

The last three are closely related to high temperature interaction of material with the process environment and already discussed in the Sect. 2.

8.5.1 Spheroidization/Carbide Coarsening

In carbon and low-alloy steels, the structure essentially consists of either ferrite/pearlite or bainite/ferrite aggregate, depending on composition and heat treatment. In case of pearlite, the inter-lamellar spacing depends on the heat treatment used during production. At higher temperatures, carbide lamellae, being thermodynamically unstable, first tend to change its shape to a round shape followed by the formation of large spherical particles by coalescence of smaller precipitates. Figure 8.37 shows different stages of spheroidization. Similar phenomenon of coarsening of carbide particles takes place in bainite or quenched and tempered steels. The kinetics of this change, i.e. the degree of spheroidization and coalescence are temperature and time dependent, the rate increasing with increase in both

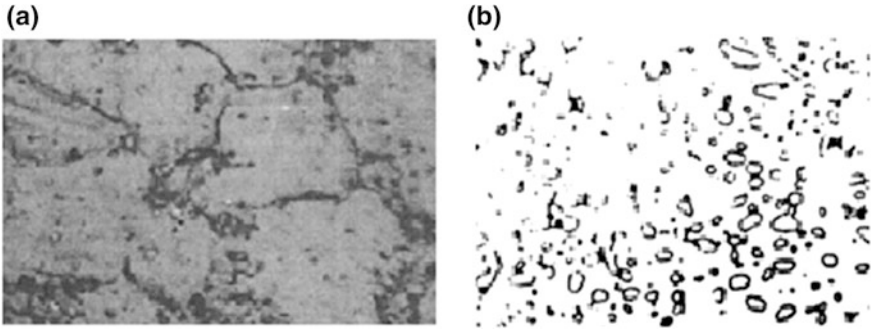


Fig. 8.37 Different stages of spheroidization. **a** Partial spheroidization. **b** Heavy spheroidization

the parameters. In case of quenched and tempered structure (where carbides are to start with, in rounded form), the coarsening occurs on long holding at lower temperatures. These changes have considerable effect on the mechanical properties because of increase in inter particle spacing. This results in degradation of mechanical properties.

8.5.2 Graphitization

Carbon and C–0.5Mo steels are composed of a mixture of ferrite and carbide. The stable form of carbon in these steels is graphite and not carbides and, therefore, at high temperature the carbides tend to decompose into and graphite. This phenomenon is known a graphitization. The reaction is time and temperature dependent and occurs at temperatures of about 430 °C and above. That is why the ASME code includes a warning note that carbon and C–0.5Mo steels are likely to graphitize above 426 and 454 °C, respectively. This phenomenon is, however, not observed in alloy steels as chromium forms stable carbides. In case of graphitization, the graphite distribution is found to be random, i.e. distributed throughout the matrix which normally does not affect the performance. Of greater concern is 'Eyebrow' type segregated distribution of carbide at grain boundaries, which leads to embitterment of steel. The latter type of distribution is not common and, therefore, there are few reported cases of failure due to graphitization. Further, unlike spheroidization, graphitization is less common. The extent of graphitization is believed to depend on the aluminium content of the steel. Both spheroidization and graphitization occur broadly within the same temperature range but with varying rate of formation as would be evident from Fig. 8.38 [51].

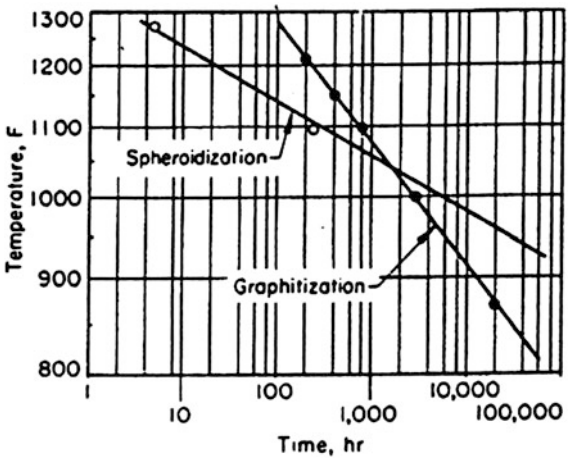


Fig. 8.38 Temperature versus time for spheroidization and graphitization

8.5.3 Phase Transformation/Phase Precipitation

In many alloys, phase transformation and/or precipitation of phases take place at high temperatures. In case of different types of stainless steels and high temperature alloys such changes have large influence on their performance. The effect is either beneficial or adverse, depending on the type of change and service. The two important types of degradation are as follows:

8.5.3.1 Sigma Phase Formation

The binary Fe–Cr alloy shows the presence of a second phase, other than alpha, having approximately equal amounts of iron and chromium (see Fig. 4.9). The alloys containing high chromium, such as, ferritic stainless steel, or low nickel austenitic stainless steels containing some amounts of ferrite (Type 304, 316, 309), and many high temperature alloys are susceptible to sigma formation. This occurs over long periods of service in the temperature range of 530–815 °C, when the ferrite gets transformed into sigma. Sigma has a complex structure, is non-magnetic and appears as needle shaped precipitates. Formation of sigma marginally affects the mechanical properties but toughness and ductility are drastically reduced that results in cracking due to stresses generated during start-ups and shutdowns. The material being embrittled, the weld repair becomes very difficult because the degraded material is not able to withstand the welding stresses. The formation of sigma is a reversible process and the ductility can be restored by subjecting the degraded material to a special heat treatment, which consists of heating to about 1100 °C, followed by rapid cooling. The other remedial measure is to use an alloy having a composition substantially free from ferrite.

8.5.3.2 Carbide Precipitation

Austenitic stainless steels are also prone to metallurgical degradation due to precipitation of chromium carbide in the temperature range of 400–815 °C, (there may be slight variations in the temperature range between different grades) resulting in intergranular corrosion and intergranular stress corrosion cracking. The mechanisms have been discussed earlier in this Chapter. Because of the required high temperature strength, wrought H-grades, e.g. 304H, 321H, 347H (0.1%C max) are specified. Carbide precipitation during welding and operation makes these alloys susceptible to grain boundary corrosion and polythionic acid cracking during shut down. Normally, 300 series of stainless steels are procured in solution-annealed condition. This does not fully prevent precipitation of chromium carbide during high temperature service. To counteract it, a stabilizing annealing is given which consists of heating in the temperature range of 870–900 °C, followed by rapid cooling. The purpose of this heat treatment is to precipitate a major amount of carbon as carbides of titanium and niobium in 321 and 347, respectively, in order to prevent subsequent precipitation of chromium carbide.

In heat resistant Fe–Cr–Ni cast alloys, where carbon content is high, i.e. in the range of 0.3–0.5% (for different grades), precipitation of secondary chromium carbide takes place in service, normally as fine carbides within the austenite grains. These have initially beneficial effect in increasing creep resistance and also the room temperature mechanical strength. On prolonged heating, the secondary carbides coalesce, forming massive carbides. The ductility is decreased markedly at room and medium temperatures resulting in brittle failure under the influence of thermal and other stresses. Improved ductility can be achieved along with better creep rupture strength by the addition of niobium and increasing nickel content, e.g. 24Cr/24NiCb and 25Cr/32NiCb HP-Mod grades. A study by the author on effect of temperature on difference in morphology of precipitated carbide is shown in the replica microstructure (Fig. 8.39) of top (low temperature) and bottom (high temperature) sections of a hydrogen reformer tube exposed for more than 50,000 h. In the bottom section subjected to high temperature the carbides have coagulated and

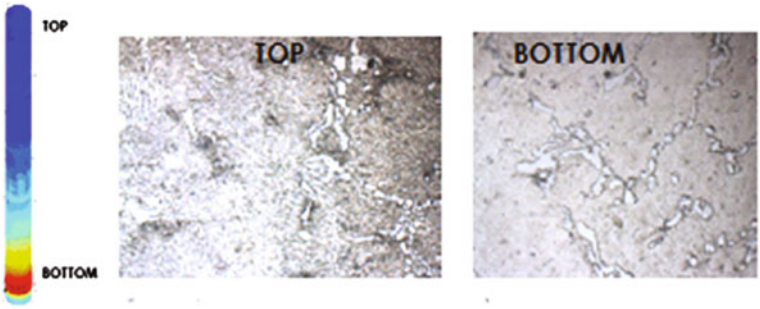


Fig. 8.39 Morphology of precipitation at the bottom and top of reformer tube after 50,000 h

secondary carbide has almost disappeared unlike top section which shows high density of secondary carbide as temperature is much lower.

8.5.3.3 Chi Phase Formation

Molybdenum promotes formation of the complex cubic chi phase, which contains approximately 33% chromium, 33% iron and 33% molybdenum and forms in the temperature range of 700–1000 °C in many corrosion resistant alloys, especially duplex stainless steels, with lower nickel content. It can be minimized by higher nickel and nitrogen additions to the alloy composition. Its presence leads to embrittlement, loss of ductility and reduced corrosion resistance. It may be eliminated by high temperature heat treatment above 1150 °C, combined with hot working at temperatures above 1000 °C.

8.5.3.4 Other Intermetallics

Duplex stainless steels are highly prone to damage due to various changes occurring at high temperatures. These can be divided into two groups, high and low temperature phases. A schematic TTT curve for precipitation in duplex stainless steels, illustrating the temperature ranges over which the various phases may form and the effects of increasing alloy content is shown in Fig. 8.40 [52]. As expected, these changes follow C-curve. The figure also shows the elements which shift the nose to left, broadens the temperature range and increases the chances of phase formation. The problem faced in DSS is not due to phase formation during service at high temperatures (operating temperature is kept below <300 °C) but during the welding

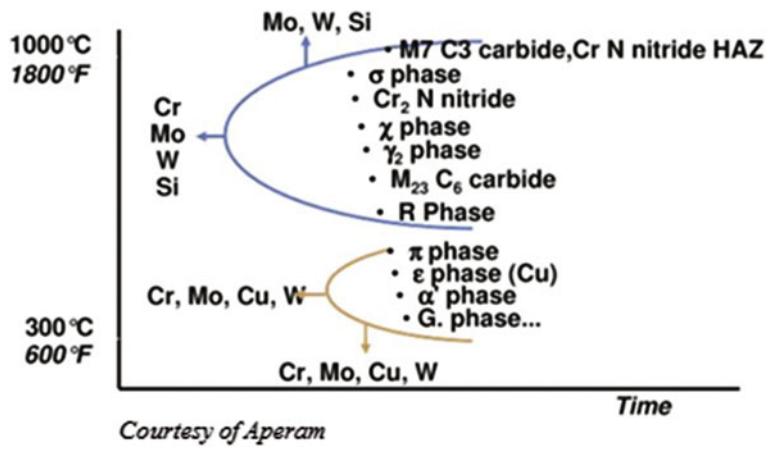


Fig. 8.40 Schematic TTT curve of precipitates that form in DSS [52]

process. However, some of these phases like G-phase, Z-phase (CrNbN), etc. are formed in high temperature alloys during service and each of them have either positive or negative effects on material properties.

8.5.4 Temper Embrittlement

Temper embrittlement as metallurgical degradation has been well known since the development of heat treatable alloys containing Mn, Ni, Cr, Mo, V, etc. singly or in combination. It was observed that steels containing Ni–Cr–Mo, or Cr–Mo–V develop brittleness on tempering in the temperature range of 345–590 °C. It was further found that embrittlement also occurs during PWHT or service exposure in the susceptible range. It has no effect on normal tensile and yield strengths, elongation or hardness of material but the impact property is severely affected. The change in impact property is reflected in the shift in the impact transition curve to higher temperature, the practical indicator of which is a shift in 54*J* (40 ft lb) transition temperature (TTΔ54) or the fracture appearance transition temperature (ΔFATT).

Considerable research has been carried out on the mechanism of temper embrittlement [53–55] and it has been established that embrittlement occurs due to the preferential segregation of phosphorous and residual (tramp) elements like antimony (Sb), tin (Sn) and arsenic (As) at prior austenite grains. The effect of different elements varies in decreasing order of Sb, P, Sn and As. Generally, Sb is not present in steel and the effect of As is minimal. Therefore, P and Sn can be considered to be the elements of concern. As regards alloying elements present in steel, manganese, silicon, nickel and chromium increase the tendency of grain boundary segregation of the residual elements. As addition of Ni and Cr cannot be avoided, for any particular alloy steel composition, control of manganese and silicon content becomes of primary importance. Some beneficial effect of Mo and W has been observed, which is considered to be primarily due to their scavenging effect on P. The specifications of normal grades of various heat treatable alloys recommend P-0.04% max. Si 0.2–0.35%, and Mn 0.5–1.0. The high contents of these elements are related to normal steel making practice. Temper embrittlement in such steels during the process of heat treatment is avoided by controlling the heat treatment cycle. Being diffusion controlled process, temper embrittlement obeys a C-curve behaviour, i.e. embrittlement occurs rapidly in a smaller temperature zone, which for commercial steel of interest lies between 455 and 510 °C. Thus by rapidly cooling after tempering from above 600 °C, the embrittlement can be suppressed.

Most of the low-alloy steel steels are to be given PWHT after welding where rapid cooling is not possible. Further, many of the equipment/components are operated in the temperature range where in-service embrittlement can occur during prolonged exposures. Some of the commonly used materials in this category in

refining and fertilizer industries are 5Cr–0.5Mo, 2.25Cr–1Mo, 1.25Cr–0.5Mo, 3Cr–1Mo and high temperature bolting materials. Of the various Cr–Mo steels, 2.2.5Cr–1Mo and 3Cr–1Mo steels are most susceptible to temper embrittlement. In these materials compositional control, i.e. lower Si and Mn and low level of P and tramp elements like Sn, As, Sb are given the maximum importance. Though normal steel specification do not mention about tramp elements, the modern steel making practices do keep a control on these because of their deleterious effect, such as, temper embrittlement, reheat cracking, fracture toughness, etc. The final objective of these special steel making processes is to contain the toughness degradation effect of detrimental elements within a small limit. The requirement for temper embrittlement resistant steel is commonly expressed by the so called J and $\overline{X}$ (X-bar) factor for base and weld metals formulated by Watanabe [56] and Bruscato, respectively [57].

(i) For base metal J factor = (Si + Mn) × (P + Sn) × 10^{-4} (All concentration in weight percentages)

(ii) For welds $\overline{X}$ (X-bar) = 10 P + 5B + 4Sn + As × 10^{-2} (All concentration in ppm)

The J or X-bar factor gives a direction to the material user and producer on the quality of steel with regard to the change in service exposed toughness. As per API 934A [58] the J factor for a shift in DTB temperature (ΔFATT) at 40 ft lb (55J) shall be ≤ 100, though some of the earlier specification used the limit of J = 150 max. The modern steel manufacturers produce steels with J factor much below 100. This limit is applicable for conventional 2.25Cr–1Mo and 3Cr–1Mo steels and also enhanced 2.25Cr–1Mo, 2–1/4 Cr–1Mo–0.25 V, 3Cr–1Mo-0.25 V–Ti–B, and 3Cr–1Mo–0.25 V–Cb–Ca steels. Resistance to temper embrittlement of welds is of same or greater importance than the base metal. Quality of deposited weld metal should therefore meet the requirements of X-bar factor which is presently specified as 12 ppm against earlier figure of 20 ppm [59].

The earlier materials were manufactured without any control on J and X-bar - factors and, therefore, damages related to temper embrittlement were experienced soon after the high temperature, high pressure processes were introduced. In 1960s this problem was recognized as a result of failures experienced in thick walled 2.25Cr-0.5Mo hydrocracker reactors. In hydrogen service, embrittlement due to hydrogen also occurs, which has an additive effect. To counteract the combined deleterious effects of temper and hydrogen embrittlement, start up and shutdown procedures were formulated and in extreme cases the vessels had to be derated (decrease in operational severity). Continuous developments have taken place in quality of steel since then and historically this can be divided into four generations between 1970 and 1989, and during this period the average J factor has come down from 231 to 61. The problems related to temper embrittlement in hydrocracker, hydrodesulphurizer, fertilizer and other industries have been considerably reduced in the recent years due to the use of improved grades of steel, which can be called 5th generation steel.

In spite of all the care, the user would like to be sure that the material has the requisite resistance to embrittlement over long periods of service. To predict the long term behaviour based on short-term tests, a stepwise heat treatment has been developed for the power industry where similar damage is experienced in heat treatable alloy steel turbine shaft during service. The same approach is being used for 2.25 Cr–1Mo, 1.25Cr–0.5Mo and 3Cr–1Mo in process industry also. The step cooling cycle, details of various steps given in API 934A is shown in Fig. 8.41 [60]. Charpy impact transition temperatures of the material before and after subjecting to step cooling have been related by a mathematical expression

$$\mathrm{AF} + 2.5\,(\mathrm{SC} - \mathrm{AF}) \tag{8.5.1}$$

where

AF As formed Charpy 54 J temperature
SC Step cooled Charpy 54 J temperature

If the resultant value is <38 °C it ensures that the material will not develop unacceptable temper embrittlement during service. This relationship is used for the construction of pressure vessels operating in the embrittling temperature range [61].

In addition to possible catastrophic failure of temper embrittled materials, their weld repair in case of any damage becomes difficult. The welding stresses are sufficient to result in the development of cracks in adjacent areas of repair. The adverse effect of temper embrittlement is, however, a reversible process and the toughness can be restored by subjecting the component to a heat treatment consisting of heating to about 620 °C followed by rapid cooling. However, such a procedure is dependent on the nature of components and severity of embrittlement.

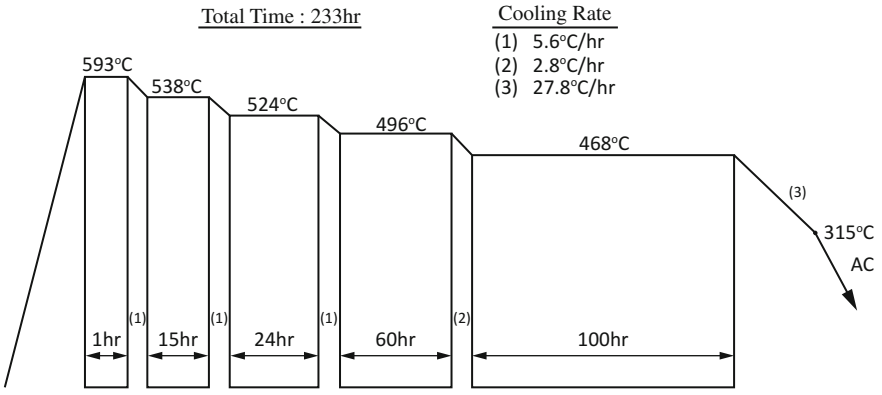


Fig. 8.41 Step cooling process for temper embrittlement susceptibility [60]

8.6 High Temperature Degradation

8.6.1 Oxidation

Unlike corrosion, which occurs in an aqueous environment, oxidation is high temperature degradation due to reaction of a dry gaseous environment with metals and alloys. The reaction is generally on surface but in some cases it can occur under the metal surface (internal corrosion) also. While oxygen is the most common agent, the reaction of metal with other gaseous constituents like carbon dioxide, hydrogen sulphide, chlorine also occurs. In the process of surface oxidation, a scale builds up on the metal surface and this scale controls the further oxidation rate. If the scale remains intact, the progress of oxidation is by transport of ions and electrons through the scale. In a way, therefore, oxidation and corrosion process are comparable.

Oxidation behaviour of any pure metal is dependent on the stability of oxides. That is, the higher the energy of oxide formation, more readily a metal will oxidize. For example, iron and aluminium will oxidize more readily than gold or platinum. However, once an oxide scale is formed, the rate of further oxidation will depend on the properties of the scale. In one of the earliest scientific studies of oxidation, Pilling and Bedworth proposed that oxidation resistance should be related to the volume ratio of oxide and metal per gm. atom of metal [62]. A volume ratio of less than 1 produces insufficient oxide to cover the metal and is not protective. Similarly, it was argued that a ratio of much greater than 1 will introduce large compressive stresses in the oxide, which will reduce oxidation resistance due to cracking and spalling of scale. The ideal ratio, according to these investigators, would be close to 1. This ratio, however, does not accurately predict oxidation resistance, although there is some qualitative agreement. In general, metals with volume ratios of less than 1 form non-protective oxides, as do those with very high volume ratios (2–3). This approach is considered as an empirical criterion as there are other more important requirements which determine oxidation resistance. To be protective to oxygen reaction, an oxide must possess good adherence to base, a high melting point and a low vapour pressure, good high temperature plasticity to resist cracking, and low electrical conductivity or low diffusion coefficient to metallic ions.

8.6.1.1 Electrochemical and Morphological Aspects of Oxidation

Oxidation by gaseous oxygen, like aqueous corrosion, is similar to an electrochemical process. Oxidation is not simply the chemical combination of metal and oxygen on a molecular scale, $M + 1/2\ O_2 \rightarrow MO$, but consists of two separate processes in the sequence given below:

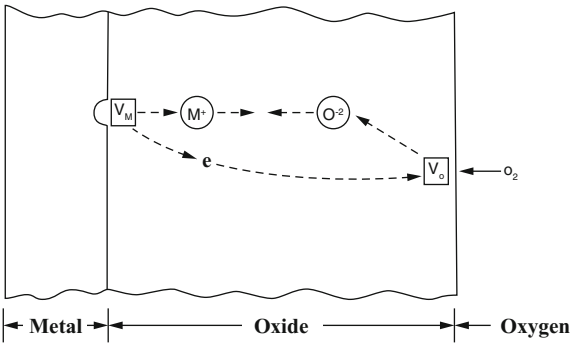


Fig. 8.42 Illustrates schematically electrochemical processes during oxidation

$$\begin{aligned} &M \rightarrow M^2 + 2e^- (\text{metal oxidation at metal-scale interface}) \\ &\text{Electron diffuses through scale to scale-gas interface} \end{aligned} \tag{8.6.1}$$

$$1/2O_2 + 2e^- \rightarrow O^{2-} (\text{oxidation reduction at scale-gas interface}) \tag{8.6.2}$$

$$M + 1/2O_2 \rightarrow MO (\text{overall}) \tag{8.6.3}$$

As ionization of metal and movement of electron similar to aqueous corrosion are involved, gaseous oxidation may be considered as dry corrosion process. Because all metal oxides conduct both ions and electrons to some extent, this electrochemical reaction occurs without the necessity of an external electronic conductor between the local anode and the local cathode. Figure 8.42 shows that the oxide layer serves simultaneously as (1) an ionic conductor (electrolyte) and (2) an electronic barrier through which electrons pass and ions migrate over defect lattice sites (V_m and V_o). Many metal-oxygen phase diagrams indicate formation of several stable binary oxides. For example, iron may form compound like FeO, Fe_3O_4 and Fe_2O_3 and copper Cu_2O and CuO. The growth of oxide scale takes place at gas/oxide interface and therefore in the formation of oxide scale on pure metal, the most oxygen-rich compound is found at the scale–gas interface and the most metal-rich compound at scale–metal interface which in case of iron can be stated in the order, $Fe/FeO/Fe_3O_4/Fe_2O_3/O_2$. Thickness of each phase is determined by the rate of ionic diffusion through that phase.

8.6.1.2 Growth of Oxide Scale

Most oxides of metals do not conform to stoichiometric composition. The oxide may be either 'metal excess', with corresponding excess of free electrons, or 'metal deficit' with vacant lattice sites. Normally, parabolic law (Fig. 8.43) is followed in most of the cases as the rate is controlled by diffusion of metal ions through the scale, which is expressed by:

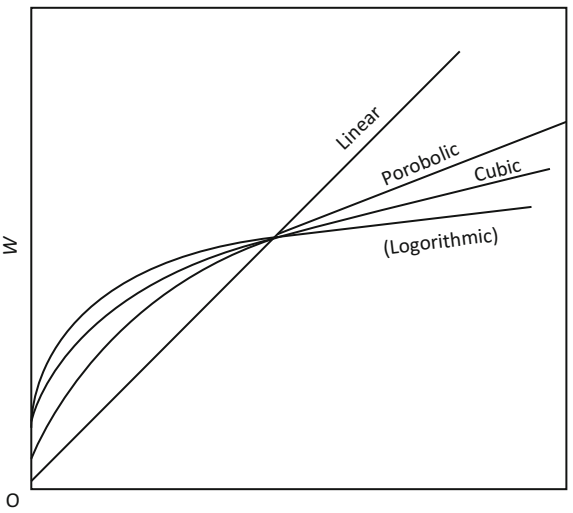


Fig. 8.43 Various oxidation laws but parabolic is more common

$$x^2 = k_1 t + k_2, \tag{8.6.4}$$

where x is the scale thickness, t is the time and k_1 and k_2 are constants.

There are some metals like aluminium which form stoichiometric composition (e.g. Al_2O_3) and, therefore, are neither metal excess or metal deficit. In such a case, the oxides formed on pure metal or an alloy containing critical concentration of the solute would develop defect free protective oxide layer which would reduce further growth of scale.

8.6.1.3 Effect of Alloying

Alloying is the most common method for increasing the oxidation resistance. Alloys which are generally used above 540 °C are known as high temperature alloys. In case of most of the engineering iron and nickel alloys, the resistance to oxidation is achieved by adding chromium. If we consider ferrous and nonferrous metals, the general approach to increase oxidation resistance is to alloy with those elements which

* would form an alloy rich oxide layer below the scale thus reducing diffusion of metal ion through the scale and restricting further oxidation,
* on addition of a critical amount of solute the formation of oxides of solvent will completely stop and in turn an impervious layer of oxide of the solute will be formed. This will be evident from Fig. 8.44 [63] which shows the effect of addition of increasing chromium to iron on its oxidation resistance. During the oxidation there are changes in the nature of

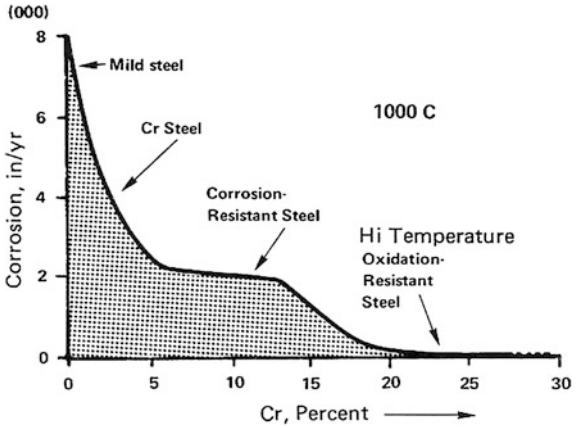


Fig. 8.44 With increasing chromium the oxide scale gets richer in chromium and increase oxidation resistance [63]

oxide layer from iron oxide with zero chromium to 100%Cr_2O_3 with 18%Cr. At lower chromium concentrations the scales consists of the mixture of iron and chromium oxides but with increase in chromium content Cr_2O_3 in oxide layer progressively increases till no iron oxide remains. The oxide of chromium has stoichiometric composition and therefore acts as effective protective scale. The Cr_2O_3 scale also gets effectively interlocked with metal due to the process of internal oxidation which prevents the spalling and cracking of the scale.

Most of the high temperature oxidation resistance alloys belong to three basic families of iron, nickel or cobalt base alloys. The reason for this limitation is that under most of the service conditions these alloys should not only have high resistance to oxidation but should have good mechanical properties including creep resistance. For these alloy systems, the main alloying element imparting resistance to oxidation is chromium. Aluminium and silicon are more effective but can be added only in limited quantities because of their adverse effect on mechanical properties. However, in chromium bearing iron and nickel-base alloys maximum 2%Si is added to further increase oxidation resistance. In some cases, small amounts of aluminium are also added. For very high and super alloys, small amounts of other alloying elements are added, not for resistance to oxidation but to improve the overall performance. Alloys used in process industries for high temperature operations are, low and medium alloy Cr–Mo steels up to 675 °C and austenitic stainless steels like Types 304H, 321H and 347H up to 800 °C. For temperatures above 800 °C, both chromium and nickel are increased with additions of small amounts of Al, Ti, Nb and W. These fall under HX alloys, where X stands for H, K, T, P, etc. some of which have been given in Table 1.2B and relevant portions of other Chapters.

8.6.2 Catastrophic Oxidation/Fuel Ash Corrosion

In boilers and heaters, burning fuel oil or coal, a type of corrosion known as catastrophic oxidation is experienced, where high temperature alloys suffer excessive loss much below their highest limiting temperature. Tubes, tube supports and other internals of heater and boiler are affected. The fossil fuels used contain as impurities sodium, potassium, and sulphur in coal and small amounts of sodium, vanadium, and sulphur in fuel oil. On firing with fuel oil, oxides of the alkali metal and vanadium are formed. These compounds react with each other and form a number of eutectic mixture having very low melting points with sodium vanadyl vanadate ($Na_2O.V_2O_4.5V_2O_5$) having melting point of as low as 550°C. Similarly on burning of coal various alkali compounds are formed. As the metallic elements in the oil/coal remain as residue (ash) after burning, this type of attack is also known as *oil/coal ash corrosion*. The mechanism of catastrophic oxidation in such service is explained on the basis of nature of fuel ash. The molten ash deposits on the water and super heater tubes and internals of boilers and process heaters. The molten slag mixture, like any slag, has high solubility for oxides. The viscous slag deposited on the resistant alloys dissolves the protective oxide film. In addition, the diffusion of oxygen through this layer is high. The net effect is very high rate of oxidation.

8.6.2.1 Prevention of Fuel Ash Corrosion

There are two approaches in protection against fuel ash corrosion, that is, use of a resistant alloy or changing the nature of oil ash formed. High chromium of the order of 40–60% is required to build up a highly protective layer of Cr_2O_3. The addition of such a high amount of chromium is possible only in nickel and not iron base alloys. Special alloys like 50Cr48Ni1.5Nb (IN 657™), where Nb gives the required creep strength, are used for furnace tube supports where accelerated oil ash corrosion occurs. The other approach is to avoid formation of liquid vanadates. A number of studies have been carried out on effect of various additives and results of test carried out by the author have shown that most effective compound is MgO followed by CaO (Fig. 8.45) [64]. In this case magnesium has been found to be very effective where it reacts with vanadium to form compounds having high melting point, which render the vanadate non-reactive. Commercially both magnesium oxide powder and oil soluble organic compound of magnesium have been successfully used.

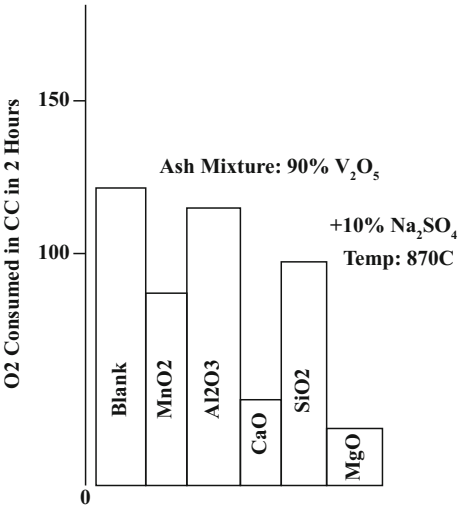


Fig. 8.45 Effect of various additives on oil ash corrosion [64]

8.6.3 High Temperature Hydrogen Attack

In processes using hydrogen, one of the important causes of material damage is hydrogen. This type of damage can occur both at high and low (in presence of water) temperatures. Low temperature hydrogen damages have been discussed in Chapt. 10. Molecular hydrogen at high temperature and pressures gets partially dissociated into atomic hydrogen. It is a reversible reaction and at any particular pressure and temperature conditions, equilibrium exists between the molecular and atomic hydrogen:

$$H_2 \leftrightarrow H + H \tag{8.6.5}$$

Atomic hydrogen is soluble is steel and enters its lattice, the solubility controlled by Sieverts Law [65], which states that under equilibrium condition the solubility of a diatomic gas in metal is proportional to the square root of the partial pressure of the gas. Thus equipment in hydrogen service absorbs hydrogen and after some time the inner surface gets saturated with hydrogen. Due to the concentration gradient between the inner and outer surfaces, the hydrogen diffuses inside the steel towards the outer surface. This diffusing hydrogen not only accumulates at any discontinuities as molecular hydrogen, causing blistering, but also reacts with cementite in steel to produce methane:

$$Fe_3C + 4H = CH_4 + 3Fe \tag{8.6.6}$$

Methane being a molecule cannot diffuse through metal and accumulate at the location of formation, normally grain boundaries, forming bubbles (voids) of

accumulated gas. The density of voids grows with time and become grain boundary fissures. This reduces the effective cross section to sustain the load, resulting in rupture.

8.6.3.1 Prevention of High Temperature Hydrogen Damage

Blister Formation

The formation of blisters is related to the cleanliness of the steel. To avoid damage of a component due to blistering it is necessary that special care is taken during manufacturing of steel to avoid the presence of lamination, voids and slag inclusions at the interface of which hydrogen accumulates. The plates, skelp and pipes should be checked ultrasonically for the presence of the above defects.

High Temperature Hydrogen Attack (HTHA)

The problem of hydrogen attack is taken care of by changing the composition of iron carbide to a carbide which would not be attacked by hydrogen at the concerned temperature and pressure. This is achieved by mainly adding chromium and some molybdenum to steel. The carbides of these elements are more stable in the increasing order of Mo and Cr. Thus with increasing hydrogen pressure and temperature, the alloy suitable for hydrogen service is to be progressively upgraded to C–0.5Mo, 1Cr–0.5Mo, 1.25Cr–0.5Mo, 2.25Cr–0.1Mo and 3Cr–1Mo, etc. The suitability of various alloys has been plotted into series of curves as temperature versus hydrogen partial pressure, originally prepared by Nelson of Shell USA in 1949 (earlier known as Nelson Chart), and later accepted by API and issued as API 941 in 1970. These curves have been developed based on plant experience and some laboratory tests and for practical purposes they form the guideline for selection of material in hydrogen service. As regards C–0.5Mo the feedback from industry was negative due to instances of failure experienced. Taking note of this, in 1977 API revised the curves by lowering of C–0.5Mo line by 55 °C (100 °F) at lower pressure and gradually decreasing by about 28 °C (50 °F) at higher pressure.

Performance of Cr–0.5Mo Steel

As number of equipment was constructed with C–0.5Mo, various studies were initiated [66–68] based on which the following major conclusions were arrived at:

(1) Susceptibility to attack is related to the actual composition of carbide with respect to Mo and not the bulk metal composition.
(2) Normalized and tempered or quenched and tempered steel gives satisfactory level of resistance to hydrogen attack but not the annealed one.

(3) PWHT at 625–650 °C increases resistance to attack.

Most of the Cr–0.5 Mo equipment have unpredictable resistance to hydrogen attack and therefore it has been deleted as a permitted alloy in the API 941 [69].

Dearburization

Under the influence of hydrogen environments, dearburization reaction can take place on the metal surface at higher temperatures. Here carbon in the metal diffuses to the surface and reacts with the surrounding hydrogen environment to form CH_4 which escapes in the atmosphere. This phenomenon of surface decarburization is indicated in Nelson Curve by dotted lines. As will be evident, surface decarburization is favoured by lower hydrogen partial pressure and higher temperatures. Under extreme conditions this reaction can also lead to thru thickness decarburization. Decarburization reduces the strength of material and thus the reliability of material can be severely affected. As would be evident, decarburization temperature increases with increase in chromium content. Similar reaction also occurs under oxidizing conditions due to surface reaction between carbon and oxygen to form CO_2. Thus under oxidizing conditions, in heater tubes, super heater, etc. a layer of low carbon zone develops on the external surface.

8.7 Cost of Corrosion to Society

Corrosion is an all pervasive irreversible natural degradation process. Process of corrosion results in loss of metals and alloys and other different modes of damage which adversely affect the useful life of structures, equipment, infrastructure, pipelines, process industries, buildings, transport vehicles, etc. which are integral part of modern human life. Action against corrosion is of utmost importance. As it is a natural process we cannot prevent it but can control it. There are various methods available today by which corrosion can be controlled and monitored. The overall effect has been that the cost the society has to incur to control corrosion has correspondingly grown. This has led to determining cost of corrosion to the economy of a nation.

8.7.1 Estimation of Cost of Corrosion

1. The first attempt to determine the cost of corrosion was made by Prof. H.H. Uhlig, who estimated the cost of corrosion to USA in 1949 as $5.5 billion. The first systematic study was, however, made in 1972 in UK by the T.P. Hoar Committee when cost of corrosion in UK was estimated as £1365 billion for 1969–1970 (amounting to 3.5% of GNP) of which 23% was potentially avoidable.

Subsequently, studies have been made in many countries like Federal Republic of Germany (19 billion DM as 3% of GNP in 1968–1969), Soviet Union, Russia (6 billion Rubles as 2% of GNP in 1969), Australia (A$22 billion in 2009), Japan (Yen 2500 billion as 1.8% of GNP in 1976–1977); Persian Gulf Region ($10–15 billion per year), India (Rupees 1.54 billion in 1960–1961), etc. The above information have been dealt in detail by Kruger [70]. A study of corrosion in China in 2001 estimated the annual cost at 498 billion Yuan (US$61 billion). China's GDP that year was 9.6 trillion Yuan. That put China's cost of corrosion even higher than the industrialized nations at 5.2% of GDP [71].

2. The cost of corrosion has been estimated using different methods to estimate (i) Direct Cost and (ii) Indirect Cost of corrosion. The direct cost includes protective organic and metallic coatings, chemical treatment and corrosion inhibitors, cathodic protection, corrosion resistant alloys, non-metallic like polymers, etc. Also included are corrosion control and monitoring instruments, R&D and education and training on corrosion. Indirect cost, on the other hand, includes cost of labour and equipment for corrosion related activities, loss of revenue due to loss of production, cost of loss of reliability and litigation, etc.
3. In one of the recent study made in USA by Federal Highway Authority (as included under Transportation Equity Act for the twenty first Century (TEA-21), which was passed by the U.S. legislature in 1998) [72] the corrosion cost was determined on the basis of data for industries in five major categories like infrastructure, utilities, transportation, production and manufacturing and government. The total direct cost added up to $137.9 billion and of these cost related to hydrocarbon and process industries were arrived at the following figures (in billion $):

    - Gas and liquid transmission pipelines 7.0
    - Oil and gas exploration and production 1.4
    - Petroleum refining 3.7
    - Chemical, petrochemical, pharmaceutical 1.7
    - Hazardous material transport 0.9
    - Hazardous material storage 7.0

The corrosion cost worked out to 1.57% of GDP which on extrapolation (non-linear) to the national GDP consisting of other industries and services, gave cost of direct corrosion to be 3.1% of GDP. The survey also assumed that indirect cost is equal to the direct cost, thus arriving at a figure of 6% of GDP as total (direct + indirect) cost of corrosion.

8.7.2 Formation of World Body

The overall conclusion is that cost of corrosion worldwide is estimated to exceed $U.S 1.8 trillion, which translates to 3–4% of the Gross Domestic Product (GDP) of industrialized countries. Overall figures for different countries can vary in the range

of 2–5% of GDP depending on the countries' industrialization, economy, living standard and awareness of general public, industry and government about the losses due to corrosion. Most of the corrosion problems are environmental specific and not national specific. This makes it easier for the problems to be tackled timely if proper communication and transfer of information is maintained. Passing on and sharing of knowledge among individuals and societies in this connection is very necessary, through interaction at seminars and conferences, in-house training, technical journals, R&D, improvement in education both in corrosion control and corrosion management, etc.

A positive step in this direction was taken in 2006 to form The World Corrosion Organization(**WCO**) which is an international association of societies and organizations such as, Australasian Corrosion Association (ACA), the Chinese Society for Corrosion and Protection (CSCP), the European Federation of Corrosion (EFC), and NACE International, involved with corrosion management and control. Today it has 27 member organizations representing more than 50,000 corrosion scientists, engineers, and technicians from all over the world. In addition to the various aspects of actual corrosion damage and corrective measures, the WCO would like to give stress on corrosion education, R&D and training, and also develop certified competence in the field of corrosion and corrosion control. These have been discussed in the 2009 WCO report by Günter Schmitt [73], The important points highlighted in the report are the lack of seriousness by industry and the government in realizing the importance of the problem and the lack of basic education in corrosion and corrosion protection in university curricula, even in highly developed countries. In case of the latter, the report states "*Even more disappointing is that in places where corrosion education is included in the natural sciences or engineering curricula, or even established as separate studies, university leaders and faculty deans refuse to support this important subject. Available chairs for corrosion and corrosion control are no longer continued as such, but rather converted into positions for teaching 'more future oriented' subjects such as biotechnology and nanotechnology. Such trends are observed specifically in Europe and the United States*". The report further states that "*The WCO aims to foster the education of technologists and engineers who should be knowledgeable in corrosion, including undergraduate majors in the field of materials science and engineering (MSE); engineers who should be aware of corrosion, including undergraduate majors in non-MSE departments such as mechanical, civil, petroleum, and chemical engineering; corrosion experts (those earning an advanced degree specializing in corrosion); and practicing engineers with Bachelor level degrees*".

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Chapter 9
Material Selection and Performance in Oil and Gas Industry

Abstract In oil and gas production, the main corrosive constituent is CO_2 and corrosion rate increases initially with increase in its partial pressure and temperature and then decreases beyond a temperature due to film formation. The rate is also affected by characteristic of produced water, flow rate, oil/water ratio, oxygen, etc. Number of predictive models have been developed which have been classified as mechanistic or empirical. However, the prediction under different models quite often varies. Carbon steel with inhibitor addition is the preferred MOC, but corrosion-resistant alloys (CRA) like 13 Cr, DSS, SDSS and nickel alloys are used depending on severity. Coated or CRA-cladded carbon steels are also being used. In presence of H_2S, the materials are susceptible to cracking for which resistant alloys are used. Handling of gas involves drying followed by separation of different constituents. All lines and offshore structures are protected against external corrosion by coating and CP. This chapter presents various aspects of problem experienced and action taken in oil and gas industry to increase the performance of materials. Emphasis has been on the offshore oil and gas installations, where the conditions are more severe and cost of operation and maintenance much higher than similar installation onshore.

Keywords CO_2 corrosion · Corrosion prediction model · Sour service · CRA · Corrosion monitoring · CP · Intelligent pigging

9.1 Introduction

Crude oil is a naturally occurring viscous flammable liquid in geological formation beneath the earth surface consisting of a mixture of hydrocarbons of various molecular weights along with smaller amounts of other liquid organic compounds. In many cases, the crude oil also contains gaseous hydrocarbons of lower molecular weight. Crude oil in an unrefined state has been utilized by humans for 1000s of years to keep fires ablaze, and also for warfare. The first recorded instance of oil (sixth-century BC) describes its use as weapons of fire by the army of Kir II, first

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Shah of Achaemenid Empire (present-day Iran). Subsequently, there have been various mentions including use of flaming torches by Alexander the Great. In earlier days, people used oil which seeped out of ground at different locations. Attempts to extract using hand dug wells of a few feet are reported to have been attempted from time to time. Major thrust on the oil getting a status of industry occurred after a process to get kerosene from crude was developed and kerosene lamp was invented in 1857. Initially, all oil refineries were set up to produce primarily kerosene and fuel oil. The year 1867 changed the scenario completely with the invention of 4-stroke engine and subsequent introduction of gasoline powered automobiles in Europe by Karl Benz and Wilhelm Daimler and in USA by Henry Ford. This created additional markets for gasoline which was earlier used as a cheap solvent produced as a by-product of kerosene distillation. With industrialization and growth of automobile and aviation industry the need for middle distillates and other associated products like lubricants, greases, wax, etc., resulted in the introduction of new processing techniques in oil refining industry. During this period the gas (associated gas) had little role and most of it was flared till its use as an alternate source of industrial and domestic energy was realized.

After the Second World War, the demand of oil increased manifolds because of worldwide rapid industrial development leading to search for new oil fields. The emphasis shifted from shallow to comparatively deeper onshore wells. During this period, offshore fields were operating only in a few shallow beds of Gulf of Mexico and Caspian Sea. In the meantime, the importance of gas as an alternate environmentally clean energy source and as feed for the production of fertilizer and petrochemicals was established. In 1973, the price of crude dramatically increased which made higher investment in exploration and production of oil and gas profitable. As comparatively shallow onshore reserves depleted and few new fields were discovered, the worldwide search for new sources of hydrocarbons turned to deeper reservoirs onshore. Simultaneously, the industry ventured from shallow to deeper waters beyond continental shelf which can be termed as ultra-deep water (Fig. 9.1).

Deeper the formation, higher is the pressure and temperature which can also be designated as high temperature/high pressure (HPHT) and extreme high temperature/high pressure (EHPHT) wells. With higher depth there is greater likelihood of encountering higher percentages of acidic gases like CO_2 and H_2S. These changes have led to increased emphasis on selection of materials and corrosion protection methods adopted because of exposure to very aggressive environments. Table 9.1 summarizes the various types of wells and conditions encountered.

Global proven reserves of oil at the beginning of 2009 were at 1.342 trillion barrels, of which about 10% is projected to be in deep water. Thus, worldwide trend today is for offshore exploration which has increased the cost of exploration and well completion manifold as given in Table 9.2 for UK Continental Shelf (UKCS). Onshore wells, on the other hand, cost $1 million to $15 million for shallow to very deep and difficult wells. If we add to this the cost of gathering and product transport lines, offshore platforms and processing facilities it will be clear that return on

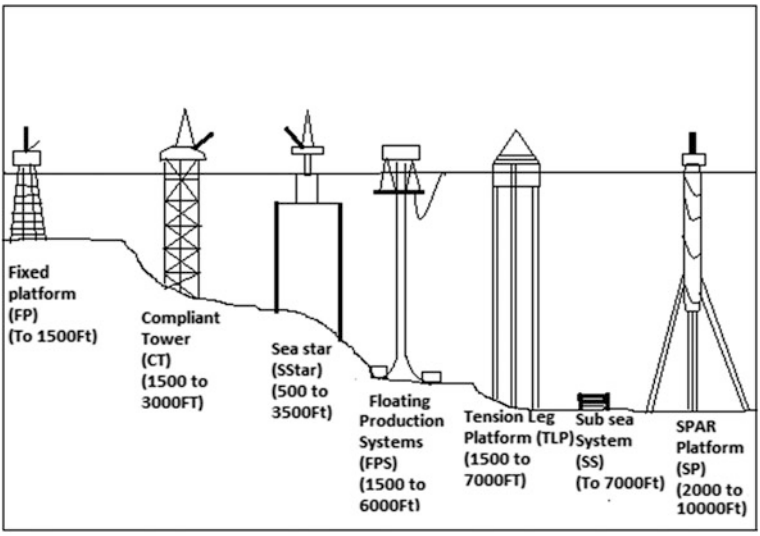


Fig. 9.1 Schematic illustration of offshore field depths

Table 9.1 Summary of nature of various oil and gas wells presently in operation

Nature of wells	Description	Remarks
Depth of reservoir	Shallow <3000 m Deep 3000–6100 m Ultra deep >6100 m	Record as of 2106—10,421 m Exploration well—16,000 m
Offshore—depth of water	Shallow <300 m Deep 300–1500 m Ultra deep >1500 m	2000–3000 m depth of water not uncommon in Brazil and Gulf of Mexico
HPHT	Bottom hole temperature 200 °C Bottom hole pressure 103 MPa	
EHPHT	Bottom hole temperature 230 °C Bottom hole pressure 206 MPa	

Table 9.2 Typical well costs (without testing) for the UK continental self in 1998 (Ref: http://www.edinformatics.com)

Well location	Typical cost (in millions of £)
Northern North Sea	8–12
West of Shetlands	5–15
Southern North Sea	7–12
Irish Sea	2–3

investment will depend on how long the production facilities last. In other words, the equipment, piping and structures need to be protected against deterioration due to corrosion to get maximum life.

One additional important consideration in offshore operation is its much higher cost of maintenance compared to onshore fields. Thus, a material which with normal maintenance will be cost effective in case of the latter may not be suitable under similar conditions for offshore fields and use of greater corrosion control becomes necessary. Thus corrosion control plays an important role, amongst others, to justify investment in the development of any new oil and gas fields, whether onshore or offshore. There have also been other developments like introduction of FPSO (Floating Processing, Storage and Offloading Vessel), where offshore processing platform is not possible or justified. The processing equipment on top of FPSO is similar to that on an offshore platform. These are especially suitable for deep and ultra-deep fields where subsea production wells are connected to it with the help of series of flow lines. The other advantage is that once a field is abandoned the FPSO can be moved to another location.

9.2 Summary of Oil and Gas Production Facilities

The oil and gas industry basically concerns exploration and production operation. Typical functions in this connection include:

1. Drilling of production wells starts after the capacity of the reservoir is established. First, the well is drilled in which casing is placed and cemented. In most cases, several casings with decreasing diameter are required. This is followed by introduction of production tubing through which well fluid is conveyed to the surface. There are two main types of oil-producing wells: artificial lift and self-flowing, depending on the pressure at formation level. On the other hand, gas wells are free-flowing wells, because of high pressure at formation level.
2. From the production tubing, the well fluids pass through series of pressure reducing valves (known as Christmas tree) to reduce the pressure (where necessary) and then to the gathering system. The gathering system consists of flow lines from various wells going to a central processing facility.
3. The well fluids coming out of well in case of oil wells are crude oil, produced water (water present in the oil or gas reservoir strata) and gas known as associated gas. Gas wells, on the other hand, contain gas along with condensate, but with or without produced water. Crude oil, condensate, gas and produced water are separated in the processing facility.
4. The separated crude, condensate and gas are exported to downstream industries like gas processing, oil refinery, fertilizer, petrochemical, power plants, etc.

The various stages as described above are illustrated in Fig. 9.2. Normally, the oil and gas are dried before transport to avoid corrosion of pipeline though transportation of wet gas through pipeline is presently being used in offshore fields.

Thus facilities in oil and gas production installations can be divided broadly into wellhead and surface equipment. In traditional production methods (in onshore

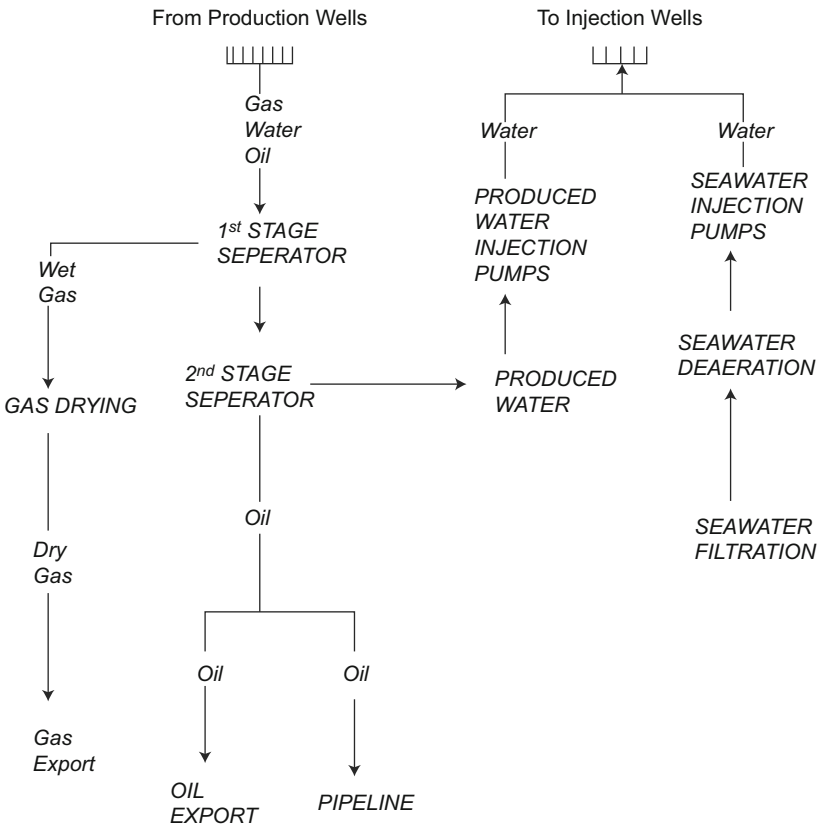


Fig. 9.2 Simplified flow processing of oil & gas

wells of comparatively lower depths), well equipment must be completely replaceable. These periodic changes in hundreds of shallow wells become necessary for the optimization of production by abandoning old wells and drilling new ones. However, this does not hold good to the same extent for deep and offshore fields, unmanned platforms and subsea production where periodic changes are not possible and, therefore, the wells are designed to last longer. As regards surface installations, these are designed to last the lifetime of the operating field, with limited replacements. This period may be anywhere between 20 and 30 years. Damage of any processing facility will bring the production to a complete stoppage unlike an individual well which can be stopped without affecting the production.

9.3 Corrosion Damage in Oil and Gas Production

Materials used in the oil and gas production, processing and transportation, depend on number of factors, the important amongst which are strength and toughness, resistance to environmental damage (primarily corrosion), amenability to corrosion control and finally cost. Historically from the very beginning carbon steel has been extensively used, mostly without inhibitor addition, as these were shallow oil wells with high oil and low-water content. Subsequently, with exploitation of deeper formation and greater emphasis on gas production from onshore and offshore fields, the importance of better material and stringent corrosion control became necessary because of higher severity of operating conditions.

Oil and gas are non-corrosive and corrosion depends on other corrosive constituents present in it and the temperature and pressures at which the materials are exposed during different operations. The most important role is that of CO_2 and H_2S along with pressure and temperature. Temperatures as high as 230 °C and very high partial pressures of CO_2 and H_2S have been encountered in some fields. Because of the presence of formation water, which increases with the age of a well, and introduction of recovery systems, e.g. water injection, CO_2 injection or in situ combustion, or lift gas, the conditions prevailing initially and that at a later date become quite different. Further, it is now believed that a well which initially does not have any H_2S can on ageing get contaminated with H_2S. Thus a material selected originally may not be compatible with conditions encountered at a later date. In addition to well fluids, oil well casing and pipelines are also subjected to soil and/or seawater corrosion. Further, in some instances presence of polysulphides, organic acids and elemental sulphur can create special problem.

Thus the overall approach to material selection can be stated as follows:

1. Use wherever possible carbon and low alloy steel to meet the requisite strength and required resistance to corrosion to give design life.
2. Where the corrosion-resistant conditions are not met use carbon and low alloy steel with inhibitor and coating, where applicable and necessary. Higher than normal corrosion allowance (CA) can also be provided to give additional life.
3. If the above steps do not give satisfactory and economical life, upgrading of metallurgy to corrosion-resistant alloys becomes necessary, which in oil and gas industry are termed as CRA to encompass different alloys.

9.3.1 Corrosivity of Reservoir Well Fluid

The first step in selection of material is to know the expected corrosivity (corrosion rate) of well fluid. Corrosion due to the presence of formation water and CO_2 corrosion were not a big issue in industry so long as shallow oil wells were being exploited. As early as 1949 the industry, based on then available field experience,

began developing rule of thumb to assess the corrosivity of oil wells. Initially the emphasis was on water cut, and it was believed that wells often have corrosion problems when the total water cut exceeds 85%, which was later revised to 50%. As late as 1958 it was stated in NACE-API publication that "wells usually become corrosive when water production reaches 40–50%" because the tubing is not wetted with oil [1]. Presently, it is believed that below 30% water cut protective effect of oil is possible under some conditions [2, 3].

As exploration of gas wells and oil wells with large amounts of associated gas was started, it became clear that it is necessary to give greater attention to the presence of CO_2 and its effect on corrosion. Accordingly, effect of CO_2 partial pressure on corrosion intensity was introduced and the following empirical rule [1, 4] was suggested on the basis of field data:

1. Carbon dioxide partial pressure below 7 psi (0.5 bars) is non-corrosive.
2. A partial pressure between 7 and 30 psi (0.5–2.0 bar) may indicate corrosion.
3. A partial pressure above 30 psi (2.0 bars) usually indicates corrosion problems.

These rules of thumb were applied rather broadly, but have been considered as too general in nature. Industry experience led to the need of finding a technically more reliable approach to estimate the corrosion rate taking into consideration different chemical and physical characteristics of flowing well fluid. Hydrocarbons are non-corrosive towards metals but main role is of CO_2 and H_2S present in gas phase of the well fluid. If the gas contains only CO_2 it is termed as sweet gas. However, if H_2S is present (with or without CO_2), the gas is termed as sour gas. In addition to the above two, the presence of chemicals in formation water (chloride, bicarbonate, etc.), temperature, pressure and flow rates also have large influence on corrosion rate. The role of different factors affecting corrosion is discussed next.

9.3.1.1 Carbon Dioxide

Though reported in 1920s, the problem of corrosion due to CO_2 has come into prominence only much later in the history of oil and gas industry. This was primarily because shallow oil wells operated at low pressures and had higher oil content, limiting corrosion within manageable level. CO_2 is an acid gas and it depresses pH when it is dissolved in an aqueous solution. Corrosion severity, therefore, increases with CO_2 partial pressure. This increased aggressiveness results from the decrease in the pH with increase in the partial pressure of CO_2. The first serious attempt to study the role of CO_2 in corrosion was made in early 1970s by de Waard and Milliams [5, 6] in connection with corrosion of gas transmission pipelines. Based on the study up to temperature of 65 °C a nomogram was prepared which related corrosion rate with temperature and partial pressure of CO_2. The application of nomogram data to a large extent confirmed actual failures experienced in gas transmission line. However, when applied to oil and gas systems, the result was disappointing.

de Waard and Lotz [3] carried out further study to establish the role of higher temperature on CO_2 corrosion. In presence of water, as per Henry's Law, CO_2 is dissolved in it to the extent proportional to the partial pressure of CO_2. The resultant solution forms carbonic acid, which, being weak acid, partially dissociates. For this reason it is generally believed that the predominant cathodic reaction is not reduction of H^+ but involves direct reduction of the non-dissociated acid to carbonate [3]:

$$H_2CO_3 + e^- \rightarrow H + HCO_3^-, \text{followed by } H + H \rightarrow H_2. \tag{9.3.1}$$

The overall effect of anodic reaction is to form iron carbonate:

$$Fe + H_2CO_3 \rightarrow FeCO_3 + H_2 \tag{9.3.2}$$

The formation of iron carbonate scales occurs by the process of precipitation when water gets supersaturated with respect to iron carbonate. The protectiveness of the scale, however, depends on its denseness which in turn is controlled by precipitation rate, corrosion rate under the scale and temperature. Corrosion under the scale tries to create voids in it which gets simultaneously filled up. The scaling tendency can be represented as

$$ST = CR/PR \tag{9.3.3}$$

where

ST is scaling tendency
CR is corrosion rate and
PR is precipitating rate.

Thus, increase in rate of precipitation compared to corrosion rate results in the formation of thin (~ 1 μm) protective coating compared to a situation where corrosion rate is higher than precipitation rate. In the latter case, even a thick scale (~ 100 μm) is unable to provide protection. Scales form slowly at lower temperatures (<60 °C) and therefore are not protective but above 60 °C precipitation proceeds rapidly forming very protective scales. However, high super saturation is not sustained for long at high temperature [7].

Laboratory tests have confirmed that with increase in temperature the corrosion rate first increases and then decreases beyond a certain temperature, as shown in Fig. 9.3 [3]. Based on the study, C. de Waard and Lotz modified the original nomogram to take into account the role of protective carbonate film in reducing corrosion at higher temperature as shown in Fig. 9.4 [3].

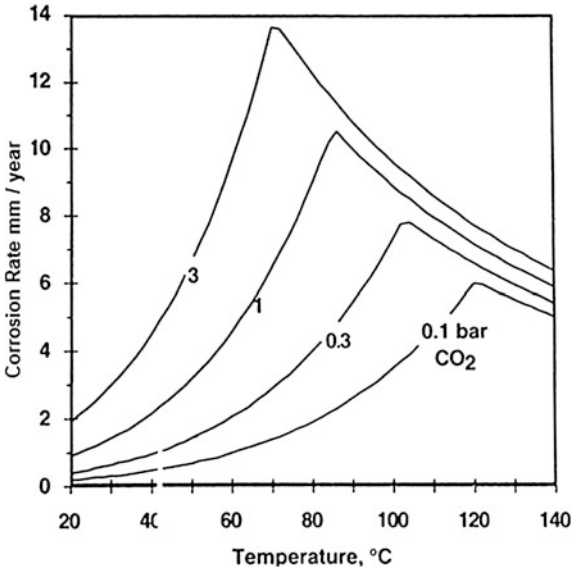


Fig. 9.3 Effect of temperature and CO_2 partial pressure on CO_2 corrosion [3]

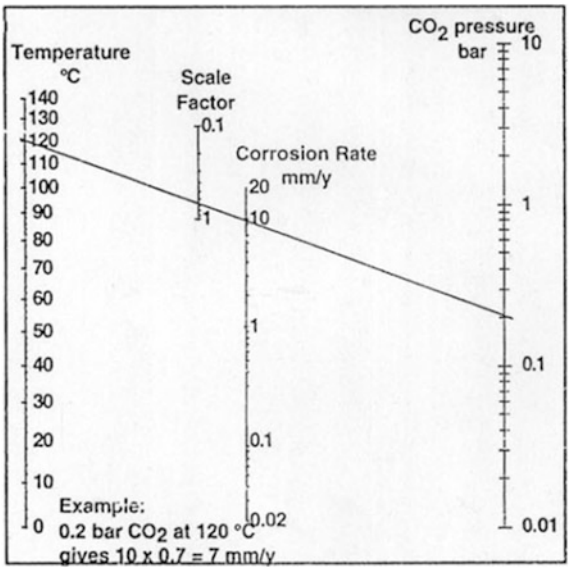


Fig. 9.4 Relation between temperature and CO_2 partial paper on corrosion rate [3]

9.3.1.2 Hydrogen Sulphide

The other important corrosive chemical present in many cases is H_2S. One of the earliest gas field discovered in 1949 was the Lacq field which had a high pressure sour gas reservoir containing 15% H_2S. Even in sweet wells presence of H_2S is

experienced at late stages when the well gets old or when some of the secondary recovery systems are introduced. H_2S is an acid gas and corrosion increases with H_2S partial pressure as in case of CO_2. Its adverse effect is less compared to that of CO_2, especially at lower temperature because of formation of a protective sulphide film. The nature of the film, however, becomes less protective at higher temperatures.

When both CO_2 and H_2S are present, no synergetic effect is observed. It is the relative partial pressures of the two which determine whether H_2S or CO_2 will control corrosion rate. It was found that the presence of small amounts of H_2S resulted in a marked reduction in general corrosion rate to the extent of 10–100 times lower than their pure CO_2 equivalent. In presence of H_2S, depending on the environment chemistry and the prior state of the underlying metal, a variety of iron sulphides can be formed. But in the present case the reduction is related to the formation of very thin protective sulphide film of mackinawite, having general formula of Fe_xS_y. This effect is primarily at temperatures less than 80 °C. At higher temperatures the characteristic of sulphide film changes to non-protective iron sulphide pyrrhotite, resulting in higher corrosion rates [8]. There are, however, different opinions as to at what ratio of CO_2 to H_2S the dominant corrosion species change. While some predict this ratio to be 500, some others suggest that a sharp change in corrosion occurs but not always at a ratio of CO_2 to H_2S above 500 [9]. It has also been suggested that at normal lower temperatures, encountered under most field conditions, the dominant mechanism should be considered to be CO_2 corrosion, wherever the CO_2 to H_2S partial pressures are greater than 100. Studies on comparison of the various CO_2 corrosion models have been undertaken by the Institute of Energy Technology, Norway as Joint Industrial Project Guidelines for prediction of CO_2 corrosion in oil and gas production systems [10]. It recommends that the corrosion rate would be controlled by CO_2 in case of CO_2/H_2S ratio of >500–1000.

9.3.1.3 Bicarbonates

The bicarbonate ions in produced water act as a buffering agent and, when present, increase the pH of the solution (Its presence is typically measured in milli-equivalent/litre (meq/l), one meq/l represents 0.061 g of HCO_3 in one litre of solution). The presence of bicarbonate, therefore, decreases the acidic effect of CO_2 and H_2S (when present) by increasing the pH of the system as shown in Fig. 9.5 [11]. Bicarbonates in production environments range from 1 to 100 meq/l. This is one of the important reasons why CO_2 dissolved in the formation water in most cases is less corrosive than that in distilled water.

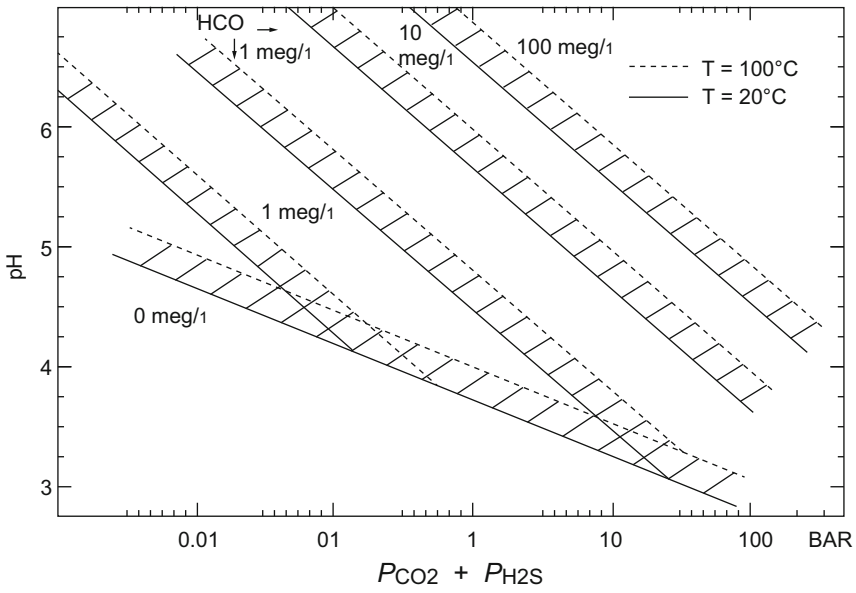


Fig. 9.5 In-situ pH based on partial pressure of CO_2 + H_2S [11]

9.3.1.4 Chlorides

In naturally deaerated production environments brines with low chloride content (i.e. <10,000 ppm) are less corrosive but corrosion rate increases with increasing chloride ion content in the range 10,000–100,000 ppm especially above 60 °C. This combined effect results from the fact that chloride ions can destroy the surface corrosion product films. The chloride content has an effect on the effectiveness of chemical corrosion inhibitors. Therefore, in many cases, more careful selection of inhibitors and inhibition procedures must be performed where high levels of chlorides are present.

9.3.1.5 Effect of Acetic Acid

Quite often organic acids are found in production fluids and low molecular acids like acetic acid have significant influence on CO_2 corrosion. Acetic acid is present as un-dissociated acid HAc or dissociated acetate ion Ac^-, and the extent of this is dependent on pH, such as, HAc %/Ac^- being 88.0/12.0 and 6.0/93.2 at pH 4.0 and 6.0, respectively [12]. The corrosion rate in presence of acetic acid is influenced by the un-dissociated HAc and therefore its effect is more pronounced at higher temperatures and low pH conditions. The effect of HAc in increasing corrosion rate and increase in sensitivity to 'mesa' attack has been attributed to the reduction in

protectiveness of the scale due to its instability [13]. A strong effect of velocity is also observed on the overall corrosion rate [14, 15].

9.3.1.6 Role of Oil–Water Ratio

It has been apparent from practical experience that under certain conditions CO_2 corrosion in the presence of crude oil is much lower. This is primarily related to the emulsification effect by which water is retained in oil as emulsion and does not wet the metal surface. Beyond a certain velocity the crude oil entrains up to certain percentage of water in oil/water mixture and thus fully protects the steel against corrosion. Based on the study by Efird [16] (Fig. 9.6), C. de Warrd and Lonz in their CO_2 corrosion model assumed no corrosion when the water cut is below 30% and liquid velocity is above 1 m/s [3]. Later, studies have shown that the critical velocity for entraining the water to eliminate the corrosion problem is influenced by number of factors as the conditions in a flowing mixture of water and oil gives rise to total, intermittent and zero wetting of metal surface. These three modes of flow have been found to be influenced by a number of factors like percentage of water cut, pipe diameter, interfacial tension, viscosity and density of oil [17, 18].

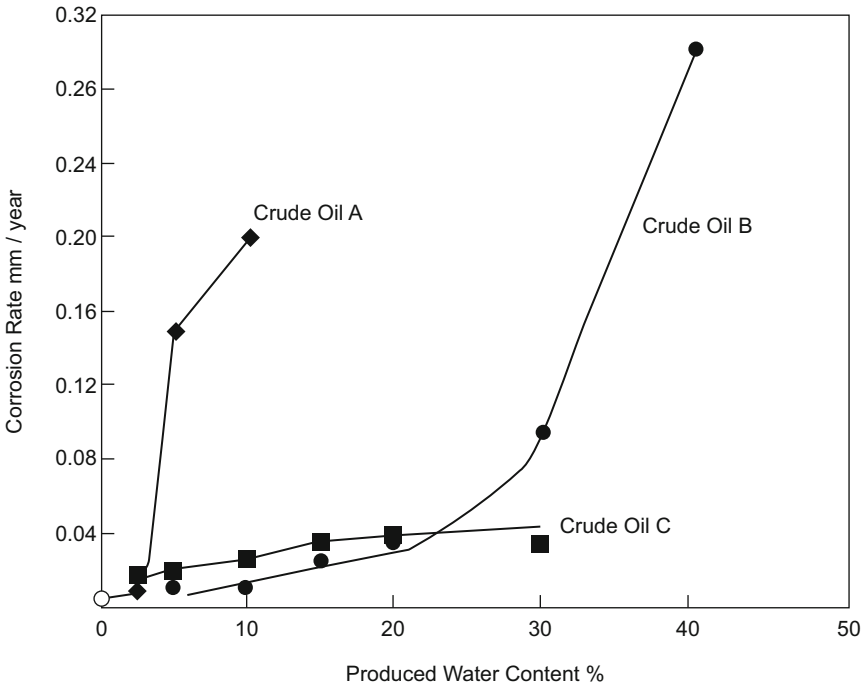


Fig. 9.6 Corrosion rate versus water content of produced water [16]

With higher water cut or lower velocity the metal surface is first intermittently and then continuously wetted, leading to significant corrosion. It has been experimentally established that the corrosion rate under intermittent wetted condition is half of that under continuously wetted state [19]. It was also found that the oil type has a significant effect on the transition from stable oil wetting to intermittent wetting and that much of the influence can be ascribed to the physical properties of the oil: density, viscosity and surface/interfacial tension. C de Waard's original model has been modified taking into account the role of different physical properties of the oil. It may be mentioned that the role of oil water ratio has however not been taken in all the CO_2 prediction models and where it has been considered there is no consistency of degree of influence. For example, in the Hydrocor model no corrosion is assumed at water cut below 40% and above 1.5 m/s liquid velocity [20]. On the other hand, Predict Model considers low corrosion rates below 50 and 5% water cut for highly persistent and non-persistent oils, respectively, while ECE Model assumes 40–50% water cut for heavy crude oils and close to zero for light condensate. This aspect has been discussed for various models under clause Sect. 9.3.3.

9.3.1.7 Elemental Sulphur

In some reservoir fluids, where H_2S content is high, elemental sulphur can be present. Sulphur acts as a strong oxidant and both carbon and low alloy steels and also many corrosion-resistant alloys are susceptible to pitting and cracking.

9.3.1.8 Mercury Corrosion

Presence of mercury in oil and gas is not common but its presence, both in elemental and organo-compound form, has been detected in some fields in Europe, South America, Africa, Indonesia, Malaysia, Brunei, etc. The quantity of mercury detected varies from 50 to 400 μg/m^3 in gas and 50–1200 μg/kg in liquid (oil or condensate) [21, 22]. The incidence of mercury corrosion in natural gas was first reported after a catastrophic failure of aluminium heat exchanger at Skikda, Algeria. Later, the gas separation plant at Map Ta Put in Thailand remained shut down for a period of 4 months because of corrosion damage of some parts due to mercury damage. The problem is considered of great concern in natural gas industry because many equipment are made of aluminium, especially the heat exchangers and aluminium is attacked by free or a mercury compound.

It is generally agreed that the mercury is present in gas in elemental form, but in condensate and petroleum liquids organo-mercury compounds are significant, and in some cases may also be the predominant one. Corrosion of aluminium by mercury occurs by process of amalgamation which, in turn, is readily attacked by water as shown in equations below:

$$Hg + Al \rightarrow AlHg \tag{9.3.4}$$

$$2AlHg + 6H_2O \rightarrow 2Al(OH)_3 + 2Hg + 3H_2 \tag{9.3.5}$$

Because of generation of Hg as a part of the reaction, the attack continues resulting in high rate of attack. Such amalgam does not form in case of iron and, therefore, Hg has a minor effect on corrosion of iron. Tests have shown that in Hg solution in cyclohexane at ambient temperature, the corrosion rate of iron was 0.5 mdd against 236.5 of that of aluminium [23]. The results further showed that:

- Dimethylmercury (DMM) in methanol or petroleum ether gave similar corrosion patterns to the elemental Hg solution.
- The attack was in general uniform on iron and localized on aluminium.
- Presence of trace amounts of HCl or H_2S further increase corrosivity of aluminium in DMM.

Prevention Against Mercury Corrosion

There are limited preventive methods available once mercury enters the system and the conditions become conducive to corrosion. Normally, whenever its presence is suspected, careful monitoring for mercury is carried out using analytical techniques. Considerable work is going on to find out a cost-effective method for removal of mercury. Such a method is useful where the mercury content is substantially high. One of the methods claimed to have been successfully used in case of fields having high level of mercury, is based on absorption.

9.3.1.9 Oxygen

Oxygen is normally not present in the formation layer but if present in quantity more than 10 ppb, heavy general and localized corrosion can occur in carbon steel and also sometimes CRAs. Oxygen has also a large role on pitting and stress corrosion cracking of iron base austenitic and duplex stainless steels. In the absence of oxygen the damages of this nature are highly reduced. However, as the oil and gas can get contaminated during production and processing either from leaking pump seals, casing and process vents, or use of inadequately deaerated seawater and produced water used for injection, this aspect should be given due weightage.

9.3.1.10 Microbial-Induced Corrosion (MIC)

Different organisms thrive on different nutrients including inorganic (e.g. sulphur, ammonia, H_2S) and organic (e.g. hydrocarbons, organic acids) substances. As many

of these are available in oil and gas bearing strata, biological activities can lead to corrosion, especially in the presence of sulphate reducing bacteria (SRB). Injection of chemicals to suppress MIC is provided against such corrosion.

9.3.1.11 Glycol/Methanol

Glycol and methanol in significant amounts are added to pipelines for prevention of hydrate formation in gas. Though much study has not been done it is believed that glycol/methanol has an inhibiting effect on corrosion because of dilution of the water phase.

9.3.1.12 Flow Rate

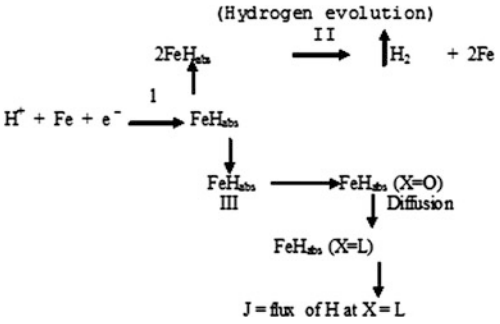
Well-produced fluids are in many cases liquid/gas multi-phase flow containing oil, gas and water. The distribution of these phases depends on the nature and quantity of each fluid, system geometry and hydrodynamic conditions. Under similar velocity conditions, the flow rate of gas will be higher than the liquid phase giving rise to different flow patterns like stratified, slug and annular, which have large influence on corrosion rate. Thus, corrosion rate increases beyond a certain velocity when shear stress due to flow exceeds the bond between the film and the metal concerned. In the presence of protective iron carbonate film, the effect of turbulent flow will be either to interfere with formation of surface film or increase in shear stress, leading to removal of protective film and subsequent increase in corrosion rate.

Quite often sand particles from the formation are also carried along with the production fluid. This results in erosive effect. In high-pressure wells, this is often controlled by deliberately limiting the fluid velocity to control the risk of sand production. Under such conditions and also in the case of depleted oil wells or young gas wells, shallow, wide and flat bottom pits, and grooves with steep sides (shallow pitting or 'mesa' type attack) are observed. The effect of this form of attack is less severe than intense localized pitting.

9.3.2 Embrittlement Effect of Hydrogen Sulphide

The major role of H_2S is not so much on corrosion, but its effect on inducing brittleness in not only carbon and low-alloy steels, but in many high-alloy steels including some nonferrous alloys. As a matter of fact, the role of H_2S was studied in detail since late 1940s and after Lacq gas field in France was discovered not because of corrosion but because of cracking of drilling and casings experienced in H_2S-containing wells. This type of attack is related to hydrogen atom produced as a result of corrosion. While under normal conditions these hydrogen atoms adsorbed

on metal surface recombine as molecular hydrogen, in the presence of H_2S, the recombination step is drastically inhibited and atomic hydrogen gets sufficient time to get absorbed in the metal. The steps described above are represented below:



The hydrogen produced as a result of corrosion process diffuses through steel and causes various kinds of damage which can be classified as:

- Delayed Cracking or Hydrogen Embrittlement (HE or HC)
- Sulphide Stress Corrosion Cracking (SSCC or SSC)
- Step-Oriented Hydrogen Induced Cracking (SOHIC)
- Hydrogen Induced Cracking (HIC) or Step Wise Hydrogen Induced Cracking (SWHIC)
- Blistering.

More than one type of failures can occur in a material during service. Figure 9.7 shows hydrogen blister with SWHIC at the edge of the blister in a caustic wash vessel studied by the author.



Fig. 9.7 Shows **a**: Blister in caustic LPG wash vessel. Indication of SWHIC at edge of blister and **b**: A typical HIC macro-crack

9.3.2.1 Controlling Hydrogen Related Damage

SSSC and SOHIC

These types of failures are related to strength of material; the higher the strength, the greater the susceptibility. Ultra-high strength materials can fail even during atmospheric corrosion (in the absence of poison) due to small amounts of hydrogen produced at cathodic sites. Alloys having bcc structures are more prone to failure than fcc structure. In practice, SSCC is controlled by limiting the hardness (an indirect indication of strength) of the base metal and also welds. NACE issued in 1975 detail guideline MR-0175 [24] for selection of various ferrous and nonferrous alloys for resistance to SSCC in oil and gas production. However this standard has now been replaced with MR 0175/ISO/15156, combining the ISO & NACE approaches [25]. Here sour service has been defined as "If the partial pressure of H_2S is equal to or greater than 0.05 psi (0.3 kPa)". This standard is divided into three parts;

Part 1 General principles for selecting cracking-resistant materials
Part 2 Cracking-resistant carbon and low-alloy steels
Part 3 Cracking-resistant corrosion-resistant alloys (CRA) and other alloys.

As severity varies with increasing H_2S partial pressure, MR0175/ISO15156 also gives three regions of environmental severity with respect to carbon and low alloy steels (Fig. 9.8) [26]. The classification of severity was not part of the original NACE MR0175

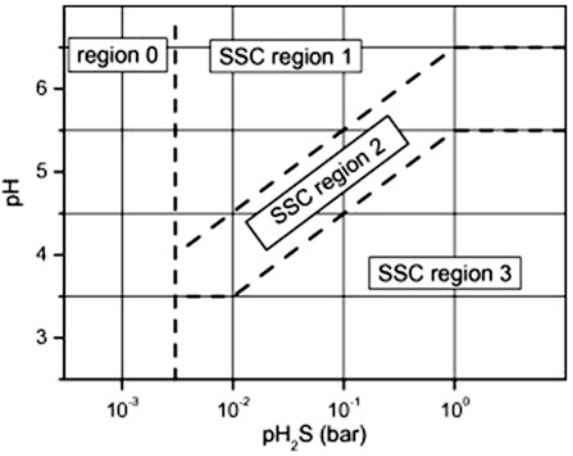


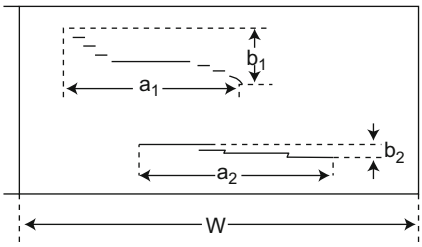
Fig. 9.8 Regions of different severity with respect to SSCC of carbon and low-alloy steels [26]

Blistering and HIC

These are connected with the nature, type and extent of inclusions in material and independent of material strength. For carbon or low-alloy steel plates, sulphur content of the steel is brought down to 0.005–0.002% against normally specified 0.04% max. Further, calcium treatment is carried out to change the shape of sulphide inclusion, from elongated to round one. Such a control markedly improves resistance to HIC. HIC resistance is evaluated by NACE TM0184-2011 in test solution of pH 5.0 and the result is expressed as sensitivity ratio (CSR), thickness ratio (CTR) and length ratio (CLR) as shown in Fig. 9.9. Where conditions are more severe, the test solution is replaced with that of NACE TM01-77 having pH of 3.0. For practical purpose CLR values are used as acceptance criteria. The recent trend, depending on severity, is to specify pH 3.0 with CLR acceptance criteria, of 15, 10 or 5%.

To summarize, for sour service the requirements to prevent hydrogen damage is use of clean low sulphur steel ultrasonically examined for internal defects like laminations as per SA-578 level1, including supplementary requirement S1 (100% scanning). Additionally:

1. For carbon and low-alloy steels
   For SSC—Hardness control of Rc22 maximum, with CE of $\leq$0.43% for carbon steel
   For HIC—Clean and extra low sulphur ($\leq$0.002%), sulphide shape (spherical)-controlled steel, CLR >5% for critical service
   For Blistering—Clean steel ultrasonically examined for internal defects like laminations as per SA578 level 1, including supplementary requirement S1 (100% scanning).
2. For corrosion-resistant alloys (CRA) the main consideration is the resistance to SSCC. For this both maximum H_2S partial pressure and maximum hardness limits are to be met as per Part 3 of MR0175/ISO15156.



$$\text{Sensitivity Ratio (CSR)} = \frac{\sum a + b}{W \,.\, T} .100\%$$

$$\text{Length Ratio (CLR)} = \frac{\sum a}{W} .100\%$$

$$\text{Thickness Ratio (CTR)} = \frac{\sum b}{T} .100\%$$

Fig. 9.9 Evaluation of HIC susceptibility after NACE test

9.3.3 Development of CO_2 Corrosion Model

9.3.3.1 CO_2 Corrosion in Multi-phase System

As a corrodent, CO_2 has a much bigger role than H_2S. Subsequent to the development of first Nomogram by de Waard et al. [3], in-depth studies on the influence of the various parameters were initiated in many companies and research institutions. The main objective shifted since late 1980s to develop prediction models for CO_2 corrosion, which can form the basis for material selection. As a result of these studies, a number of computer models have been developed, some of which also incorporate inputs of field experience.

The prediction models may be categorized as either being mechanistic or empirical/semi empirical:

- A mechanistic model takes into account the chemical, electrochemical and transport processes while,
- An empirical model starts with some simple empirical correlations followed by inputs of practical experience.

Application of various models to a particular situation unfortunately did not give the actual measured corrosion rates. For a more comprehensive study on CO_2 corrosion models, The Institute of Energy Technology (IFE), Norway undertook Joint Industrial Project with the participation of companies in Europe and USA. The objective was to compare the predicted corrosion with actual corrosion rates and establish, if possible, a system where the corrosion prediction models would help the corrosion engineers to make decisions for the design of oil and gas production and treatment facilities. Sixteen models, such as, de Waard, NORSOK (Statoil, Saga, Hydro), HYDROCOR (Shell), CORPLUS (Total), Predict (InterCorr), MULTICORP (Ohio University), etc. were included in the study. In this project, field data with actual corrosion measurements were gathered from the participating oil companies. The different available CO_2 corrosion prediction models were evaluated by performing sensitivity studies, running the different corrosion models for a set of the field cases. On comparing both predicted corrosion rates actual results large variations were obtained in many cases. However, at the end of the study application limits and strong and weak points of each model could be identified. Though both mechanistic and empirical models use laboratory testing and field data (though to different extent) different models have a different approach as to how the various mechanisms and parameters are treated or given weightage as shown in Table 9.3 [27]. As would be evident from Table 9.3, the role of different parameters is not only not given similar weightage in all models but completely neglected in some. Of these, the influence of protective corrosion films and oil wetting is believed to be the reason for large differences observed in the prediction of corrosion rate by different models [27, 28]. Thus, for wide range of conditions there may be accuracy of ±50% [28].

Table 9.3 Important factors in CO_2 different corrosion prediction models①

Model	DW	NO	HY	CO	CA	KS	MU	EC	PR	TU	UL	CP	OL	SW
Lab data, field data model, mechanistic model	L	L	M	F	L	M	M	L	L	M	F	L	M	L
Scale effect formation water[a]	N	M	N	W	W	M	M	W	S	S		M	W	W
Scale effect condensed water[a]	W	M	W	W	W	M	M	W	S	S		M	W	W
Effect of pH on corrosion rate[a]	W	M	W	M	W	M	M	W	S	S	S	M	W	W
Risk for localized attack				Y		Y			Y		Y			
Oil wetting effect crude oil[a]	S	N	M	M	N	N	S	S	S	N	S	M	N	N
Oil wetting effect condensate[a]	N	N	N	M	N	N	M	M	M	N	S	M	N	N
$CaCO_3$ correction for pH				Y			Y						Y	
Effect of organic acid on corrosion			Y	Y	Y		Y	Y	Y		Y			
Top of line corrosion	Y		Y				Y	Y			Y			
Effect of H_2S on corrosion rate[a]	N	N	W	N	N	N	M	S	S	N	W	N	S	N
Multi-phase flow calculation[b]	N	P	M	P	N	N	P	M	P	P	M	M	N	N
Max. temperature limit °C	140	150	150	150	140	150	100	140		115		150	120	120
Max. CO_2 partial pressure bar	10	10	20	20	10	20	20	20	70	17		10	20	
Open, commercial, proprietary	O	O	P	O	O	O	P	C	C	P	P	P	C	P

[a]*S* Strong effect, *M* Moderate effect, *w* Weak effect, *N* No effect

[b]*P* Point calculation, *M* Multi-phase profile calculation, *N* No multi-phase flow calculation

①Name of models: *DW* De Warrd, *NO* NORSOK—506, *HY* Hydrocor, *CO* Corplus, *CA* Cassandra, *KS* KSC, *MU* Multicorp, *EC* ECE, *PR* Predict, *TU* Tulsa, *UL* ULL, *CP* CorPos, *OL* OLI, *SW* SweetCor

Based on the study IFE has brought out guidelines for estimating CO_2 corrosion for use in design and engineering practice [29]. The document is sufficiently flexible and sets minimum guidelines which can be used by any designer. The document points out that the major problem is that during design stage availability of input data is limited or based on a few samples, which may not tally with actual operating parameters. The predicted corrosion rates in design phase have, therefore, been categorized on the basis of severity level and not as actual corrosion rate as given below:

Severity level	Unmitigated[a] corrosion rate (mm/year)
1	<0.01
2	0.01–0.10
3	0.10–1.0
4	1.0
5	>10.0

[a]Free of any chemical inhibition

It has been stated in the report that the severity level should be determined in two steps; first, when limited data are available and second, when maximum data are available. The first should be used for preliminary and the second involving rigorous analysis for the final design. Some of the parameters to be used for the two stages, given in the guidelines are given in Table 9.4. To find the position within the severity range for a given corrosion prediction, the severity index can be calculated.

9.3.3.2 Corrosion in Gaseous Phase

Gathering lines, separators, and gas handling system in the oil and gas production handle multi-phase system (oil/condensate; produced water; and gas-containing CO_2) where corrosion occurs both in the liquid and gaseous phases. In the gas phase, which is not in contact with water, corrosion can occur only if there is condensation of water and therefore the controlling factors in this section are quite different. From the point of view of corrosion, the condition existing on pipe wall having stratified flow can be divided into broadly two parts as shown in Fig. 9.10:

1. Bottom portion up to the liquid level, where corrosion is due to acidic gases dissolved in water, can be minimized by inhibitor addition.
2. Portion above the liquid level, where corrosion occurs in the presence of thin film of water condensed on metal surface. This part, unlike the bottom portion, does not get the protective effect of oil, bicarbonate and any inhibitor added.

The gas portion of the metal surface can be subdivided into two, that is, top and sidewall where the condensed water drains to the bottom. The nature of corrosion in the bottom and side wall is uniform but that in the top section suffers localized

Table 9.4 Parameters to be used in each step for the evaluation of severity level

Factors to be considered	Input parameters	Notes
Step I		
CO_2	P_{Total}; $\%CO_2$; $f_{CO_2} = a$; P_{CO_2}	(1)
CO_2/H_2S ratio	$P_{CO_2}/P_{H_2S} = > 500-1000$	
Temperature	T	
Calculated pH	HCO_3; P_{CO_2}/P_{H_2S}; total organic acidic species	(2), (3)
Prediction model	P_{CO_2}; T; pH	(4)
Step II		
Protectiveness of film	T; P_{CO_2}; and pH for $FeCO_3$ film	(6)
Flow factors	Flow regime and velocity	(7)
Type of corrosion	General or pitting	
Wetting effect	Oil/water wetting properties	
Organic acids impact	Total organic acid species; pH (impact on the protectiveness)	(8)
pH effect	Total organic acid species; consistency check of formation water	(3), (9)
Prediction model	Operator defined	(4)

Notes

1. If model allows the use of fugacity of CO_2, this should be used rather than partial pressure of CO_2. Fugacity coefficient is available in literature
2. The effect of acetate is limited to impact of acetate on calculated pH. There is no further adjustment on the predicted corrosion rate in Step 1
3. Default values of acetic acid are given in Appendix 2
4. Any model evaluated for this purpose. A brief description for some of the models is given in Appendix 1
5. Level II corrosion prediction assessments carry a varying degree of complexity and are Principal and situation specific. Some of the parameters situation and references are provided for information only and their use should be reviewed by Principals Subject Matter Expert
6. Any model having the required module (see Appendix 1)
7. Any model having the required module (see Appendix 1) or dedicated flow models
8. HAc is amount of non-dissociated acetic acid (i.e. non-dissociated part of total acetates
9. Check formation water chemistry for electro neutrality, the differentiation between, HCO_3^-, acetate and alkalinity, calcium carbonate saturation under reservoir condition. Values may have to be adjusted if they do not make sense, which may affect the pH

(The Appendix mentioned in the notes is part of the original Table and not the manuscript)

attack [30]. However, in the presence of acetic acid the nature of corrosion changes with uniform corrosion at the top of the line and localized corrosion at the bottom [31].

Factors which control corrosion in the gas phase mentioned above are not only important to explain the multi-phase flow, but also the in the handling of wet gas and the well-known top of line corrosion (TLC). Due to the presence of water in the system, the gas is in saturated condition and, therefore, condensation of water shall occur if there is any drop in the temperature. The important point here is that condensation is not related to the drop in system temperature (bulk temperature of the flowing medium) but that of the metal wall temperature. Drop in the internal

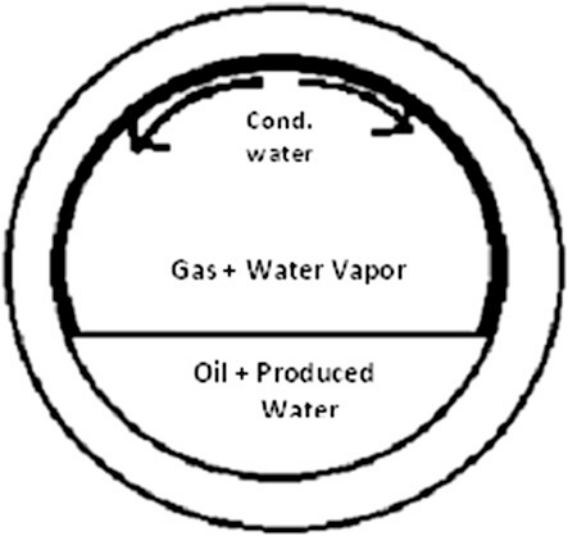


Fig. 9.10 Corrosion in gaseous phase due to condensation of water

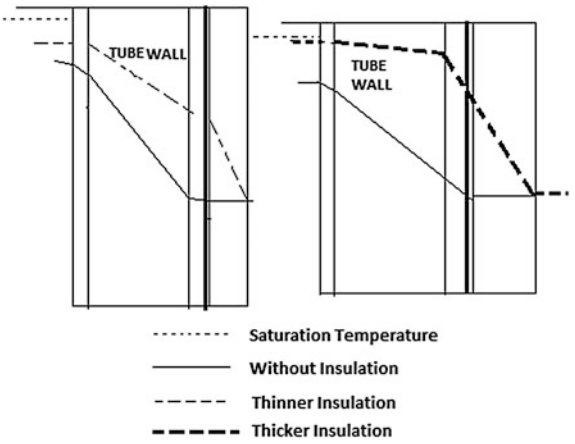


Fig. 9.11 Effect of insulation in suppression of inner tube wall below dew point

metal wall temperature, on the other hand, is related to the cooling effect from the external surface (OD) and there are various parameters which influence this and corrosion rate in a complicated way. Some of the important parameters which would control the condensation and its rate are:

- Temperature difference between internal and external surfaces. This would vary depending on climatic conditions, geographic location, underground or offshore line and shallow or deep water.
- Presence or absence of insulation. Figure 9.11 illustrates how efficiency of insulation affects the extent of drop in temperature below the dew point. This analogy is applicable for item 1 (difference in temperature) also.
- System temperature/pressure/CO_2 partial pressure.

- Nature of medium, that is gas or liquid and their heat capacity.
- Mass and velocity of flow on inside and outside surface.
- Increase in difference between the dew point and ID wall temperature which would increase condensation rate.

Once the condensation occurs, the process of corrosion starts which involve number of steps which control corrosion rate. The condensed water is pure and once CO_2 is dissolved, the water becomes acidic (having typical pH of <4) and this results in the initiation of corrosion. Corrosion results in increase in solution pH and enrichment of the corrosion product iron carbonate, takes place in thin layer of electrolyte. Once saturation is reached, iron carbonate tends to precipitate and form a protective film which helps in reducing corrosion. The protection afforded depends on temperature and rate of condensation.

(1) At low rate of condensation there is marginal effect on renewal of water film which flows down slowly. Under this condition if the temperature is low, the process of precipitation is very slow and scales obtained are not sufficiently protective even under high super saturation condition.
(2) Conversely under low condensation rate, at high temperatures (e.g. >60 °C) increase in corrosion rate hastens super saturation of the thin film and precipitation of carbonate film proceeds rapidly and dense and very protective scales are formed even at low super saturation. Thus while initial corrosion rate is high the rate decreases with time [7].
(3) At high condensation rates the situation changes. Because of continuous condensation, saturation of iron carbonate in film is not reached and high rate of corrosion of several mm/year can be experienced. Thus, the corrosion rate under such a condition is governed by the two opposite effects of the rate of the corrosive reaction (increase in iron in the film) and the rate of condensation (diluting effect of condensing water).

Studies have been conducted to find out the role of various parameters to determine corrosion rates in the gaseous phase. The Shell model takes into account the condensation factor (Fcond) to determine CO_2 corrosion. The factor vaies from 1.0 to 0.1 at high and low condensation rates of 2.5 and 0.25 g/m^{2}s respectively [32]. These factors can be used to determine corrosion rate in the gas phase.

9.4 Material Selection and Corrosion Control for Gas and Oil Wells

The first step in oil and gas production is called *exploration,* which includes all activities connected with drilling, casing, introducing production tubing, pumping facilities, internals and the well head choke or T. Corrosion resistance and strength of material are two important considerations in case of wells. The major corrosion

problem experienced in these systems, based on which material selection is made can be summarized as follows:

1. General and pitting corrosion due to presence of CO_2, H_2S, and chlorides in formation water,
2. Localized corrosion due to breakdown of protective film, condensation of water in gas wells, exposure to soil, etc.,
3. Hydrogen damage like SSCC, HIC and blistering in case of sour conditions.

These are related to either process side conditions or external environment. Consideration is also to be given to increased severity faced with depletion of well (resulting in high water cut) and appearance of H_2S with ageing and use of secondary recovery operations which may involve injection of formation water, sea water, CO_2, etc.

9.4.1 Well Completion

Once the viability is established the well is 'completed' to enable the flow of oil and gas out of the formation to the surface. There are some special requirements which oil and gas wells are to fulfil. These are:

- Prevention of collapse of the well hole by strengthening its side.
- Prevention of seepage of oil and gas out of the well hole,
- Prevention of any other fluid or gas to enter into the formation.

For this purpose, various steps are needed before the well starts operating. Completion of well involves installing the well casing, tubing and the wellhead components. The tubular drilling, casing and tubing are seamless tubes which in the oil and gas industry are known as OCTG (oil country tubular goods). If the well is not free flowing, then it is also necessary to install lifting equipment. Broadly the process consists of drilling of a shallow 20′–30′ deep well (15–20″ diameter in onshore and 30–52″ in offshore) to which a metal pipe, called *casing*, is cemented. Depending on the depth and the nature of soil, several deeper casings of progressively smaller diameter are placed and cemented as shown in Fig. 9.12. External pressure acting on the casings is directly proportional to the depth of the well. Hence, strength of material used for casing increases with the depth of the well. These materials are covered under various API grades of carbon and low alloy steels (Table 9.5) [33]. Steels with yield strengths below 620 MPa (90,000 psi) generally will not fail in sour environment but when required, deleterious effect of high strength can be compensated in some case by increasing the thickness of lower strength material or by using high strength SSCC resistance casing such as API L-80 and C-90. Once the casing is completed, production tube is installed through which petroleum products flow from formation to the surface. This is followed by well completion and placing of packer. Well head components like casing head and

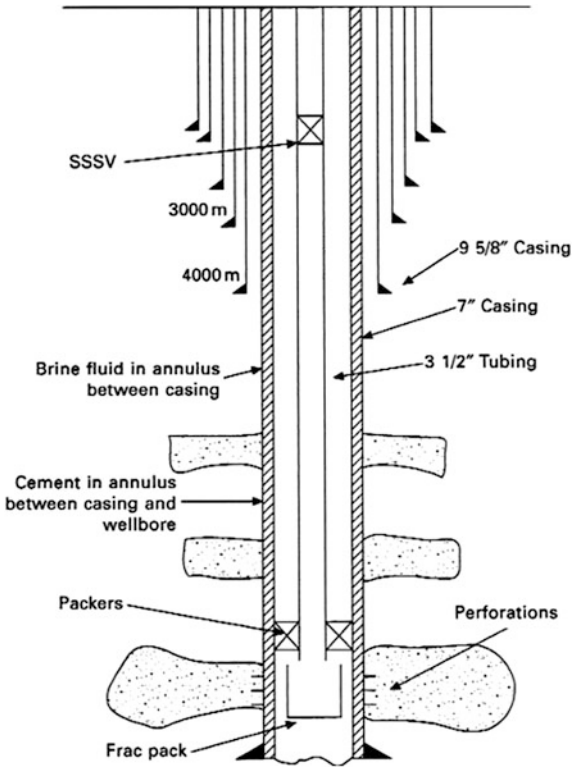


Fig. 9.12 Wells having casings with successively reduced diameters

Table 9.5 Oil country tubular good (OCTG) carbon steel and lowalloy grades

% Alloy content									
Yield strength (ksi)	API grade code	C	Mn	Ni	Cr	Mo	Cu	Yield strength (0.2% proof stress) (N/mm^2)	Tensile strength min (N/mm^2)
40	H40	0.5	1.5					276–552	410
55	K55	0.5	1.5					379–552	655
75	C75-1	0.5	1.7	0.5	0.5	0.40	0.5	517–620	665
90	C90-1	0.35	1.9	0.9	1.2	0.75		620–724	690
95	T95-1	0.35	1.2	0.9	1.5	0.85		655–758	724
125	Q125	0.35	1	0.9	1.2	0.75		860–1035	930
140	H40	0.3	1	0.5	1.6	1.1	0.05	965–1171	1034

tubing head, are then installed at the opening of the well. These prevent leakage of well product and prevent blowouts. To control the flow of well fluids valve is then fitted on the top of the casing and tubing heads. The system has special construction with many branches containing tubes and valves and resembles a tree and therefore called ‘Christmas tree’. In ‘Christmas tree’, corrosion erosion condition exists and,

therefore, fluid exposed surfaces are lined with erosion–corrosion-resistant lining. Smaller internal components are of solid erosion-corrosion-resistant alloy. If the springs, which have higher strength and hardness, do not meet the requirements of MR0175/ISO15156, these should be made of cobalt or nickel base alloys.

In offshore wells, the well head components and Christmas tree are on well platform but in case of ultra-deep and some deep waters, the well head components are on sea floor, the operation is controlled from FPSO. There are almost no possibilities of undertaking any maintenance job at these locations and therefore these should not only be of highest quality but also high corrosion resistant to last the working life of the well. These are also required to be externally protected by good coating and cathodic protection. Where naturally good flow of products from the formation does not occur, arrangements for lifting (pumping) is to be made. In case of onshore oil wells it is common to use rod pumping, where cable and rod are moved up and down using 'horse head' or conventional beam pump to get oil from the formation.

9.4.2 Corrosion Control in Oil and Gas Wells

9.4.2.1 Casing

The casing is protected internally against corrosion by cementing and drilling mud left behind. As inhibitor is used in the mud during drilling, the same also acts as protective agent during the lifetime of the well. As regards external surface of the casing, cathodic protection has been successfully used in many onshore fields. Its performance in deep wells is not likely to be as effective as in case of shallow wells. As the anode bed is placed on the ground level (Fig. 9.13), the throw of current shall not be to the desired extent. NACE standard RP-01-86 [34] describes different

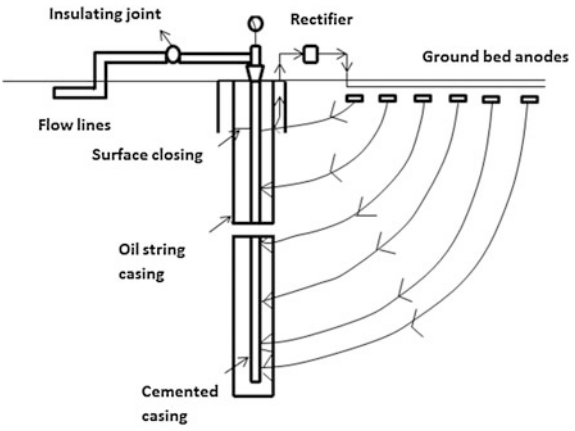


Fig. 9.13 Cathodic protection of well casing against soil side corrosion

methods for designing and monitoring cathodic protection systems for well casings. Of these potential profile survey is the only technique in which the flow of protection current at depth can be confirmed.

9.4.2.2 Production Tubing

As regards production tubing, the material selected would depend on corrosivity of the fluid. Commonly used rule of thumb methods for corrosion control are:

- Carbon steel in case of low water cut and no CO_2,
- Use of carbon steel with inhibitors (if corrosion rate can be brought down to about 0.1–0.15 mm per year),
- Use of corrosion-resistant alloy if corrosion rate is higher.

Protection by Inhibitors

The present-day practice to evaluate inhibited corrosion rate is based on inhibitor availability, which is considered as the time the inhibitor is present in the system at a concentration at or above the minimum dosage. To quote NORSOK Standard M-001 [35], corrosion allowance (CA) should be based on the percentage availability (A%), which can be calculated as follows:

$$\mathrm{A}\% = 100 \times (\text{inhibitor available time})/(\text{lifetime})$$

$$(\mathrm{CA}) = (\text{the inhibited corrosion allowance}) + (\text{the uninhibited corrosion allowance})$$

$$\mathrm{CA} = (\mathrm{CRin} \times \mathrm{A}\%/100 \times \text{lifetime}) + (\mathrm{CRun} \times \{1 - \mathrm{A}\%/100\}\text{lifetime}),$$

where

CRin inhibited corrosion rate and
CRun uninhibited corrosion rate.

The inhibitor availability to be used in a design calculation depends on the planned corrosion management program, including corrosion monitoring and corrosion inhibition. According to NORSOK M-001, unless defined otherwise, an inhibitor availability of 90% shall be used and maximum inhibitor availability shall not exceed 95%. 95% inhibitor availability requires that a qualified inhibitor is injected from day one and that a corrosion management system is in place to actively monitor corrosion and inhibitor injection. Inhibitors are being used in oil and gas industries to control oil well corrosion of carbon steel for more than a century and even today it plays a major role.

The effectiveness of inhibitor cannot be predicted with confidence and before selection their performance should be evaluated to assess their effectiveness under

the conditions these will be used. Various test procedures are available as indicated below:

1. NACE Publication ID196 (latest revision), "Laboratory Test Methods for Evaluating Oilfield Corrosion Inhibitors"
2. ASTM G 170.01a (latest revision), "Evaluating and Qualifying Oilfield and Refinery Corrosion Inhibitors in the Laboratory"
3. ASTM G 184 (latest revision), "Standard Practice for Evaluating and Qualifying Oil Field and Corrosion Inhibitors Using Rotating Cage"
4. ASTM G 185 (latest revision), "Standard Practice for Evaluating and Qualifying Oil Field and Corrosion Inhibitors Using the Rotating Cylinder Electrode".

Application of Inhibitors

For down hole tubular, the following methods are commonly used:

- *Batch Inhibition*: Inhibitor is added in the flow system periodically by displacing the fluids in the well bore with the inhibitor and its carrier. A strongly persistent filming inhibitor is usually used. However, use of this technique is limited where high temperature >120 °C (>250 °F) and high flow rates exist.
- *Squeeze Treatment*: Squeeze treatments are modifications of batch inhibition. Instead of just displacing the tubing with inhibitor and its carrier fluid, the squeeze treatment also forces the fluid under pressure into the surrounding formation. This has the benefit of extending the duration between batch treatments. However, in other cases, squeeze treatments can also interfere with the well's production by plugging the formation.
- *Continuous Inhibition*: In this case, the inhibitor is continuously injected into the tubing at bottom of the string or through a subsurface injection valve. The rate of injection is regulated to provide the inhibitor at a required concentration to mitigate corrosion. While more costly and requiring more equipment than batch inhibition, continuous inhibition has been shown to be more effective particularly in deeper high temperature wells and in more severe corrosive conditions. At high flow rates, continuous inhibitor injection may become costly and possibly ineffective. One advantage of this method is that the functioning of inhibitor persists on ground facilities also.

Use of Corrosion-Resistant Alloys

If design life cannot be obtained with inhibitor addition, then a suitable grade of corrosion-resistant alloy (CRA) will have to be used. Intensive studies carried out since early 1980s have shown that increasing chromium increases resistance to CO_2 corrosion. Based on various studies 9% Cr and 13% Cr (API Gr) and 13% Cr super martensitic stainless steels (SMSS) have been developed and accepted by industry.

Table 9.6 Iron chromium alloy oil country tubular good (OCTG) steels

API grade	C	Mn	Ni	Cr	Mo	Cu	YS (0.2% proof stress) (MPa)	UTS min (MPa)
9% chromium alloy steel								
L80-9 Cr	0.15	0.6	0.5	9	1	0.25	552–655	665
13% chromium stainless steel								
L80-13 Cr	0.22	0.6	0.5	13		0.25	552–655	655
SMSS-1	0.04 max	0.6	4	13	1.5		655–758	724
SMSS-2	0.04 max	0.6	5	13	2.5		758–896	827

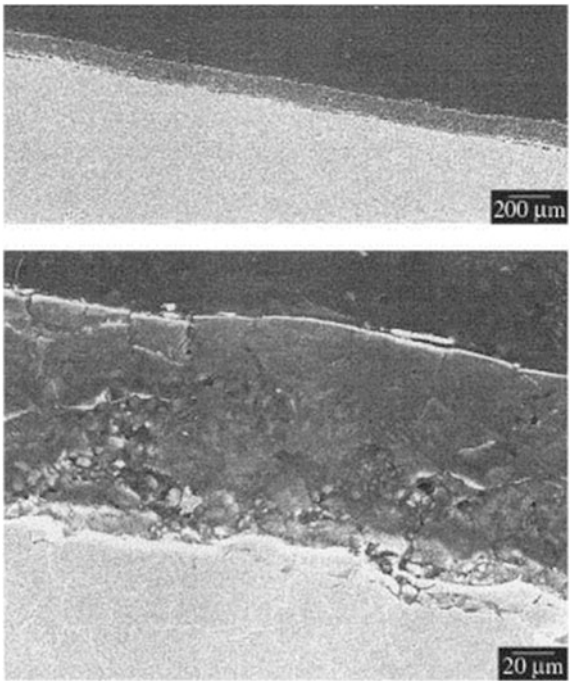


Fig. 9.14 SEM image of dense protective film in 3%Cr containing steel at two magnifications [36]

These are being used for down hole tubing (Table 9.6). As regards gathering lines, 13 Cr Super Martensitic Stainless Steel (SMSS) is the first choice for CRA against CO_2 corrosion. Studies conducted have shown that in low carbon steels good resistance to CO_2 corrosion can be achieved even with as low as low as 3% Cr containing alloy. The beneficial effect of chromium is believed to be due to replacement of $FeCO_3$ film with more protective Cr^{3+}–OH film. In the Joint industry sponsored study the role of chromium was found to be formation of an adherent and defect free protective film even in the presence of 3%Cr in steel as shown in Fig. 9.14 [36]. The behaviour of chromium-containing alloy in CO_2

Table 9.7 Corrosion-resistant alloys for oil and gas production and processing

Group	Alloy (common name)	Nominal composition, wt%
Martensitic stainless steel	410, 420 (13 Cr)	12 Cr
Super martensitic stainless steels	Super/hyper 13 Cr	12–13 Cr, 4–5 Ni, 1–2 Mo
Duplex stainless steels	2205	22 Cr, 6 Ni, 3 Mo
Super-duplex stainless steels	2507, DP3W	25 Cr, 7 Ni, 3.5 Mo, N, W
Nickel base alloys	825, 2242	22 Cr, 42 Ni, 3 Mo
	2550	25 Cr, 50 Ni, 8 Mo, 2 W, 1 Cu
	G50	20 Cr, 52 Ni, 9 Mo
	C276	15Cr, 65Ni, 16Mo, 4W
	718	20 Cr, 52 Ni, 3 Mo, 5 Cb, 1 Ti, 0.6 Al
	925	21 Cr, 42 Ni, 3 Mo, 2 Ti, 2 Cu, 0.4 Al
	725	20 Cr, 57 Ni, 8 Mo, 3 Cb, 1.5 Ti
Titanium alloys	Grade 5 (Ti-6-4)	6 Al, 4 V
	Ti-6-2-4-6	6 Al, 2 Sn, 4 Zr, 6 Mo
	Grade 19 (Beta C)	3 Al, 8 V, 6 Cr, 4 Zr, 4 Mo

environment is found to be similar to carbon steel with decrease in corrosion rate above certain temperature. However, the temperature at which maximum corrosion occurs progressively increases from ~80 °C for carbon steel to ~225 °C in alloy containing 13% Cr.

With increase in CO_2 partial pressure it becomes necessary to switch over to higher grades of CRA. While austenitic stainless steels have good resistance to CO_2 corrosion, these are liable to suffer chloride stress corrosion cracking and pitting in case of ingress of oxygen in the system. From this point, different grades of duplex stainless steels are preferred. If the conditions are extremely severe and if H_2S is also present then one has to use higher alloys, including nickel-based alloys.

In case of deep and ultra-deep wells one has to additionally consider the strength of alloys, as the casings are not only required to sustain very high internal pressures but also tension loads and collapse pressures. In future, explorations to higher depths are being planned where bottom hole conditions of Extreme HPHT and Ultra HPHT (>204 °C and >138 MPa) will be experienced. The problems involved in case of these wells have been discussed in detail by Bruce Craig [37]. Of the various CRAs (Table 9.7), nickel and titanium-based alloys have also been suggested as candidate materials. There are concerns about the possibilities of the high alloy stainless steels and nickel alloys losing toughness over 20–30 years of exposure at temperatures in excess of 204 °C due to the precipitation of sigma, mu and laves phase. This is due to the fact that temperature versus time relation for the transformation of these phases follows 'C' curves and their formation at lower temperatures will take long time for which no data are available for temperatures

expected in deep wells. Any long-term adverse effect on mechanical properties of these alloys becomes a matter of uncertainty.

9.5 Material Selection and Corrosion Control of Gathering Lines

Gathering lines connect the different wells to a central location which can be either a receiving station or processing station. In case of lift wells, the pressure and temperatures are not high. Being downstream of 'Christmas tree' in free-flowing wells, the pressure is much lower than in the production tubing though there is not much decrease in temperature. In both cases, however, the fluid composition in production tubing and flow lines remains the same. In other words, we can say that corrosive condition in flow lines is milder compared to the well conditions. Considerations in material selection and corrosion for flow lines are similar to the well production tubing. The various alternatives are:

(a) Use of carbon steel with inhibitor,
(b) Use of corrosion-resistant alloys (commonly grouped as CRA),
(c) Use of internal coating and
(d) Coating and cathodic protection for external protection.

9.5.1 Application of Inhibitor in Flow Lines

For flow lines, inhibitor is added using the following procedures.

9.5.1.1 Continuous Inhibition

Inhibitor is continuously injected into the flow stream. This may be applied in both down hole and surface production systems. This method is preferred where the flow velocity is greater than 10 ft/s (3 m/s) or where the amount of water is high.

9.5.1.2 Batch Inhibition

Inhibitor is added in the flow system periodically in batch treatments between two pigs. A strongly persistent filming inhibitor is usually used which can reduce corrosion rates effectively during the period between batch treatments. This technique is more effective where the velocity is not high and used as supplement to other inhibition techniques.

9.5.1.3 Pigging

For cleaning, application of inhibitor, gauging of diameter and inspection of pipeline, a vehicle is propelled through it using the pressure of the flow of the product. This vehicle is known in oil and gas industry as 'pig' and the process 'pigging'. The advantage of pigging is that long lengths of pipe can be covered without stopping pumping of the product. Inhibitor for corrosion control of pipeline is also applied using pig. Further, as flow lines are horizontally laid there is likelihood of solids settling down especially where flow velocity is low. In some cases stratified flow also can occur and, most importantly, when a well is temporarily shut down, water can settle at low points. All these conditions can reduce inhibitor efficiency and also cause under deposit corrosion leading to leakage which is not only hazardous but cause environmental damage. To avoid this, pipes are also periodically cleaned by pigging to remove water and deposits from the bottom of the pipe.

9.5.2 Use of Corrosion-Resistant Alloys

Corrosion-resistant alloys (CRA) in case of flow lines are used as solid pipes though in the recent years use of clad pipe is increasing because better reliability and comparatively lower cost have been attained with the introduction of advance techniques.

9.5.2.1 Solid CRA

In addition to the limit to which corrosion can be controlled by inhibitor addition, there is increase in operating cost and close control on operation of the system to meet the require % inhibitor availability. One has, therefore, to consider the use of CRA at some stage in spite of higher investment. This is especially important in offshore operation where it is difficult to ensure the required degree of inhibitor availability from isolated unmanned oil wells. If life-cycle cost is considered, then use of CRA can be justified. In this connection, an alloy, modified 12 Cr super ferritic stainless steel (Table 9.7), has become quite popular for gathering lines in the recent years. The alloy having composition of 0.01C–12Cr–5Ni–2Mo–0.01N has good strength, good resistance to CO_2 attack and SSCC resistance in H_2S partial pressure of 10 kPa (1.5 psi). In addition, the alloy has good weldability requiring no pre or post weld heat treatment. The preferred welding processes for 12–13% are automatic pulsed gas metal arc (PGMA) and gas tungsten arc welding (GTAW) [38]. Matching consumables have been developed, but have not proved to be successful for large scale use. For lower strength grades, nickel alloy fillers or 22%Cr duplex stainless steel can be used. Brief PWHT, e.g. at 650 °C for five

Table 9.8 Rough cost factors of stainless steels relative to carbon steel based on 1992 prices

Material	Cost factors on weight basis	Cost factors on strength basis
Carbon steel	1	1
13%Cr (AISI 420)	2	1.8
Mo-free duplex	4	4
Stainless (316L)	4–6	9–14
22%Cr—duplex	6–8	6–8
25%Cr—super-duplex	9–11	7–9
Stainless steel (254SMo)	10–12	15–18

minutes, to prevent intergranular corrosion of HAZ that are exposed to hot acidic fluids, is advisable.

Where conditions are more severe, especially in the presence of H_2S, the metallurgy is required to be further upgraded and 22Cr DSS/25Cr SDSS for lightly sour (NACE MR0175/ISO 15156) conditions and Alloy 825, Alloy 625, Alloy C276, etc., for highly sour conditions need to be considered. Increasing numbers of fields that are being explored and developed these days cannot be made operative without the use of CRA materials. An idea about the cost factor can be had from 1992 data given in Table 9.8 [32]. The data is only comparative because the cost depends on a number of factors and is not likely to be applicable in 2012. However, the extra cost to some extent is compensated due to reduction in recurring expense of inhibitor, reduced maintenance cost and life-cycle cost [39]. Further cost reduction can be achieved by using CRA-lined/clad carbon or alloy steel piping instead of solid alloys. One other advantage of clad pipe is that stainless steels, which are susceptible to CSCC, can in many cases be used as cladding in the presence of chloride.

9.5.2.2 Clad Corrosion-Resistant Alloy (CRA) Pipeline

The transportation of highly aggressive crude oil and gas by inhibited carbon steel line is quite often not justified. In such cases it becomes necessary to look for an alternative and that is selection of a suitable corrosion-resistant alloy (CRA). In cases where the CRA is identified as different types of stainless steels or nickel alloys, for final selection the strength and cost of alloys have to be given due consideration. In addition to their high cost, many of the CRA have low strength when compared with various line pipe steels. If solid CRA is used high pressures can only be handled if very heavy walled pipe is used. In such cases the use of solid CRA becomes unviable because of cost factor.

In order to partially balance out the two apparent disadvantages, the use of clad pipe becomes necessary. In this case high strength carbon steel outer pipe (backing steel) is provided with an inner layer of corrosion-resistant alloy. Despite higher capital expenditures it does works out to be more cost-effective solution because of lower inspection and maintenance cost over long years of service. The clad pipes

generally have ~3 mm thick CRA lining over the backing steel made from normal high tensile ferritic steels conforming to various API grades; the latter taking care of internal and also external pressure in case of deep water wells.

Types of Clad Pipe

Clad pipes are categorized into two types:

1. *Metallurgically Clad Pipes*
   - In case of seamless clad pipes, the CRA internal cladding and the external pipe material are bonded together metallurgically using techniques like co-extrusion of a composite billet of CRA pipe inserted in a steel pipe, explosive bonding, centrifugal casting of backup steel followed by that of CRA, hot isostatic pressure (HIP) cladding using powder or solid lining to get a diffusion bond between two.
   - Metallurgically clad welded pipes, on the other hand, are manufactured from hot rolled clad plates or explosive bonded rolled plates. The pipes are finally made from clad plates by forming followed by welding or by using UOE process (see Chap. 3).
2. *Mechanically Clad Pipes*
   Mechanically clad pipes are normally made using two processes, that is hydroforming and rolled lining. Though details of steps involved may vary for different manufacturers, the broad steps involved are given below.
   - Hydroforming process consists of inserting a CRA liner pipe into the base metal outer pipe to bring together the two in mechanical contact. The inner liner is then subjected to high water pressure resulting in expansion of both the pipes and producing a tight mechanical fit after de-pressurization. A compressive stress is produced in inner pipe due to higher elastic resilience of outer pipe. Maximum compressive stress is developed at interface of two when yield stress of liner is about 50% of the yield strength of the outer pipe. However, this method of production is not suitable for CRA having high yield strength like DSS and SDSS but suitable for 316L, 825 and 625.
   - Rolled lined pipe does not have the disadvantage of limit of material strength as in case of hydroforming. In case of rolled lined pipe the carbon and CRA plates are rolled together into a cylinder and then longitudinally rolled. The steps involved are shown in Fig. 9.15 [40].

Economic Aspects

For economic comparison of metallurgically and mechanically bonded pipes estimates based on the year 2007 price is quoted below [41]:

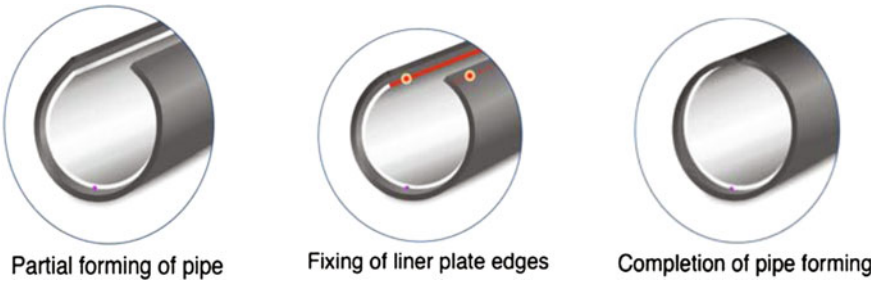


Fig. 9.15 Steps involved in the production of rolled lined pipe [40]

This scenario involves pipe for transporting natural gas. The OD is 12 in.; the working pressure is 150 bar (2176 psi); the contaminants are hydrogen sulphide and chlorides. The three cases are as follows:

1. *Homogenous (solid) pipe made from 316L*
2. *Metallurgically clad welded pipe: API X 65 outer pipe, 316L inner pipe*
3. *Mechanically clad seamless pipe: API X 65 outer pipe, 316L inner pipe.*

Case 1*. The wall is approximately 0.59 in. thick and the pipe weighs about 81 lbs./ft. This is the reference case. The cost is 100 units per meter.*
Case 2*. The outer pipe is approximately 0.39 in. thick; the liner is about 0.12 in thick. The pipe weight is 71 lbs./ft. Relative to Case 1, Case 2 costs 80 units per meter.*
Case 3*. As in Case 2, the outer pipe is 0.39 in. thick and the liner is 0.12 in. thick. Compared to Case 1, the cost for this pipe is 46 units per meter.*

Therefore, mechanically clad pipe represents a cost reduction of 54% compared with a homogenous pipe and a cost reduction of 42.5% compared with a metallurgically clad pipe.

Another area of potential cost reduction is in welding, because clad pipe has thinner walls than homogenous pipe, and so requires less welding time. In this scenario, the clad pipes are 0.39 in. thick, whereas the homogenous pipe is 0.59 in. thick, a 13% difference.

It is claimed that cost wise there is marginal difference between the metallurgically and mechanically clad welded pipes. However, during continuous laying of mechanically clad pipe one has to ensure that the pipe is not subjected to a bending radius of smaller than desired value to avoid wrinkling and subsequent localized detachment of cladding. In addition, it should be noted that in mechanically clad pipe the wall thickness of the inner lining cannot be measured from outside using ultra-sonic technique.

9.5.2.3 Material Selection Standard for Oil and Gas Production

NORSOK Standard M-001 [35] is the only standard available to general public specifically dealing with materials selection for the oil and gas industry. This standard was first developed in 1994 in Norway by the concerned operators and engineering companies active in the North Sea area. There are in-house standards on material selection for internal use of large companies engaged in the oil and gas industry but the same are not in public domain. In such a case, NORSOK M-001 is being used in several projects outside Norway also. Need was, therefore, felt for international standardization, where possible, with the inputs of the concerned companies. For this purpose, a joint group was formed consisting of members from different oil and gas companies in Europe, the USA and Middle East. ISO has published the conclusion of the joint study as a standard ISO/CD21457 [42] which includes all equipment from and including the wellhead, to pipeline for stabilized products but excluding down hole components. The standard gives guidance for oil and gas production, produced water, gas/water injection and utility systems, in the areas of:

- corrosion evaluations;
- materials selection for specific applications and/or systems;
- performance limitations for specific materials;
- corrosion control;
- qualification of materials and manufacturers.

The standard provides guideline and does not recommend any specific material, but lists typical and proven materials and final selection is left to the user's judgment. The future of this standard will depend on how far it is accepted by the oil and gas companies for material selection. This ISO standard has already been accepted and incorporated in British Standard [43]. Compared to NORSOK M-001, it can be summarized that:

- The ISO 21457 is a guideline.
- Material selection for down hole is not covered.
- The tables giving recommended material grades are split in multiple tables, but the content is in general the same.
- Temperature limits for SCC in marine environments are modified.

9.5.3 Protection of Carbon Steel Gathering Lines by Internal Coating

9.5.3.1 New Lines

Under comparatively milder conditions the gathering lines can be protected to a large extent by combination of internal coating and inhibitor addition. With selection of modern coating systems it may also be possible to dispense with inhibitor injection. Coatings used should have good adhesion, stability (low rate of degradation), and resistance to softening by hydrocarbon. Lining materials that can be considered are single coat epoxy, multi coat epoxy and polyurethane but of this single coat epoxy is considered to be preferable because it is cost effective and efficient. In case of getting Teflon-like finish reduction in pumping cost along with a minimum of 6% increase in flow is claimed to be achieved [44]. However, the internally lined pipes have inherent problem with providing branch connections and are a better option for straight run pipe. It may be mentioned that techniques like 'Rotolining' has been developed for branch fittings where the non-metallic lining is applied uniformly inside the fitting and branch connections.

9.5.3.2 Old Lines

In cases where the thickness of gathering line shows considerable deterioration due to internal corrosion there are two options, either replace the line or take steps to minimize further corrosion. Where possible, the latter alternative by providing coating in situ is more attractive, especially for offshore lines. This avoids additional high cost of pipe lying. For in situ coating, the internal wall of pipe is first cleaned using either abrasive blasting or using suitable chemicals. Several coats of protective coating are then applied. Though high performance epoxy coating is normally used, other types can also be applied. For coating instead of spray, pipeline pigs are used. In situ internal coating is claimed to cost 15–20% of replacement cost of an offshore line. On the other hand, the major disadvantage is that the unit price is not justified primarily because of cost of resource mobilization. The pipeline diameters of 4″–30″ have reportedly been successfully coated.

9.5.4 External Protection of Gathering Lines

9.5.4.1 External Coating

The gathering lines are either buried in soil (onshore) or sea bed. These lines are protected against soil and seawater corrosion by combination of coating and cathodic protection. TWI has conducted detail review of protection of offshore

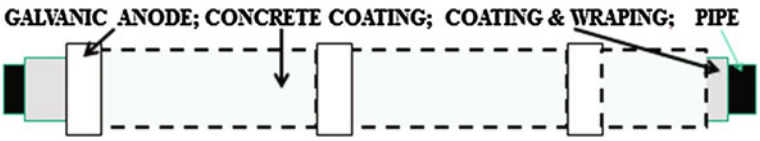


Fig. 9.16 Shows the coating system along with galvanic anodes (schematic)

pipelines against corrosion [45]. As per the report commonly used coatings are based on coal tar epoxy resin, fusion-bonded epoxy (FBE) and 3-layer polypropylene or polyethylene (3LPE). While coal tar epoxy resin has performed reasonably well, FBE and 3LPE are presently preferred material. While FBE is more popular in the USA and the U.K. 3LPE is preferred by European companies. The data of 2006 give the worldwide preference for 3LPE coatings for new pipelines [46].

- Most areas of the World—65–90%
- Africa and Middle East—45–50%
- The USA and Canada—15%.

For onshore line, fusion-bonded epoxy coating is also used. In case of offshore lines, additionally concrete coating is applied with the primary objective of providing extra weight against floating up of the line due to buoyancy effect. Figure 9.16 shows schematically the corrosion protection coating system of offshore lines. Large diameter pipes laid underground are also to be similarly provided with concrete where ground water table is high. The two ends of gathering lines in offshore (at well head and process platform ends), are subjected to extreme conditions as these fall in tidal and splash zone. Extra thick pipeline coating provided in this zone has not been found to be successful. The special rubber coating like Polychloroprene (Neoprene) has provided good protection to splash zone of riser pipes connecting the subsea pipeline to well head or well head to process platform. In addition splash zone section of a riser is subjected to stresses due to wave action which can damage normal coatings. The Neoprene is a preferred coating as it is flexible, highly resistant to abrasion and impact damage, and seawater ingression. As per the manufacturers, if required, special anti-fouling coatings can be integrated in the rubber to prevent marine growth [47]. Metallic sheathing of 90 Cu–10 Ni can also be given over the coating.

9.5.4.2 Cathodic Protection of Offshore Lines

For offshore underwater flow lines it is not possible to use impressed corrosion system because it is not practical to provide anode bed and corresponding power source in the sea bed. Thus, practical considerations require that galvanic system with anodes fitted on the line itself be used. The anodes are fitted during the laying of the pipe for which bracelet type anodes of aluminium (generally Galvanum III) is used.

Thus, the total protective system of a carbon steel line consists of coating and wrapping followed by concrete coating for additional weight against buoyancy. After coating of the pipe, bracelet anodes are fitted. As per DNV-RP F103 [48], in ISO 15589-2, Sect. 7.1, maximum anode distance of 300 m is advised for pipeline CP design. Distance of larger than 300 m can be used after design (appropriate potential attenuation calculations), taking into consideration the metallic resistance of pipe wall. Depending on pipe size, mean values of cathodic current densities, coating break down factors, and the nature of galvanic anode, the total weight of anode is decided to get the design life. Such an estimate is important as the galvanic anodes have finite life and retrofitting is to be avoided, though not always possible. For pipelines of a few kilometre lengths, impressed current system has been tried. There are some instances where combination of galvanic and impressed current (anode bed being at shore end of the impressed system) have been used. There are also reports of Sled anodes having being successfully used.

Cathodic protection is also used for protection of CRA in seawater environment. However, in such cases there have been some instances of failure of 13Cr SMSS, DSS and SDSS due to hydrogen embrittlement caused by hydrogen evolved on metal surface as a result of galvanic current [45, 49], where the galvanic anode used was aluminium alloy without control of applied potential. Details of some of the failures are given in Table 9.9 [49]. It is also well known that over potential can cause discharge of hydrogen at cathode which results in softening and de-bonding of coating on carbon steel [50]. In case of CRA having hard structure, hydrogen entering the alloy can cause cracking if stresses are present. Industry sponsored scientific studies are also underway to provide data on design and safety of cathodically protected sub-sea components.

Because of possibilities of pipe failure, anodes are not directly welded to CRA pipes like SMSS and DSS. For this, a circular doubler plate made from an austenitic material (like 316L) is welded to the pipe and then on top of the doubler plate the anode bracket is welded. However, failures have been experienced at the fillet weld toe due to the combined effect of welding stresses and strains and hydrogen embrittlement. For prevention of such failures, it is essential that the protective potential range requires to be substantially reduced. Recommended protective potential ranges for cathodic protection of various materials in seawater have been given in, ISO Standard 15589—2:2004 (Table 9.10) [51], which include the guidelines of NORSOK M-503 [52]

The main reason for failure of 22Cr and 25Cr DSS under CP is due to combination of load/stress and local hydrogen embrittlement (HISC). It has also been established that materials with coarse austenite spacing are more susceptible to HISC than those with fine austenite spacing. Requirements relevant for measurement of austenite spacing are given in paragraph 17 of ASTM E112-96 [53]. DNV has, therefore, prepared a separate standard DNV-RP-F112 for design of CP for DSS [54].

Table 9.9 Failure of SMSS flowlines in the North Sea

Initiation of cracks(s)	Propag. phase	Failure type and direction	Phase detected	Filler type	PWHT	OD (mm)	H source (s)	Total H level (ppm)	Measured YS (MPa)
Doubler plate weld HAZ	Pressure testing	1 transverse crack	Pressure test	SDSS	n	259.8	CP	5[a] 10–16[a, d]	758
Doubler plate weld HAZ	Pressure testing	1 transverse crack	Pressure test	SDSS	n	259.8	CP	2 12–15[d]	708
Anode pad fillet weld	Pressure testing	1 longitudinal crack	Pressure test	Ni-base	n	323.9	CP	3 9.5[d]	782 770
Girth weld	Pressure testing	1 longitudinal crack	Pressure test	SMSS	n	323.9	CP	2–3	898[c] 1007[c]
Doubler plate welds	Pressure testing	2 shallow transverse cracks	After recovery	SDSS	n	268.6	CP	–	–
Doubler plate welds	Pressure testing	2 shallow longitudinal cracks	After recovery	SMSS	n	323.9	CP	–	593 608

[a]Transverse base material specimen
[b]Samples tested after being kept at RT for two weeks
[c]Transverse weld metal specimen
[d]Hydrogen level of adjacent weld metal

Table 9.10 Recommended protective potential against Ag/AgCl reference electrode as per ISO standard 15589—2:2004

Pipeline material	Environment	Least—potential (mV)	Most—potential (mV)
Carbon steel <500 MPa	Aerobic	−800	−1100
Carbon steel <500 MPa	Anaerobic	−900	−1100
Carbon steel >500 MPa	All	Determine by HSIC testing	Determine by HSIC testing
Stainless steels			
Austenitic			
NPRE ≥ 40	All	−300	−1100
NPRE <40	All	−500	−1100
DSS	All	−500	If HISC possible −800
12Cr martensitic (SMSS)	All	−500	If HISC possible −800

9.5.4.3 Cathodic Protection of Onshore-Gathering Lines

In onshore fields gathering lines are laid underground. Because of safety considerations the lines are coated and then provided cathodic protection. Normally, impressed current cathodic protection system is used. The protective potential of carbon steel against $Cu/CuSO_4$ of—850 mV minimum is maintained. If a CRA like 13Cr SMSS or DSS is specified and requires to be cathodically protected (due to soil condition) then the design (galvanic or impressed current system) will be such that at no point the potential exceeds—800 mV or goes below the minimum specified in Table 9.10. Insoluble anodes, especially platinized titanium is preferred. Power source used is transformer rectifier, or solar battery, depending on location and the current requirement.

9.5.4.4 Galvanic Anodes for Cathodic Protection

Commonly used galvanic anode in offshore is aluminium alloy though zinc alloy is also available. The properties of three alloys, two of aluminium and one of zinc, are given in Table 9.11 [55].

Table 9.11 Properties of galvanic anodes

Property of alloy	AI–Zn–In	AI–Zn–Hg	Zinc Mil. 180001 H
Potential (−) volts versus Ag/AgCI	1.08	1.05	1.05
Galvanic capacity A. Hrs. lIb.	1150	1280	355
Galvanic efficiency %	85	95	95
Mud performance	Good	Unpredictable	Good

Table 9.12 Anode chemistry for cold water

Element	Typical	Cold water
Iron (Fe)	0.10% max	0.007% max
Zinc (Zn)	2.8–7.0%	4.75–5.25%
Copper (Cu)	0.006% max	0.005% max
Silicon (Si)	0.20% max	0.10% max
Indium (In)	0.01–0.03%	0.015–0.025%
Cadmium (Cd)	Not specified	0.002% max
Others (each)	0.02% max	0.02% max
Aluminium	Remainder	Remainder

In offshore, aluminium alloys are preferred because of their higher galvanic capacity compared to zinc. It has also the advantage of lower weight.

Cathodic Protection in Deep-Water Installations

For deep-water CP, special considerations are required because of substantial differences in conditions, compared to that at lower depths [55]. Another important point is that once installed, any future corrective measures at >1000 feet depths become difficult (as only ROV) can be used and, therefore, continuous good performance of the anodes is to be assured. The most important difference is decrease in temperature with depth which (i) decreases the electrical conductivity of seawater and so the CP current output, (ii) the extent of calcareous deposit on cathode (component being protected) is decreased resulting in the formation of less dense deposit) and (iii) reaction rate of seawater is decreased. The overall effect is that more numbers of anodes are required to get the required degree of protection and for the design life. For deep water, the preferred anode is Al–Zn–In alloy, because it has higher driving potential compared to mercury containing alloy and good performance in mud and silt of sea bottom. However, for good performance the composition of alloy is tailored for cold water as shown in Table 9.12.

9.5.5 Non-Metallic Reinforced Thermoplastic Pipe (RTP)-Gathering Lines

Use of reinforced piping is now being used in oil and gas industry mainly for gathering line and injection line systems. Since API has published API RP 15S [56], the use of RTP has risen significantly. The main technical advantages of RTP are:

- RTP is flexible and supplied on long-length coils, allowing a simple and very fast installation.
- It has very good resistance to corrosion in oil and gas environment.

- It can withstand high pressures.
- It has very high impact strength and is suitable for field/rough handling.

The unique combination of properties of RTP stems from its 3-layer construction:

1. A thermoplastic liner pipe, usually High-Density Poly Ethylene (HDPE), to provide a leak free and corrosion-resistant pipe,
2. Cross-wrapped layers of high strength synthetic fibre or high strength steel wire reinforcement provide the required strength to withstand hydrostatic pressure,
3. An HDPE cover layer, to protect the pipe from mechanical damage and UV radiation.

Typically, RTP is supplied in the diameter range of 3″–6″ and a pressure rating up to 150 bars (2200 psi). Steel wire reinforced RTP (just) floats when empty, and just sinks when filled with water. To sink pipe to the seabed during installation, and also to ensure sufficient stability on bottom while in operation, weight is attached to the pipe.

9.5.6 *Umbilical for Operation of Well Heads in Deep Water Sea Bed*

In case of deep sea wells, the conventional well platforms are absent and all facilities are situated at sea bed. Here a host production platform connects to wells scattered over long distances on the sea floor. Operation of these sub-sea systems is controlled through *umbilical.* Typically more than a mile in length and 140–175 mm (5–8 in.) in diameter, umbilicals are essentially large hoses or pipelines containing a cluster of smaller, high pressure hydraulic hoses as well as electrical and optical cables that connect to sub-sea wellheads for remote operation of valves. The hoses and cables are placed within free-floating stainless steel tubing covered with an extruded thermoplastic overwrap. This arrangement is suitable for operations up to a depth of about 2150 m (7000 ft).

9.5.7 *Instrument, Chemical Inhibition and Other Tubing*

Tubing transferring instrumental process data from any particular location to the Central Control room is an important part of any process plant. Such small diameter tubing is also used for chemical inhibition, hydraulic lines, and utility applications. Because of the critical nature of their service, integrity and long life of material selected for such lines are to be ensured. These lines are subjected to external corrosion and some also to internal corrosion, depending on service conditions. In case of offshore platforms and onshore plants located very near the coastal line,

the conditions are very severe with respect to the external corrosion due to highly saline atmosphere. The most commonly used MOC is 316 stainless steel up to a maximum temperature of 60 °C considering its susceptibility to CSCC. As per Statoil guidelines [57], for sheltered tubing, the temperature limit can be raised to 70 °C. The major problems experienced around the world under different climatic and environmental condition are:

- *Pitting*: Pitting is localized corrosion which can result in perforation of tubing. Susceptibility of stainless steel to pitting in presence of chloride depends on its composition with respect to the chromium, molybdenum and nitrogen content and expressed as PREN. Of the various alloys, the minimum alloy suitable for tubing is the molybdenum containing 316 stainless steel having PREN value of 26.
- *Crevice Corrosion*: Crevices are impossible to avoid because tubing are to be supported for installation using clamps and supports. Mostly, tubing is laid side by side on a tray, with narrow gap because of constraint of space. Accumulated deposits between adjacent tubing and also the tray and tube are likely to act as crevice. In general, susceptibility to crevice corrosion decreases with increase in PREN and CPT of the alloy but crevice corrosion is more severe than pitting type of corrosion attack and the CCT is lower than the CPT (see Chap. 8). Instrument line of 316 stainless steel is mainly affected by crevice corrosion and proper care is needed to minimize this type of attack. NACE standard SP0108-2008 under Section 13 also discusses the corrosion control of small bore stainless steel tubing [58].

Some of the important points to be considered with respect to the instrument tubing are:

1. Prevention of crevice corrosion and pitting:
    - Avoid use of plastic tubing clamp because it deforms around the tubing and creates tighter crevices which, in turn, promotes crevice attack because of limited availability of oxygen.
    - Use marine aluminium alloys 5XX or 6XX series (such as 5052, 6061, etc.) for tubing supports and clamps. In one of the designs, the rows of tubes rest on aluminium alloy strip (plain or corrugated), placed on FRP tray and the tubing is held with an aluminium alloy bar [59]. In such case, galvanic corrosion of aluminium can occur but these are replaceable and can be changed as and when necessary.
    - Discontinue use of tape for labelling piping systems to minimize the risk of crevice formation.
    - Space tubes on parallel runs of tubing on pipe rack so that it is possible to have access to every connection point and cleaning of pipe surface periodically.
    - Handle tubing so as not to damage the surface with scratch or dents, which may act as site for initiation of pitting.

2. Application of liquid protective coating:
   - Normally, coatings are too thin and get easily damaged. This has been tested but found to be unworkable in actual field trials.
   - Tubing jacketed with thermoplastic polyurethane have been found to be cost-effective provided some important conditions, such as, resistance to impact and abrasion, resistance to UV-degradation, ease of joining, etc., are met.
3. Change of material:
   - Stainless steels with better resistance to pitting and crevice corrosion have been evaluated. The two alloys which have been found to justify use of costly alternative are super DSS (Type 25Cr) and 6-Mo alloys (254SMO, AL6XN, etc.). Though NORSOK M-001 includes 316 as instrument tubing, Statoil guidelines [57] recommend the use of 316 stainless steel under indoor and 25Cr DSS or 6-Mo in areas outdoor. The said table also includes the MOC of fittings and small valves.
   - It is reported that copper alloy tubes of Tungum™, a precipitation hardening copper alloy having nominal composition of 82Cu–1Al–1.1Ni–1Si–Zn Balance possess high resistance to marine corrosion. Shell International has been reported to have used instrument lines of this alloy in number of their offshore installations [60].
   - The alloy has high resistance to marine environment and is immune to pitting and crevice corrosion. However, its use is limited.

9.6 Material Selection and Corrosion Control for Oil and Gas Processing

Oil and gas produced from wells also contain produced water; condensate and these are to be first separated before further processing to get different fractions. In performing the various activities there are additional requirements of product storage, cooling and fire water systems, offshore platforms, sub-sea pipelines, instrumentation, etc. The material selection and corrosion control measures would not only have to take into consideration various factors affecting corrosion but also operator's requirement and internationally or nationally accepted safety norms.

For example, there are variations in conservatism of different operators. There are many companies who favour a design based on a corrosion-resistant alloy. On the other hand, there are other companies who are liberal in their approach and would prefer a carbon steel solution. Further, many nations have either national regulations or follow internationally accepted guidelines given by API and ISO for safety and environment. Material selection and corrosion preventive measures have

also to take into consideration these requirements. NORSOK M-001 does not in general recommend the use of inhibitor, including in processing section. According to them, "Use of corrosion inhibitors in process systems is not recommended, but can be used provided the inhibitor in each process stream satisfies the inhibitor supplier's minimum recommended concentration for each stream and flow rate. Due to complex geometries and normally high flow rates, there is an increased risk for high inhibited corrosion rates locally in process systems compared to pipelines, which will influence the need for inspection and maintenance".

9.6.1 Processing Facilities

Oil and gas from different wells come to a header via gathering lines, from where these are sent for processing. Depending on type of field and other conditions, different processing systems are provided. In case of offshore operation, processing is done normally on offshore platforms. Sometimes processing is also carried out partly offshore and partly onshore. The processing activities in oil and gas fields consist of:

- Separation of crude, produced water and associated gas coming from oil field,
- Separation of condensate, condensed water, produced water and gas from gas wells,
- Crude/condensate and produced water handling system,
- Gas handling; compression, dehydration and transmission,
- Removal of H_2S (sweetening) in case of sour gas,
- Cooling and heating system involving sea and fresh water,
- Firefighting system,
- Instrument and chemical injection system,
- Processing of condensate to produce naphtha, kerosene, ATF and gas treatment for LPG, propane, butane, ethane and natural gas/LNG.

9.6.1.1 Oil Fields

The oil from well head valve flows through the gathering lines and depending on distance from well head there is a drop in pressure and temperature. However, once the well products come on the processing area the oil, produced water and associated gas are separated in large size horizontal cylindrical vessels, known as *separators*. The separation is done often in 2 or 3 stages by reduction in system pressure. Simplified flow diagram of oil and gas separation in oil fields is shown in Fig. 9.17 [61]. In the separator the well product gets separated in 3 layers, that is produced water, oil and gas in this order from bottom to top. The MOC of separator would have to be selected on the basis of CO_2 and H_2S partial pressure in the

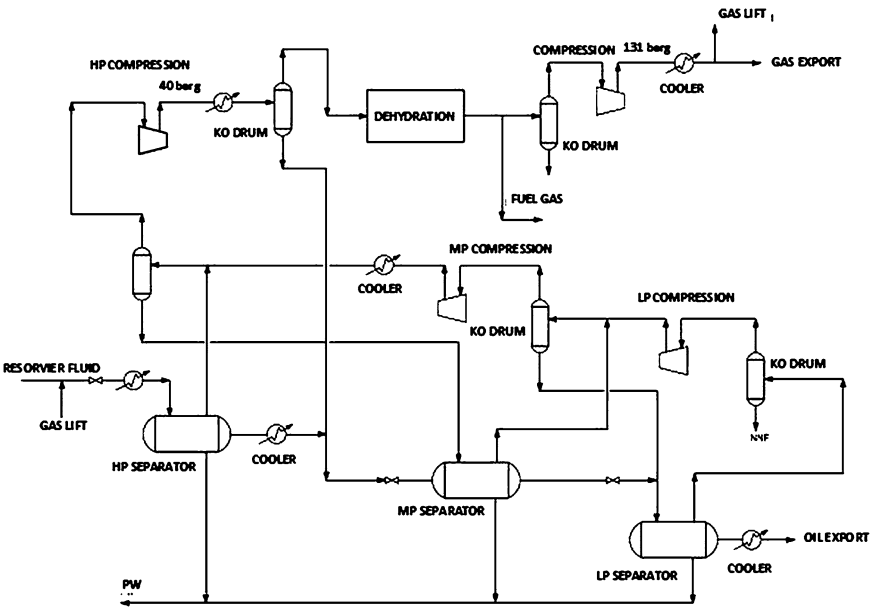


Fig. 9.17 Simplified flow diagram of oil and gas processing (oil fields) [61]

associated gas phase. The separated oil contains very small amounts of water so no corrosion of downstream oil lines is expected. As regards produced water, the same would contain dissolved CO_2 and H_2S along with high amounts of dissolved chlorides and other salts and these would have to be taken into consideration. The associated gas is saturated with moisture and corrosion in gas phase would depend on the extent and the rate of water condensation.

Handling of Well Fluid

Selection of MOC would require consideration of a number of factors which include amongst others the nature and corrosivity of fluid, location of processing facilities (onshore or offshore), design life, etc. Broadly, the general approach in material selection in processing can be stated as follows:

1. MOC for the first stage and test separator, in the absence of CO_2, will be carbon steel with bottom 40% of circumference coated with 1–1.5 mm-thick coating of glass flake filled resin.
2. In case of moderate CO_2 partial pressure and where addition of inhibitor can bring down the corrosion rate to 0.1 or 0.15 mm/year, the MOC for first stage separator would be carbon steel fully coated with 1–1.5-mm thick glass flake filled resin. Providing cathodic protection with galvanic anode in the bottom

section shall further help in reducing corrosion. Inhibitor would be injected at outlet of the main header going to test and first separator at a distance sufficient from separator for ensuring thorough mixing.

3. As a protective coating, glass flake filled resins are quite popular in the oil and gas industry. Here the glass flakes are added to epoxy or vinyl ester. The flakes are only microns thick and dispersed in layers to form dense, inert barriers as a result of overlapping layers of glass flakes. The addition of glass also increases the barrier flexibility, hardness and abrasion resistance of coatings. It is claimed that formulation with coating life of 25 years before major maintenance can be achieved. If application is proper, minor repairs may be required to give a design life of 20–30 years under moderate conditions.
4. In case of higher CO_2 partial pressure MOC would be changed to solid or clad corrosion-resistant alloys (CRA), the alloy grade depending on the corrosivity of the system. More economical glass flake resin lining can be used, but the coating may require repair a few times during the life time. It is therefore advisable to consider both initial and maintenance costs in selection of this alternative, especially for offshore installations. Estimation of life-cycle cost is recommended while selecting MOC, including the composition of CRA, in these cases.
5. In case of the presence of H_2S within the definition of sour system, the material would meet the NACE MR0175 ISO 15156 requirement. In addition, any carbon steel plates used for fabrication shall be resistant to HIC, that is extra low sulphur shape controlled steel with CLR of 10–5 (depending on H_2S partial pressure). It may be mentioned that the present day practice is to select material on the basis of minimum SSC Region1 of Fig. 9.8, even in cases where H_2S is initially absent or very low. This is because it has been experienced that with ageing and introduction of secondary steps to enhance production, many of the wells become sour. At that stage, it becomes difficult to make any large scale replacement required in MOC.
6. Due to subsequent decrease in pressure downstream of the first separator, the MOC of the second and subsequent separators (including knock out drums) would depend on the corrosion rate, arrived at based on operating conditions existing in these zones.

Handling of Crude

After the separation in separators, the remaining small amounts of water in the crude is separated in electrostatic separator and then stabilized before export. The treated crude being non-corrosive containing very little water, the piping, pumps and storage tanks are made of carbon steel.

Handling of Associated Gas

Associated gas coming out of separators is water saturated, and corrosion would occur in case of condensation of water on piping ID. The gas is compressed in 2 or 3 stages up to transmission pressure (Fig. 9.17). The gas handling system consists of compressors along with inter stage coolers, knock out drums (scrubbers) and gas drier prior to the transmission of gas. For selection of material of construction, the first step would be to determine the corrosion rates in different sections as per various parameters discussed under item 7.3.3.2. The line from the separators to the compressor would handle saturated gas and may or may not have any condensation, especially if these are insulated. The line from first stage compressor to the first inter stage cooler would be hot and not likely to experience any condensation. On the other hand, the line from first inter stage cooler to the KO drum to the second stage compressor would have condensed water and, therefore, highly corrosive because of increase in CO_2 partial pressure. These conditions would prevail till the gas dehydration tower, as beyond it the gas will be dry and non-corrosive and carbon steel can be used for all related downstream equipment and piping. The MOC of piping, vessels, compressors under such condition would require careful consideration as far as use of carbon steel versus CRA considering the fact that it will not be possible to use any inhibitor to protect carbon steel in this section. MOC for wet gas shall depend on partial pressure of CO_2, temperature and the nature of equipment. In case of sour systems, the material used shall also have to conform to various requirements of NACE standard MR0175/ISO15165. Where corrosion rates are high, MOC would be upgraded to required CRA.

Various CRA can be considered depending on corrosivity and presence of H_2S. Normally, 13 Cr super martensitic steels are not used for oil and gas processing. Next choice is 316L stainless steel which can be used in onshore inland (non-marine) processing units with the temperature limit of 60 °C. Carbon steel clad 316L is a good alternative but normally not used for piping in process areas. In case of non-sour or mildly sour systems (as per NACE standard MR0175/ISO15165), DSS (22 Cr or 25 Cr) is most commonly used. In case of highly sour corrosive gas, higher iron and nickel base alloys (Table 9.7) becomes the correct choice. For exchangers, pumps, valves, etc., appropriate grades of material, compatible with MOC of lines will be selected. Scrubbers/KO drums downstream of inter stage coolers of compressor shall preferably be of CRA clad carbon steel, though glass flake lining can also be used with provision of impingement plate or deflector (former is preferable), made of CRA, opposite inlet nozzle to take care of any damage of lining and shell due to impingement attack. Compressed gas, either during intermediate or final stage, is dried before transmission.

MOC of downstream equipment after drying would be of carbon steel and would meet the requirement of NACE MR0175 ISO 15156, in case the gas is considered to be sour. This precaution is taken to avoid SSCC in the event of the gas becoming wet due to upset in the drying system. For gas lines or equipment handling gas, where de-pressurization can result in super cooling, MOC used should be suitable

for low temperature use even though the operating temperature is high. The various materials suitable for low temperature use have been given in Table 9.14.

Handling of Produced Water

Produced water is corrosive because of its high salt content and dissolved CO_2^+ and H_2S. The MOC of produced water would be based on considerations similar to that of the process fluid as far as corrosion resistance is concerned. Thus, MOC is similar to that used in case of upstream lines. Use of GRE pipes can also be considered in offshore installations provided the material conforms to require level of fire safety. Its use in onshore fields is possible if the pipes are laid underground. In the absence of CO_2 it has been a common practice, especially in onshore installations, to use carbon steel or galvanized steel. Though these have limited life, replacement can be easily done as and when required. After removing oil in cyclones (MOC similar to that of piping), the produced water is subjected to effluent treatment before being discharged. Where water injection is practiced the produced water is used for reinjection. In offshore operation it is used along with deaerated sea water.

9.6.1.2 Gas Field

In gas fields the well pressures are high to very high, and for processing, where necessary, this pressure is brought down to a low-level downstream of Christmas Tree (choke). The pressure selected is such that after deducting pressure drop, the same shall be sufficient at the outlet of the glycol contactor for transmission of dry gas to onshore for processing. In other words, considerable investment and energy for compressing the gas can be saved. The products coming out of gas well have considerably different characteristic compared to oil well:

1. Crude oil content is either none or only in small amounts.
2. Liquid hydrocarbon (called condensate) is present in considerable amounts, which is lighter compared to heavy crude.
3. Both pressure and temperature are much higher compared to oil well.
4. In deep gas wells considerable amounts of water vapour is present which condense in the well tubes as the pressure and temperature decrease. The water coming with gas can be condensed or produced water or mixture of both.
5. Generally gas wells have higher CO_2 and are likely to be sour.
6. Both material selection and corrosion protection measures are to be given due consideration.

Gas, unless dried, remains saturated with moisture with respect to temperature and pressure. Corrosion in piping or separator or vessels can occur only if there is condensation of water on inner wall. Considerations which would go into the

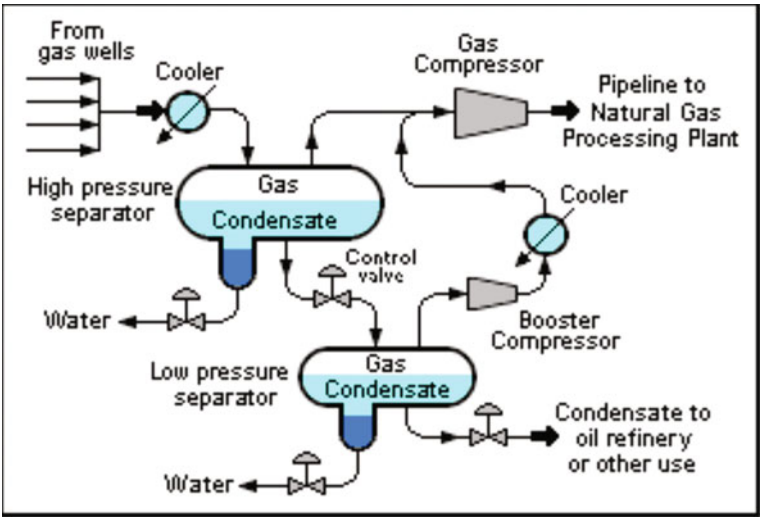


Fig. 9.18 Simplified flow sheet showing gas field processing—condensate/produced water separation [62]

selection for MOC should be as discussed earlier under handling of associated gas (Fig. 9.18) [62].

9.6.2 Gas Drying

To prevent corrosion of gas lines due to condensation of water, the water dew point of gas is brought down to a level below the lowest operating temperature in the pipeline. The dehydration process consists of contacting the gas with glycol in an absorber using counter current flow. The water-rich glycol is then heated to remove the dissolved water and lean glycol is sent back to the top of the absorber. Though ethylene, di-ethylene or tri-ethylene glycol (TEG) can be used, TEG is preferred because of its high boiling point and ease of regeneration. During the dehydration process, the water along with acidic gases like carbon dioxide and hydrogen sulphide present in the gas are also absorbed by glycol making it acidic. Glycol is also subjected to thermal degradation above 200 °C, forming organic compounds like glycolic ($C_2H_4O_3$), formic (CH_2O_2), and acetic ($C_2H_4O_2$) acids. This results in the progressive decrease in pH, and buffering of glycol becomes necessary by the addition of monoethanolamine (MEA) and diethanolamine (DEA). The MOC of the piping, pumps and glycol column is carbon steel, but with dissolved impurities it becomes necessary to add inhibitor to control corrosion as dissolved water is present in the system. As the dehydration process involves recirculation of glycol, its repeated recirculation results in increased in acidic constituents. To control

corrosion bases like borax, triethanolamine (TEA) or NACAP [63] are added to glycol. NACAP® is a 50% aqueous sodium 2-mercaptobenzothiazole that functions as a corrosion inhibitor for water, alcohol and glycol systems. This necessitates having a well-established monitoring system. Sometimes the region of water rich phase at the bottom of drier column is lined with CRA like 316L. While the general practice is to dry the gas before being exported through pipeline, in offshore operation the practice of sending wet gas to gas processing plant onshore has become popular.

The degree of dehydration of sale gas is done taking into account the ambient temperature of the area. For example, the sale gas is required to meet a specification of 7 and 4 lb of water per million cubic feet of gas in warm southern USA and cold Canada and Northern Europe, respectively. Normally, the lines are considered to be free of corrosion but it is not uncommon to get at the end of pigging black material which is known in the industry as 'black powder' phenomenon. Various explanations have been given for this type of corrosion. Some of these are (i) improper drying, (ii) co-condensation of water with TEG [64], (iii) accumulation over the years of very small quantities of TEG vapour to cause glycol corrosion [65], and (iv) effect of bacterial activity turning glycol to become corrosive due to bacterial activity [65].

9.6.2.1 Corrosion Protection of Pipelines Carrying Wet Gas

Recent trend in offshore operation is to transport wet gas or unprocessed well fluid or wet gas on shore to minimize the high cost of capital and operational expenditure on offshore platform. Depending on the corrosivity the MOC of subsea pipelines will be a suitable CRA or carbon steel with a high efficiency inhibition system with the required inhibitor availability of 95% (as per NORSOK M-001 guideline or that recommended by BP) or higher used by some others like Shell which sets the upper limit to 99%, followed by increasing the corrosion allowance, if required. The various aspects of problems connected with subsea pipeline system have been discussed in detail by Marsh and Teh [66].

Formation of Gas Hydrate

At high pressures and low temperatures there is likelihood of formation of ice-like crystals called gas hydrate in wet gas. The problem is of greater concern in the transport of unprocessed reservoir fluid flow lines or wet gas pipeline in deep-sea environment, where the surrounding temperature is very low [67]. Gas hydrates are ice-like crystals composed of gas and water which agglomerate to form large solid plug, which block the pipeline (Fig. 9.19). Depending on gas and water composition, it is possible to find out thermodynamically stable zone of hydrate.

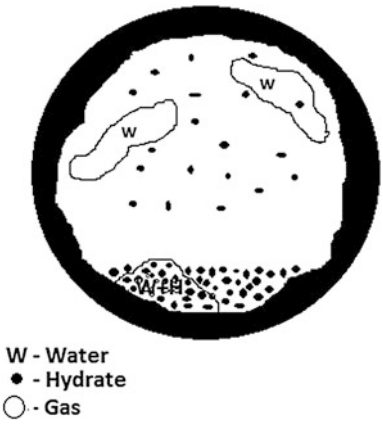


Fig. 9.19 Formation of gas hydrate

Corrosion Inhibition

The major problem with ensuring inhibitor injection to the required per cent availability is the priority it gets over transport of gas as any adverse effect of failure in injection is experienced only in the long run. On the other hand, in transporting of unprocessed gas field fluid or wet gas methanol/MEG is added to prevent hydrate formation and their injection is given the highest priority by operators because in case of injection failure hydrate formation would occur in a short period and block the line. If the inhibitor is injected along with methanol/MEG, it can be effective in successfully achieving very high levels of corrosion inhibitor availability. This concept is being used by many companies around the world [66].

pH Stabilization

In case of sweet gas production with condensed water and little or no produced water, corrosion can be controlled by pH stabilization in case MEG is injected to prevent hydrate formation. In this case pH is controlled by dosing potassium hydroxide or a suitable amine along with the MEG. However, where produced water is also present combined pH stabilization and inhibitor has been found to be effective where corrosion rate of 0.1 mm/year can be used for design [66].

Combined pH Stabilization and Corrosion Inhibition

Although pH stabilization can be effective in condensed water gas production systems, there is always the possibility of some produced water formation occurring in later life. The most recent developments in corrosion control for gas production have concentrated on the concept of combining pH stabilization and corrosion inhibition with MEG injection.

Corrosion Allowance

Where corrosivity is high, carbon steel with increased corrosion allowance of upto 10 mm as recommended by the NORSOK M-001 [36] and DNV-0S-F101 [68] should be considered. Laying of pipeline with upto 10 mm thickness is not a problem [66].

Operator Variations

Final selection of the corrosion control system depends on the users. MOC and corrosion allowance selection also depends on conservatism of the operating companies. Companies like Statoil and BP are more likely to favour CRA in aggressive environments unlike Shell and Chevron whose first choice will be inhibited carbon steel system.

9.7 Processing of Oil and Gas

9.7.1 Crude Oil Processing

Crude oil is a mixture of long chain hydrocarbons of various molecular weights having different boiling point. The crude is heated and liquids having required range of boiling points are distilled out to get naphtha, gasoline, kerosene, diesel etc. for different use. There are in addition other downstream processes including some where hydrogen is also present. The corrosion problems, material selection and material performance in refining of crude have been covered in Chap. 10.

9.7.2 Gas Processing

Gas is a mixture of lighter hydrocarbon consisting mainly of methane and smaller quantities of other heavier gases like ethane, propane, etc., which have successively lower sub-zero liquefying temperatures. Of these, methane is the lightest having boiling point of −173 °C. Others are heavier gases having comparatively higher sub-zero boiling points and are collectively known as *natural gas liquid* (NGL). Most of the processes involve sub-zero and cryogenic temperatures and approach for selection of MOC is quite different except for areas where water as liquid along with CO_2 or H_2S can be present, leading to corrosion.

9.7.2.1 NGL Extraction

There are two principle techniques for removing propane, butanes, pentanes and other heavier hydrocarbons from the natural gas, the absorption method and the cryogenic expander process. These two processes account for around 90% of total natural gas liquids production.

Absorption Process

Natural gas is passed through an absorption tower, where it comes into contact with the absorption oil which soaks up a high proportion of the NGLs. The 'rich' absorption oil consisting of propane, butanes, pentanes and other heavier hydrocarbons is heated to a temperature above the boiling point of the NGLs, but below that of the oil and fed into a tower. This process allows for the recovery of around 75% of butanes, and 85–90% of pentanes and heavier molecules from the natural gas stream. In case refrigerated oil absorbent is used, propane recovery can be upwards of 90%, and around 40% of ethane can be extracted from the natural gas stream. Extraction of the other heavier NGLs can be close to 100% if this process is used.

Cryogenic Expansion Process

Cryogenic processes are also used to extract NGLs. It is of special interest where recovery of ethane is sought. The turbo expansion process is more common. In this process, external refrigerants are used to cool the natural gas stream. Then, an expansion turbine is used to rapidly expand the chilled gases, which causes the temperature to drop significantly to −85 °C. This rapid temperature drop condenses ethane and other hydrocarbons having higher molecular weight in the gas stream, while maintaining methane in gaseous form.

9.7.2.2 Separation of Liquid Fractionation

Once NGLs have been removed from the natural gas stream, the various fractions are separated by fractionation, taking advantage of different boiling points of fractions present. The particular fractionators are used in the following order:

- **Deethanizer**—this step separates the ethane from the NGL stream.
- **Depropanizer**—the next step separates the propane.
- **Debutanizer**—this step boils off the butanes, leaving the pentanes and heavier hydrocarbons in the NGL stream.
- **Butane Splitter or Deisobutanizer**—this step separates the iso and normal butanes.

9.7.3 Natural Gas (NG)

Gas remaining after the removal of heavier fractions is primarily methane with some ethane. If not removed during earlier stage, the gas is dried and then sweetened to remove H_2S. This gas is exported to the users through underground pipelines. Alternately, the gas is liquefied (called liquefied natural gas—LNG) at about −173 °C and stored and transported in Horton spheres.

9.7.4 Material Selection for Sub-zero and Cryogenic Temperatures

In NGL processing, corrosion is not a problem in the absence of liquid water because all operations are at sub-zero and cryogenic temperatures. Because of absence of water, process side corrosion is not a consideration and primary requirement is the materials' susceptibility to brittle failure. This has been discussed in detail in Chap. 5. While on heating ferritic steels loses strength and becomes more ductile, the behaviour reverses if these are used at sub-zero temperatures as illustrated schematically in Fig. 9.20. Thus, metals can lose considerably their toughness and in extreme case fail in brittle manner. Some of the factors which affect change from ductile to brittle behaviour are:

- Crystal structure—Unlike BCC structure, metals and alloys having FCC structure (copper, aluminium, and 300 series stainless steels) retain their toughness to a large extent up to extremely low temperatures.

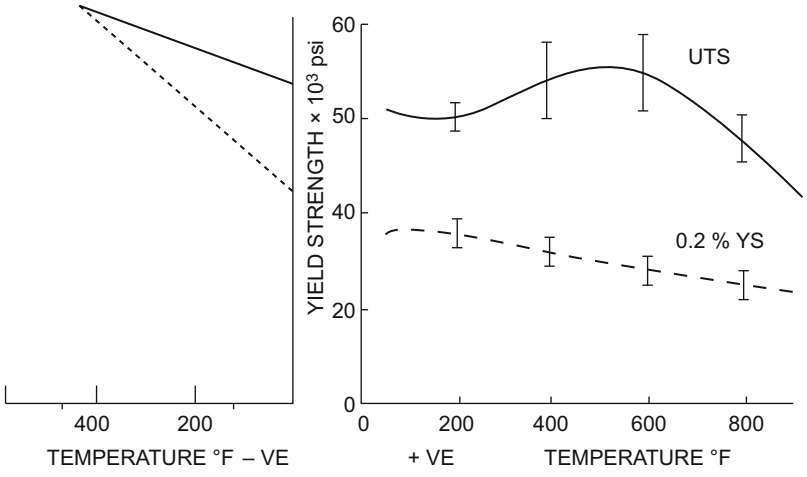


Fig. 9.20 Change in UTS and YS with temperature

Table 9.13 Boiling points of gases and list of steel for service at sub-zero and cryogenic temperatures

Commodity	Chemical formula	Approximate BP °C	Some of steels used for service at BP	Remarks
Butane	C_2H_{10}	−0.60	ASTM A 516, All Grades ASTM A 106B	
Propane	C_3H_8	−42.3	ASTM A 333, Grades 1, 6 and 7 ASTM A 516, Grades All Grades ASTM A 662, Grade A	
Ethane	C_2H_4	−83.3	ASTM A 333, Grade 3 ASTM A 334, Grade 3	
Methane	CH_4	−111.7	ASTM A 553 Type II ASTM A 333, Grade 8 ASTM A 334, Grade 8	

- Alloying with nickel lowers the ductile to brittle transition temperature DTBT of iron.
- Grain size—In case of ferritic steels, finer grain size has a large influence in increasing the toughness at low temperatures.

Thus MOC selected for the processing of NGL is to meet the requirements of the mechanical properties mentioned above. The material selected with decreasing low and cryogenic temperatures are fine grained C–Mn steel, Fe—2.25 to 5.0%Ni, Fe-8 or 9%Ni. Austenitic stainless steel and aluminium can be used up to ∼ absolute temperature. Table 9.13 gives the recommended materials for handling propane, butane, ethane and methane at boiling point under atmospheric pressure.

9.7.5 Gas Sweetening

9.7.5.1 Amine Process

Presence of H_2S in gas is not preferred because of SO_2 pollution when used as a heating medium, or acting as poison for many processes where gas is the feed. The H_2S is, therefore, removed (known as *gas sweetening*) to contain no more than 4 ppm (a quarter grain H_2S per 100 standard cubic feet) before marketing. The removal of acidic gas is done mainly by reacting with an alkaline (alkanolamines) solution of Monoethanolamine (MEA), or Diethanolamine (DEA), or Methyl diethanolamine (MDEA), or Disopropanolamine (DIPA). The gas sweetening unit consists of an absorber and regenerator/stripper operating at the temperature range is 40–60 °C and 100–120 °C, respectively. The gas at high pressure containing H_2S and CO_2 enters the absorber at bottom and comes in contact with the lean amine flowing counter current from top. A simplified flow diagram of amine treating plant

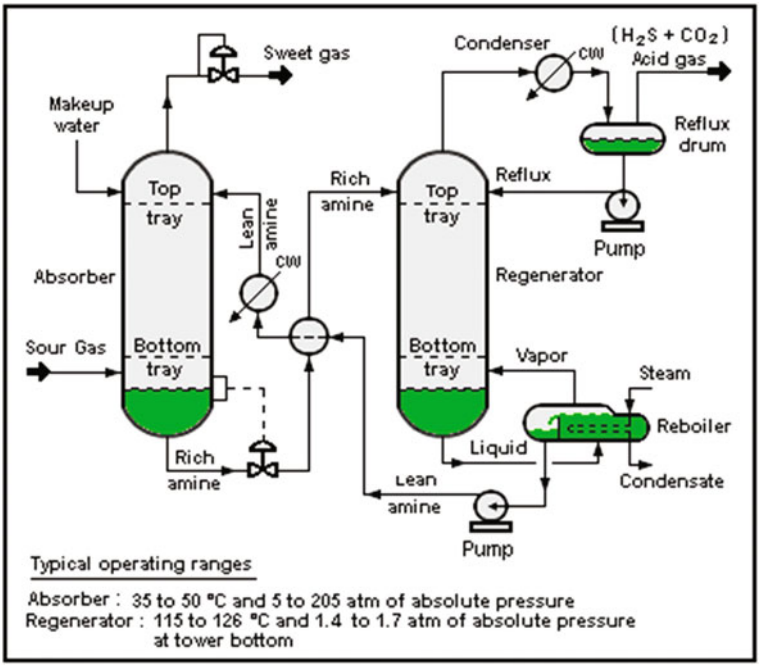


Fig. 9.21 Simplified flow diagram of amine process for gas sweetening [69]

is shown in Fig. 9.21 [69]. Though the process is operated to remove H_2S, some CO_2 is also removed in the process. The acid-rich amine from bottom is heated in rich/amine heat exchanger and the solution going to regenerator top flashes, where the dissolved acidic gases, $H_2S + CO_2$ are released. The cooled lean solution from the exchanger is fed back, after cooling to the absorber top. $H_2S + CO_2$ + water vapour are cooled in condenser and H_2S is sent to the sulphur recovery plant. The bottom and top temperature of stripper are maintained with the help of re-boiler and reflux from bottom and top respectively. Amine process is also used in treating of refinery sour water for the removal of H_2S and CO_2 in the production of hydrogen.

Amine Degradation

Amines are normally considered to have a low corrosion potential and all equipment are made of carbon steel except a few. However, corrosion is faced primarily because of contamination of the solution with high temperature degradation products of amines and to some extent from dissolved acidic gases. Known as *heat stable salts* (HSS) like formate, oxalate, acetate, thio-cyanate, etc., they not only make the solution corrosive but also affect amine solution's acid gas carrying

capacity [70, 71]. As the lean amine is fed back in the system there are possibilities of build up of corrosive salts in solution, which is to be avoided.

Amine Reclamation

According to Dow [72], purification of MEA is done by using sodium carbonate (preferred as it does not cause SCC of carbon steel) or caustic by semi-continuous distillation in a reclaimer as per the arrangement shown in Fig. 9.22. First the solution is neutralized and then heated to distil off MEA and water and neutralizing by semi-continuous distillation in a reclaimer/regenerator as part of the gas sweetening process. At the beginning of the reclaiming cycle, the reclaimer is filled with lean amine solution. During filling, a strong base such as sodium carbonate (Na_2CO_3) or sodium hydroxide (NaOH) is added to the reclaimer to neutralize the stable amine salts present in solution. Heat is then applied to the kettle and water vapour and MEA are distilled off the top. The contaminants consisting of degradation products, 1-(2-hydroxyethyl), imidazolidone-2 and N-(2-hydroxyethyl) ethylenediamine, and non-volatiles such as inorganic ions, iron sulphide, high boiling hydrocarbons, and heat stable salts are drained off from the bottom.

Corrosion Control

MOC is primarily carbon steel but use of corrosion resistance stainless steel (normally 304L) is advisable for some equipment and piping as stated below:

- Top section of stripper, where acidic gases are present, should be made of stainless steel (304L solid or clad).
- Lean/rich and re-boiler tube bindle will be of 304L.
- The reflux condenser and the accumulator will be of 304 (cladded).
- The rich solvent let-down valve and subsequent piping to the stripper will be of 304L.

In addition, some additional precautions are needed, such as:

- Acid-rich MEA is more corrosive than DEA and, therefore, the concentration of MEA and DEA should be restricted to 10–20 and 20–30 weight percent, respectively.
- As far as loading of amines with acidic gases is concerned, it should be in the range of 0.25–0.45 mol acid gas/mole MEA, and 0.5–0.6 mol acid gas/mole DEA
- Velocity of the amine solution for carbon steel shall be maximum 1 m (3.5 feet) per second.
- LP steam will be used in re-boiler to minimize formation of heat stable salts.
- Some inhibitors for amine system have been developed and are available in the market.

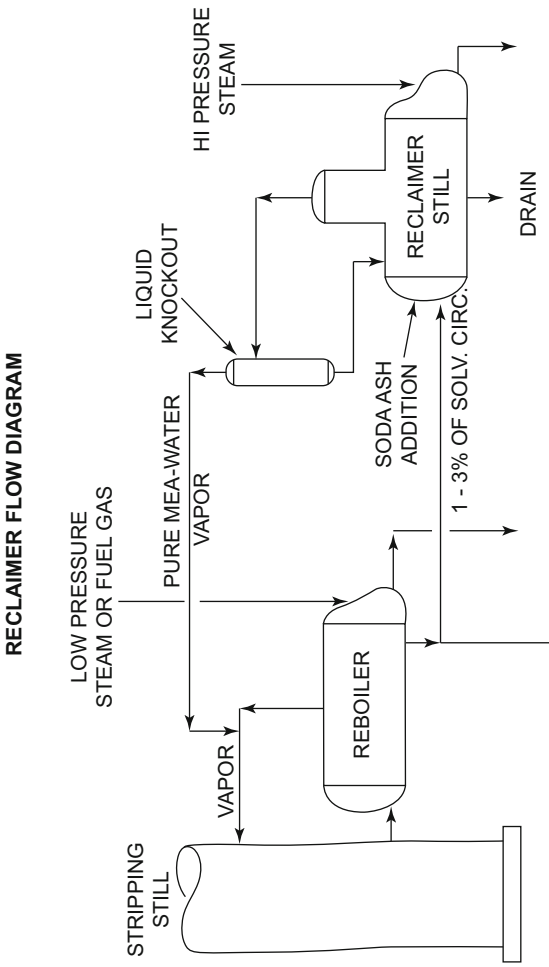


Fig. 9.22 Reclaimer section of amine process flow diagram

Stress Corrosion Cracking

Carbon steel is susceptible to SCC in amine solutions and the susceptibility depends on type of amine, its concentration and temperature and varies in decreasing order of MEA, DEA, MDEA and also DIPA. The cracking occurs at welds and to prevent this type of failure the welds are to be stress relieved. As it is 100% environment related, PWHT is to be done independent of the code requirement in all welds including attachment and repair welds. API 945 [73] recommended PWHT guideline for the prevention of SCC of carbon steel is given in Table 9.14.

If stress relieving (PWHT) is carried out locally in a pipe or vessel, it is necessary to ensure that the residual stress is lowered below threshold limit, which is quite low (172 MPa or 25 ksi) in case of amine. For this purpose, the requirements as per API 945 for pipes are given in Table 9.15. Similar approach should also be applicable for equipment which is not given PWHT in furnace and locally stress relieved.

(a) Minimum heated band width should be as follows (Table 9.15):
(b) Insulate over the total heated band width and a 230-mm (9 in.) minimum runout on both sides, using at least a 50 mm (2 in.) thick insulation blankets.
(c) In the case of flange welds, insulate the entire flange inside and out, and a 230 mm (9-in.) run out of the pipe side of the weld.
(d) If possible, close off the ends of the pipe to minimize convection currents.

In a recent meeting of Task Group of API to assess the existing status with regard to API 945, the following issues were identified [74]:

(a) The PWHT temperature range is different than the NACE document on environmental cracking and API 582.
(b) More detailed consideration on local PWHT (e.g., to reflect WRC Bulletin 452 Recommended Practice).
(c) Company practices have evolved over the past 15 years where all carbon steel equipment irrespective of amine type and temperature are subjected to PWHT.
(d) Much broader use of stainless steel.

Table 9.14 PWHT of carbon steel in amine service (API 945)

Medium	Temperature	Remarks
MEA	For all CS equipment regardless of temperature	
DEA	For all CS equipment operating above 60 °C	
DIPA	For all CS equipment regardless of temperature	Effect of heat tracing and steam out should be considered
MDEA	For all CS equipment operating above 82 °C	Only few instances have been reported above 88 °C

Note Many companies however practice PWHT of all carbon steel equipment irrespective of amine type and temperature

Table 9.15 Recommended local PWHT procedure as per API 945

Nominal pipe size	Minimum heated band width
19–25 mm (3/4–1 in.)	102 mm (4 in.)
38–76 mm (1 1/2–3 in.)	152 mm (6 in.)
102–152 mm (4–6 in.)	203 mm (8 in.)
≥203 mm (≥8 in.)	$BW = 4.12\sqrt{Rt} + 50.8$ mm or 203 mm minimum

Where,
BW Heat band width
R Pipe radius (outside diameter)
T Pipe wall thickness

(e) Corrosion experiences and mitigation methods may have evolved, including the adoption of IOW's by many operators and the new RP API 584 IOW document.
(f) Expanded surface preparation guidance prior to making weld repairs may be needed.

Based on the discussion it was decided to issue revised document by the end of 2013.

9.8 Offshore Platform

The offshore field consists of number of well heads from where the oil/gas/formation water/condensate flows to a central platform through gathering lines. These are then processed in the central platform or transported onshore to separate oil, gas and produced water. For this purpose, necessary structures are to be provided both at well heads and processing location. In case of deep waters and far off locations from shore, FPSOs, anchored at desired locations are used. A platform not only has costly installations on it but also has living accommodation of a number of staff who live and work in shifts. It is, therefore, important that health of the platforms be maintained all through its life time. In this connection major emphasis is on preventing the deterioration of the platform under harsh marine conditions.

9.8.1 Protection of Offshore Platform Against Corrosion

The platforms rest on sea bed/semi-submerged condition and their various sections are exposed to different conditions which can be divided into the following zones:

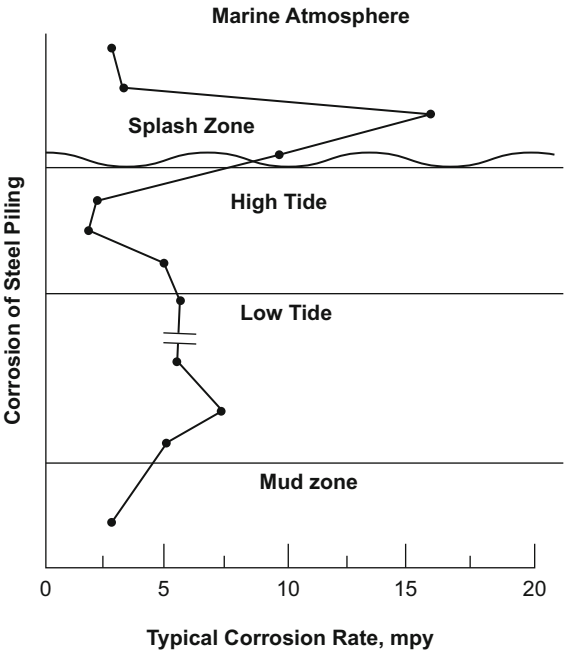


Fig. 9.23 An offshore platform and risers have zones of different corrosion rates [75]

1. Totally immersed in sea water.
2. Exposed to tidal zone.
3. Exposed to splash zone.
4. Above splash zone, exposed to marine atmosphere.

Corrosion rates of steel under these conditions vary with maximum in the splash zone as shown in Fig. 9.23 [75]. The preventive measures in different areas are, therefore, also different.

9.8.1.1 Cathodic Protection

The underwater portion of platform is not coated, but cathodically protected. Normally aluminium galvanic anode (Galvanum III) is preferred. These are fitted on the tubular cross members of the structure. The anodes are fitted during fabrication of the platform based on design calculations. If after installation at site the protective potential is not attained after a reasonable period, retrofitting is done with modified design. Retrofitting/replacement of anodes also become necessary during the lifetime of a platform because galvanic anodes have a finite life. Various retrofitting methods have been developed which can be installed with and without the help of divers.

Use of impressed current CP by normal method is limited for platform because of closeness of structural members. However, attempts have been to use anode sled placed on the sea bottom at a location which ensures proper distribution of current

to achieve the protective potential on 100% of surface. Impressed current anode sleds have been successfully installed upto a depth of 850 feet of sea water. The major problem with this system is the protection of power supply cables against damage and power generating source. In well platforms, the latter facility is not always available. The advantage of impressed current is the long life of anodes and lowering weight of the platform as the galvanic anodes add to the load.

9.8.1.2 Coating

Above mean sea level (MSL), the members in the tidal zone are intermittently exposed to sea water. Thus this section of the platform is only partially protected by cathodic protection. The corrosion rate in the splash zone falls between 0.5 and 1.5 mm/year, depending on location and season. The very high corrosion rates are caused by extended periods of wetness and high concentrations of chlorides that accelerate corrosion. Corrosion rates in the splash zone also increase dramatically at the higher surface temperatures found in hot riser pipes, which connect the production to central platform constructed from the sea floor to the platform or vice versa. At 90 °C, corrosion rates can reach very high value. Thus considerable care is to be taken to control corrosion in this zone as any leak can have disastrous consequences. The splash zone, therefore, requires heavy duty protective coating as cathodic protection is not effective in this area. As maintenance painting is difficult and costly (compared to onshore) long lasting systems should be selected. Splash zone corrosion is of similar importance for risers. Here good quality coating is a must as any leakage due to corrosion can result in fire/explosion and pollution. Neoprene is normally used in this zone though other coatings are also available. Coatings age with time and, therefore, a more reliable long lasting system is desirable. Coating selection and application have to be done with inputs from coating manufacturers, paint specialists and, wherever possible, inputs of performance under similar conditions. Finally, it is the surface preparation which determines the performance of coating. It has been estimated that 85% of failures have occurred due to deficiencies in surface preparation. Table 9.16 [76] gives some of some of the system which can be considered.

Table 9.16 Paint/coating system for offshore platform

Area	Corrosion rate (mpy)	Paint coating system				
		First coat	Intermediate coat	Final coat	DFT	
					Micro M	Mils
Atmospheric zone	3–8	Zinc rich primer	Epoxy	Poly urethane	320	13
Splash zone	8–20	Epoxy	Polyester[a]		600	24
Immersed and tidal zones	4–8	Epoxy + CP/partial effect of CP in tidal zone			450	18

[a]Use of glass flake epoxy or polyester can be considered in splash zone but only in areas which are not likely to be mechanically damaged due to boats or floating objects

9.8.1.3 Sheathing of Legs and Risers

While conventional high quality coating and wrapping form the main line of defence, many operators like to provide additional protection by providing corrosion-resistant metallic sheathing. In 1950s, during the development of Gulf of Mexico offshore fields, sheathing with Monel^{TM} was introduced and proved to be very successful because of its high resistance to seawater corrosion [77]. Use of Monel^{TM} was restricted because of its high price but with the development of cupronickel alloys, 90Cu–10Ni is being increasingly used for sheathing [78]. In case of splash zone, sheathing should span at least from below mean tide level ($\sim$2 m) to well into the atmospheric zone. The 4–5 mm thick sheet is formed and welded to the legs and risers (Fig. 9.24) using 3-bead technique to avoid dilution effect. A mechanical method to fit the sheath in old platform has also been successfully used. It consists of propelling pointed needles at high velocity, using air gun, on the sheath fitted around the legs. Galvanic corrosion at the junction of steel and Monel^{TM} or Cu–Ni alloy does occur, but the effect is not very serious and is addressed by providing heavy duty coating in the top section; the location in the submerged section is taken care of by cathodic protection provided to the structure. This approach is also applicable for the risers.

Another problem of concern in this area of legs and riser is excessive bio-fouling resulting in drag and the necessity of undertaking frequent cleaning. Wherever this problem is serious, need to control bio growth is essential. In case of high copper containing 90Cu–10Ni the slow corrosion provides sufficient copper ion at metal/sea water interface to inhibit the marine growth. It may be mentioned that the high nickel containing Monel^{TM} does not have the anti-bio-fouling property. In case

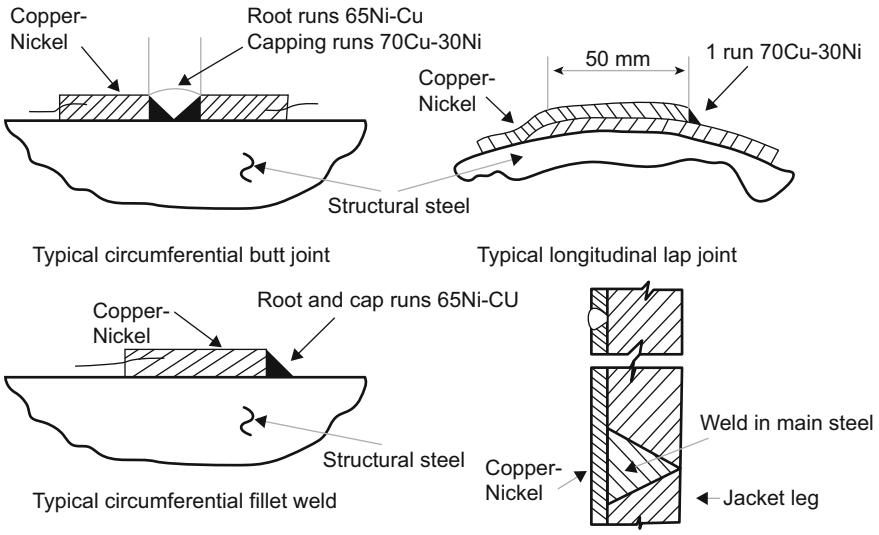


Fig. 9.24 Sheathing of platform legs with Cu–Ni alloy

where only control on bio growth is required, the cupronickel is not welded but wrapped with an insulating layer of material like neoprene, between the sheath and leg.

9.8.1.4 Corrosion Fatigue of Platform Structure

The platform is subjected to various stresses and due to wave action the platforms sways with frequency of wave motion. Anybody working on offshore platforms constantly feels the movement. This alternate movement induces alternate stress on structural members. Combined with corrosive effect of seawater, corrosion fatigue can initiate and propagate the crack. Normally, fatigue cracks occur at nodes of the platform structural members or at any defect in the structural members. The capsizing of platform Alexander Kielland in 1980 during the storm in the North Sea highlighted the importance of fatigue. Initiation and propagation of fatigue crack from a small 6 mm fillet weld of hydrophone on one of the bracing connected to the vertical column resulted in other bracings being broken off. The accident resulted in the death of 112 personnel [79]. Risers in FPSO and the special steel catenary riser (SCR) in deep sea areas need to have high resistance to fatigue as these are exposed to very large dynamic stresses from the currents and the movement of the ship, both horizontally and vertically.

9.9 Protection of Long-Distance Cross-Country Pipeline

9.9.1 Cathodic Protection

Products like crude, gas, etc., are to be transmitted to long distances through pipeline, either for local use or for export (terminals). Normally, these are laid underground and are coated and supplemented with CP. Impressed current is used by locating anode beds at predetermined distances along the pipeline. Each anode bed provides certain amount of current to protect specific length. This is shown in Fig. 9.25. The same is repeated again and again till the total length attains a protective potential of minimum −850 mV against $Cu/CuSO_4$ electrode. The distance between anode beds is determined on the basis of quality of coating, total area to be protected, soil resistivity, etc. If two or more pipes are laid side by side or cross each other, they can interfere with each other if only one line is protected. Such interference should be avoided by taking proper action otherwise the unprotected line shall also pick up the current and drain it back to protected pipe. Under this condition, the unprotected pipe shall corrode at the point of drainage.

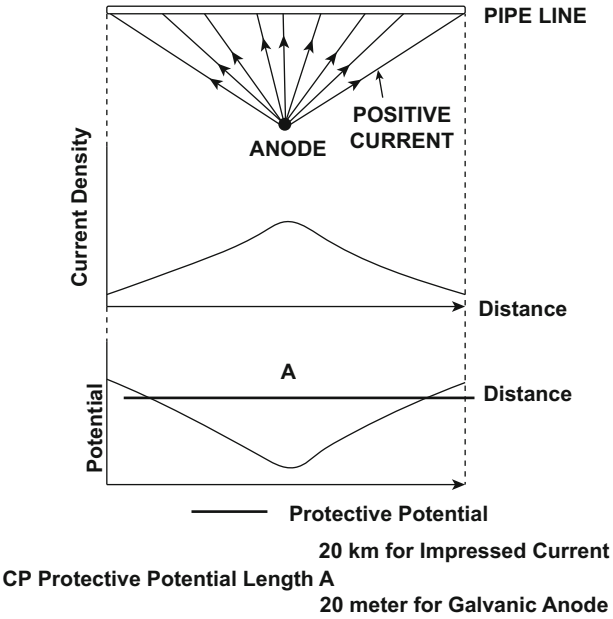


Fig. 9.25 CP of cross-country line comparing protective range of galvanic and impressed current systems

9.9.2 Soil Side SCC

In underground carbon steel gas pipelines, soil side stress corrosion cracking is experienced. The problem has been studied extensively and has been reviewed in greater detail [80–82]. There are two forms of external SCC, that is, high pH SCC and near-neutral pH SCC having intergranular and trans granular modes of cracking. Both forms of SCC develop colonies of longitudinal surface cracks that link up to form flaws of sufficient size to cause leaks or ruptures. As regards the environment, near-neutral SCC occurs in the presence of dilute groundwater containing dissolved CO_2 where pH is in the range of 6.0–8.0 and CP is either absent or not adequate. The intergranular SCC in high pH environment (>9.5 pH) is also related to CO_2 where under the influence of cathodic protection the pH of the electrolyte beneath de-bonded coatings increases. This results in CO_2 to dissolve in the high pH electrolyte and form a concentrated CO_3–HCO_3 (carbonate/bicarbonate) solution in which carbon steel is susceptible to SCC. Coating has a large role to play which has occurred both under asphalt, wax and coal tar enamel coatings and also polyethylene/polyvinyl chloride (PVC) tapes. Here the major cause is de-bonding of coating resulting in shielding of the CP current in the affected area. The near-neutral-pH form of SCC is most prevalent on tape-coated pipelines, while high pH SCC has occurred most frequently on coal tar coated

pipelines. Fusion-bonded epoxy (FBE)-coated pipelines are very resistant to SCC. As per Canadian Energy Pipeline Association (CEPA) [80], of 37 failures recorded (17 leaks and 20 ruptures) between 1977 and 2007 on Canadian transmission line most of the failures were associated with polyethylene tapes against fewer with asphalt and coal tar enamel. Figure 9.26 shows cracks in neutral pH condition aligned along the toe of the long seam weld in neutral soil under polyethylene tape coating. Table 9.17 summarizes the various factors that determine near-neutral and high pH SCC of underground pipeline. Soil side SCC failures of underground pipeline are longitudinal but six of the failures experienced in Canada were found to be circumferential in nature. On the basis of National Energy Board (NEB) recommendations CEPA examined this type of failure and their findings and recommendations form part of the 2007 report. Under near-neutral condition SCC occurs under spiral-wrap tape where tape passes over a seam or irregular contour. Here water penetrating the coating accumulates and thus increases the possibilities of cracking. The cracking is circumferential and is more likely to occur where pipeline is designed based on high maximum allowable operating pressure (MAOP) compared to one designed with lower MAOP. Any SCC to occur, the stress has to exceed a minimum tensile strength (endurance stress) and this stress can be reached in case the pipeline design is based on high maximum allowable operating pressure (MAOP) of say 72% of specified minimum yield strength (SMYS.) Pipelines designed with lower MAOP of say 30% are unlikely to develop circumferential crack.

The important steps in the prevention of soil side cracking of pipelines are:

1. Coatings with good adhesion, good resistance to disbonding, electrical insulation and low water permeability be used.
2. Preferable coatings are fusion-bonded epoxy, urethane and liquid epoxy, multilayer or composite coatings, and extruded polyethylene.
3. Coating procedure should be properly developed to ensure good adhesion and freedom from disbonding.

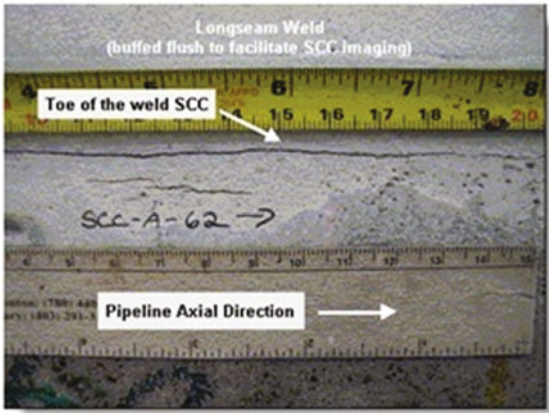


Fig. 9.26 SCC along toe of weld in near-neutral soil [80]

Table 9.17 Characteristics of high pH and near-neutral SCC of pipeline (NEB 1996)

Pipeline	High pH SCC	Near-neutral pH SCC
Location	• Typically within 20 km downstream of pump or compressor station • Number of failures falls markedly with increased distance from compressor/pump and lower pipe temperature • SCC associated with specific terrain conditions, often alternate wet–dry soils, and soils that tend to disbond or damage coatings	• 65% occurred between the compressor station and the 1st downstream block valve (distances between valves are typically 16–30 km) • 12% occurred between the 1st and 2nd valves • 5% occurred between the 2nd and 3rd valves • 18% occurred downstream of the 3rd valve • SCC associated with specific terrain conditions, often alternate wet–dry soils, and soils that tend to disbond or damage coatings
Associated electrolyte	• Growth rate increases exponentially with temperature increase	• No apparent correlation with temperature of pipe • Appear to occur more frequently in the colder climates where CO_2 concentration in groundwater is higher
Electrochemical potential	• −600 to −750 mV ($Cu/CuSO_4$) • Cathodic protection is effective to achieve these potentials	• At free corrosion potential: −760 to −790 mV ($Cu/CuSO_4$) • Cathodic protection does not reach pipe surface at SCC sites
Crack path and morphology	• Primarily intergranular (between the steel grains) • Narrow, tight cracks with almost no evidence of secondary corrosion of crack wall	• Primarily trans granular (across the steel grains) • Wide cracks with evidence of substantial corrosion of crack side wall

4. Grinding of all weld protrusion to ensure bonding of the coating with pipe wall.
5. Ensuring that maximum pipe/soil potential does not exceed—1.1 V against $Cu/CuSO_4$ electrode.
6. In case of gas transmission lines, the outlet temperature downstream of compressor station is high and most of the high pH cracking occurs in the first 15–20 km of compressor station. This section of pipeline should be provided with improved coating system.

9.10 Corrosion Monitoring

In the oil and gas production, corrosion monitoring is as important as corrosion control, especially because of large investment, scattered nature of installations, environmental considerations and different types of measures which are required to

be used. The objective of corrosion monitoring is not only to determine the corrosion rates but also to assess the degree of effectiveness of the corrosion control measures. The selection of monitoring method will depend on the expected nature of corrosion damage, type of facilities, approachability and, therefore, there is no fixed method which is to be used. However, methods which give general corrosion rate combined with periodic inspection form the core of monitoring and largely used under all conditions. Various monitoring techniques have been discussed in Chap. 8 and some of the commonly used techniques in oil & gas industry are described next.

9.10.1 Iron Count

Iron and sometimes manganese count is simple to perform and gives a broad indication and is quite popular, especially for well and pipe line corrosion. It is essential that a representative sample is collected so that iron from formation is not included as corrosion loss. If possible, a base count should be conducted on a down hole sample. If the pipeline corrosion is the objective then analysis at inlet and outlet ends of pipeline is carried out and corrosion rate established assuming uniform corrosion of line.

9.10.2 Coupons and LPR and ER Probes

These versatile methods are suitable and used extensively in most of the facilities except the down hole. The coupons or the probes can be inserted and retracted online at also very high pressures. It is important that these are placed at locations where there is presence of water phase.

9.10.3 NDE Techniques

Ultrasonic thickness measurement, radiography, flaw detection, use of normal pigging and intelligent pigging (for pipeline) are used as required.

9.10.4 Special Techniques

Electrochemical techniques, test loop, hydrogen probe, oxygen analysis, bio probe, sand probe and various other online techniques are available and are useful.

9.10.5 Monitoring of Cathodic Protection

Monitoring of cathodic protection is primarily to ensure that minimum protective potential is maintained. The technique used varies depending on the particular situation. A cathodically protected onshore pipeline is monitored by periodic measurement of pipe to soil potential at test points and recording of current and voltage output of rectifier. Use of CPL (Chap. 8) survey has increased during the last two decades. These are normally carried out after 5–6 years or when some major coating damage is suspected.

Monitoring of CP in offshore platform presents considerable challenge. In offshore platforms, the potential of galvanically protected system is best monitored by a diver. However, in case of impressed current cathodic protection system, it is preferred to permanent reference electrodes (zinc/seawater) fitted at critical locations. The leads from these reference electrodes are connected to the control room and automatic recording of potential is done. The CP monitoring of underwater piping is more difficult because of depths involved and closely spaced anodes. Manual recording of potential is not only costly but in many situations not practically feasible. Remote control Cathodic Protection Survey Systems have been developed for this purpose, the two of the popular ones being:

1. Remote Operating Vehicle (ROV)
2. Towed Fish Technique (TFT)—Not very reliable and presently not being used.

In case of ROV, a submerged vehicle carrying reference electrode array moves along the pipeline and data collected are recorded with cathodic protection survey system (CPSS) software and automatically recorded. After the vessel comes on the surface, the data are analysed. A typical plot from such a survey is shown in Fig. 9.27 [83]. This type of survey will let the operator see the condition of the line and make informed decisions regarding retrofitting. The depth up to which it can be operated depends on depth rating of the ROV. In TFT, on the other hand, the reference anode is towed along the pipeline from a boat travelling on the pipeline route at speeds up to 5 knots. Real time data with 0.005 mV accuracy are recorded. TFT method has been used upto a depth of 450 FSW, but its reliability is in doubt and presently not in use.

9.10.6 Assessing Corrosion of Underground and Subsea Transmission Line Using In-line Intelligent or Smart Pig

While normal monitoring aids like LPR and ER would give an overall idea of internal corrosion in a pipe line, it is essential to assess actual nature and extent of corrosion damage on both ID and OD of the line. The industry today also wants to know in greater detail the nature of damage and how it will affect the integrity of the

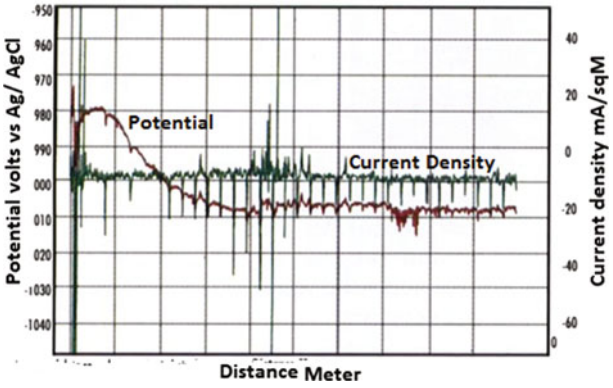


Fig. 9.27 Detailed offshore pipeline CP inspection plot [83]

line. In addition, there are some defects which might have been introduced during the construction and laying of the pipeline. As underground and submerged pipelines are not approachable from inside or outside and the lengths are long, special NDE tools are required to be used. The tool used for examination can only be propelled through the pipeline from one end (launcher) and collected at a suitable location downstream (receiver) at a distance which may vary from a few kilometres to tens of kilometres. During its passage through the pipeline, the tool measures the change in pipe wall defects along the whole circumference, identifies the location of damage and whether the same is on internal or external wall of pipe. In addition to taking the measurement, the tool has to record the same so that the data can be retracted after the tool is retrieved at the end of run. The NDE techniques used are magnetic flux leakage (MFL) and ultrasonic thickness (UT)

9.10.6.1 Magnetic Flux Leakage (MFL) Tool

The MFL tool consists of a number of strong permanent magnets placed along the periphery of a pig, so as to cover the full 360° of the pipe's circumference. The magnets are very strong so as to fully saturate the tube wall. At the locations of internal or external metal loss, the magnetic flux 'leaks' out of the pipeline, which is picked up by sensors from which the location of the defects can be accurately inferred. By this technology very small pitting defects can be detected even when the pipe surface is in poor condition. The data collected is recorded in another pig containing the recorder package. In addition there is a third pig on which the battery package is mounted. All the pigs are then connected through swivel joint for smooth running of the inspection tool. The arrangement is shown schematically in Fig. 9.28a along with an original smart pig in the process of being launched (Fig. 9.28b) [80]. For inspection, the tool is inserted in the pipe at launcher and propelled through the pipe by the transporting fluid, and then retrieved at another

point along the pipe line at receiver. The distance up to which the data is collected depends on the capacity of the battery. After retrieval the data collected is analysed using the various programs and the basic deficiencies in the pipe identified. There are programs by which the total contour and area of the localized defect is developed. The small peaks seen on left hand show the locations of pipe weld. The tool also measures the distance travelled after the same is launched and, therefore, it is possible to indicate the location of damage. In case of underground lines, pits are dug around identified locations and damage physically verified visually and by ultrasonic technique for external and internal defects, respectively. Based on the results, necessary corrective actions are planned. Similar approach is also used for offshore lines but here steps are to be taken based on depth at which the defect exists.

9.10.6.2 Ultrasonic Tool (UT)

The UT smart pig is similar in construction as the MFL tool except that ultrasonic probes are fitted in place of permanent magnets. Its advantage over MFL tool is that it measures actual wall thickness having two dimensional features. The MFL technique is sensitive to localized changes in wall thickness, but rather insensitive to very gradual and smooth changes in wall thickness, since they do not crate sufficient magnetic flux leakage signals. Consequently, direct measurement of smooth grooving or uniform corrosion goes undetected. On the other hand, UT tool measures thicknesses and, therefore, are more reliable than that calculated indirectly from MFL data. The disadvantage of the UT inspection method is that it cannot

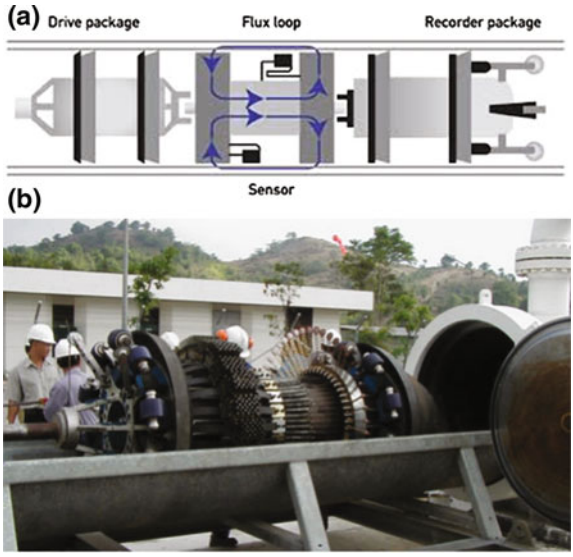


Fig. 9.28 **a** Schematic view of various components of smart pig. **b** In-line inspection tool being loaded into a 'pig launching barrel' [80]

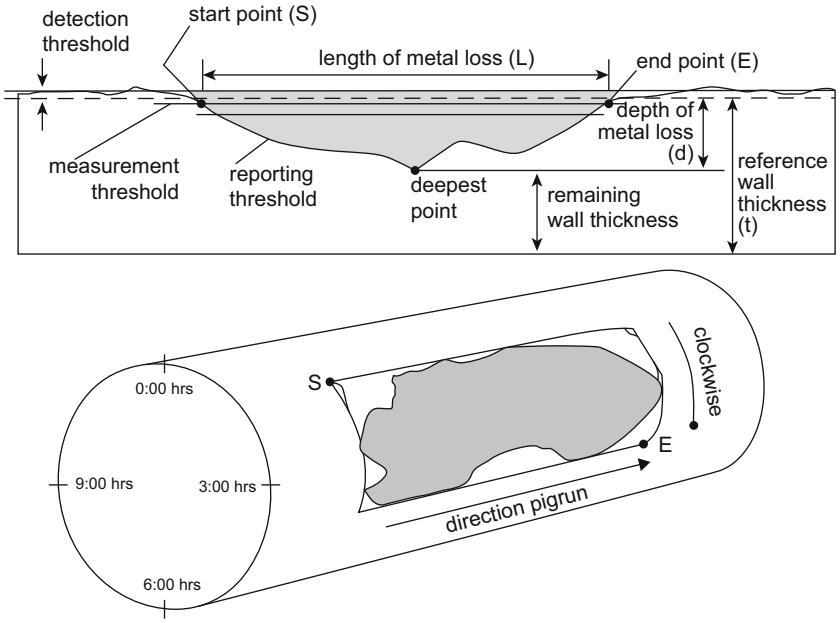


Fig. 9.29 Mapping of damage based on data collected by smart pig [84]

detect defects which are smaller than 10–20 mm in length. Further, presence of debris interferes with accuracy of result and thus significantly reducing the probability of defect detection thickness.

Smart tools were commercially introduced in 1970s. Starting with simple identification of the affected area, the technique has been constantly improved over a period and today advanced programming and software have been developed by which information on defect shape (Fig. 9.29) [84], geometric measurement, pipeline routing, metal loss, crack or other defects are detected during their passage through steel pipelines. Pipe operators today not only want to know the exact extent of damage but also combine it with asset integrity and operational risk management. Specifications on operational and reporting requirements for tools, to be used for geometric measurement, pipeline routing, metal loss, crack or other defect detection during their passage through steel pipelines has been prepared by Pipeline Operator Forum (POF) [84]. Data required for such elaborate study cannot be fully served individually by the MFL or UT tools but in combination they can provide high accuracy in length, depth and width measurements for exact defect shapes, and precise information on general wall thinning. To collect the maximum information, running of both the tools substantially increases the cost of inspection.

Table 9.18 Companies providing pipeline inspection services

Company	Country	Website
Baker Hughes/CPIG	Canada	www.bakerhughes.com/PMG
BJ Pipeline Inspection Services	Canada	www.bjservices.com
GE/PII	U.K.	www.gepower.com
Magpie/TDW	USA	www.magpiesystems.com
NDT	Germany	www.ndt-ag.de
NGKS	Russia	www.ngksint.com
Pipecare	Norway	www.pipecare.com
3P Services	Germany	www.3p-services.com
Rosen	Germany	www.Roseninspection.net
Tuboscope	U.S.A.	www.tuboscope.com

9.10.6.3 Combined MFL and UT Tool

To overcome the problem associated with running both MFL and UT tools, M/S ROSEN has developed, using in-house advanced technology, a new tool RoCorrUT™ which combines the two so that they ideally complement each other [85]. As a result, highly reliable information is provided with regards to metal loss as well as weld, geometry and pipeline wall features. In addition, both the probability of detection (POD) and the probability of identification (POI) are significantly increased compared to measurements based on a single inspection technology. It is claimed that inspection tools combining both methods show excellent detection performance for numerous metal loss flaws (e.g. pitting, axial grooving, circumferential grooving), mid-wall features (e.g. lamination, inclusions, blisters), weld features (e.g. girth welds, longitudinal welds, spiral welds), geometry features (e.g. dents, ovalities, misalignments), and other features (e.g. valves, fittings, bends).

There are a few organizations who undertake such highly sophisticated inspection job worldwide. The POF in 2005 identified the companies (Table 9.18) who can provide smart pig inspection of pipelines.

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Chapter 10
Material Selection and Performance in Refining Industry

Abstract In petroleum refining, the equipment are subjected to both high-temperature and corrosion damages. The most common high-temperature attack is related to sulphidation attack both in absence and presence of hydrogen in the processing media. The attack in the presence of hydrogen is much higher than its absence and, therefore, material of construction also varies in two cases. High-temperature attack also occurs if there is presence of naphthenic acid in the crude requiring different considerations in selection of material. The other high-temperature damages like bulging, low cycle fatigue and temper embrittlement are also experienced. Low-temperature corrosion due to presence of HCl and H_2S in the overhead system and sulphide stress corrosion cracking are also of major concern for which specific mechanical and corrosion control measures are to be implemented. The chapter presents problems experienced in different units and steps taken in material selection and implementation of suitable corrosion control and monitoring systems.

Keywords Sulfidation · Naphthenic acid · Hydrogen attack · Sulphide stress corrosion cracking · Overhead corrosion · Sour system

10.1 Short Outline of Processes

Crude oil is a mixture of hydrocarbon having different molecular weight and boiling points. The process of refining mainly involves separation of the organic compounds with different range of boiling points through distillation. The main products from an atmospheric distillation unit are LPG, naphtha, gasoline, kerosene, aviation turbine fuel (ATF), light and heavy gas oil, reduced crude oil, light hydrocarbons, e.g. methane, ethane, propane, etc. are also separated after distillation. The reduced crude oil is generally further distilled in Vacuum Distillation Column to recover vacuum gas oil as distillate. The liquid residue formed from vacuum column bottom is further treated in secondary processing units to produce

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more distillates along with other petroleum products including coke, fuel oil, etc. In addition, various grades of lubricants, wax, benzene, etc. are also produced in some refinery. A simplified flow diagram of various processing units in a refinery is given in Fig. 10.1 [1].

To maximize production of gasoline and middle distillates, secondary processes, e.g. fluid catalytic cracking and hydrocracking are used with mainly heavy gas oil as feed. The present trend is to produce very low sulphur petroleum products to minimize environmental pollution. Sulphur content in naphtha, kerosene and diesel

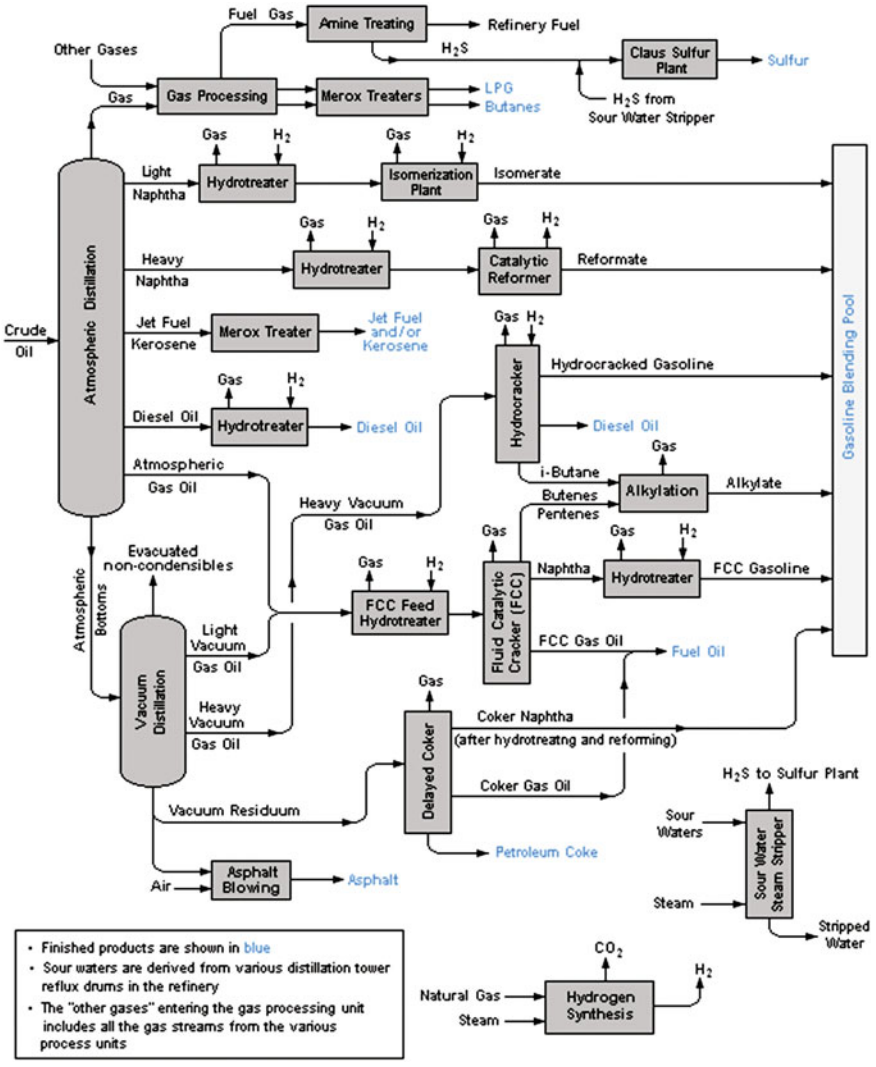


Fig. 10.1 Simplified flow diagram of various processing units in a refinery [1]

are brought down in hydro-treating or hydro-desulphurizing units. Similarly, octane number of gasoline is improved by a process known as reforming. Use of lead compound (TEL: tetra ethyl lead) as an additive for octane boosting may be avoided as it may leads to environmental and health hazards. In modern refineries, alkylate is produced and blended in gasoline to meet the recent specification, e.g. aromatic, olefin and VLI (Vapour Lock Index). In addition, various grades of lubricants, wax, benzene, etc. are also produced in a refinery.

10.2 Considerations in Material Selection

Hydrocarbon is non-corrosive. However, it contains some constituents, as a part of crude oil or extraneous in nature, which cause corrosion. The choice of materials used in refining industry depends on several variables, e.g. quality of crude with regard to sulphur, organic acidity, inorganic salts, hydrogen sulphide and also the presence of hydrogen that forms part of feed in some processes. The operating parameters of importance are pressure and temperatures. The temperature variations determine whether there will be high-temperature attack or corrosion due to the presence of an aqueous phase at the operating pressure. If we look at the flow diagrams with respect to temperature and pressure profiles, it will be apparent that some of the equipment or part of it, operating at lower temperatures, will be having a water phase while the rest will be free from it. The former will thus be subjected to wet corrosion. The equipment at higher temperatures will, on the other hand, be subjected to high-temperature attack by the process fluids. In between, will be a zone of intermediate-temperature where both types of attack will be absent or negligible. Thus for material selection we have to divide any process into three zones, i.e. high, intermediate and low-temperature areas.

10.3 Problems Related to High-Temperature Service

10.3.1 High-Temperature Sulphur Attack

10.3.1.1 Corrosive Constituents in Crude

Crude is a mixture of compounds of carbon and hydrogen having different molecular weights and boiling points. The different fractions (naphtha, kerosene, light diesel, heavy diesel, etc.) falling within a definite range of boiling points, are separated by distillation. Hydrocarbons are by themselves non-corrosive and no problem in their handling and processing is expected from the point of view of damage to the material. However, other than carbon and hydrogen, these contain impurities some of which have damaging effect on materials. The two important

constituents in this category are sulphur compounds and naphthenic acids. Of the above two, sulphur is the most abundant element in the crude and distillates. Sulphur may be present as elemental sulphur, hydrogen sulphide, mercaptans, disulphides, aliphatic/aromatic sulphides and polysulphide. The various forms of sulphur attack the material of construction only at high temperatures (except hydrogen sulphide which is corrosive at low temperatures). Sulphur attack, known as *sulphidation*, occurs above 230 °C, the rate increasing with increase in temperature.

10.3.1.2 Prediction of Sulphur Corrosion

In material selection it is essential that the corrosivity of crude can be predicted from the sulphur content of the crude. The rate of attack for the different sulphur compound, however, is not the same because of their different sulphidation potential. This is the reason why the corrosivity of sulphur in hydrocarbon is not proportional to weight per cent of sulphur as in case of a chemical mixture. If analysis of specific sulphur compounds, such as, H_2S, mercaptants, sulphides, poly sulphide is known it may be possible to predict crude corrosivity with greater accuracy. The general practice is to report analysis of sulphur in the crude or its fractions as total sulphur. Total sulphur above 0.5% (some designers use 0.2% as the limit) is known to be corrosive to carbon and low alloy steels at higher temperatures. As regards selection of material, the first choice is carbon steel which is then upgraded to alloy steels once the operating temperature reaches beyond a limit when the rate of sulphidation becomes too high. This temperature, which can be called as carbon to alloy steel break temperature, is not fixed and different temperatures have been used by refiners over the years. A summary of some of the practices are given in Table 10.1.

It has to be kept in view that in addition to temperature, other important consideration in fixing the transition temperature are the sulphur content, single or multi-phase flow, velocity/turbulence/impingement effect, and the nature of equipment. For example, the temperature limit in case of exchanger tube and pumps would be lower because of low thickness and higher turbulence respectively. On the other hand, the temperature limit would be higher for say exchanger shell, vessel because in these cases higher corrosion allowance (CA) can be provided. Transition temperatures of 260 and 290 °C would be appropriate, which is confirmed from proven performance of stainless steel 410 cladding provided up to a height above diesel draw off point in crude distillation column where temperature is ~300 °C (Diesel Fraction 220–320 °C) with column draw off temperature of ~300 °C in crude distillation unit.

The iron sulphide film formed as a result of sulphur attack is protective but beyond a certain velocity and temperature the film breaks down, resulting in accelerated corrosion. Quite early in twentieth century it was found that by alloying with chromium, resistance to high-temperature sulphur attack of iron can be increased. Based on industry experience and survey data by API effect of sulphur

Table 10.1 Carbon to alloy steel break temperature in case of sulphidation

Degree of corrosion	Temperature	Remarks	Reference
Relatively un affected	<260–290 °C		[2, 3]
Highly variable/marginal performance	290–345 °C 260–315 °C		[2, 3]
High corrosion rate	>290 °C >315 °C		[2, 3]
Corrosion rate (mils/yr.) vs. temperature for 1.1 to 2%S and $\leq$ TAN	<230 °C, 231–260 °C, 261–290 °C 2 5 15 291–315 °C, 291–340 °C 30 50	Corrosion increases above 260 °C	[4]
Beneficial effect of silicon in steel	>260 °C		[5]
Carbon to alloy steel break or transition temperature	290 °C; Also used 260 °C and 315 °C 340 °C—vessel; 290 °C—piping/heater tube; 230 °C—pump 260–290 °C		[2, 4, 6, 7]

on high-temperature attack in the absence of hydrogen was prepared which is known as McConomy curves [8]. The corrosion rates obtained from the original curves were found to be conservative and therefore modified McConomy curves were published for 0.6 wt% sulphur along with correction factor for variation in sulphur content of crude from 0.4 to 4.5% [9]. Thus to predict the relative corrosivity of crude oils and their various fractions having high sulphur (in the absence of naphthenic acid and hydrogen), normally the modified McConomy curves shown in Fig. 10.2 are used. The sulphidation attack increases with temperature and then decreases above 455 °C, which is believed to be due to coke formation on metal surface.

The scale formed on carbon steel during sulphidation has a composition of $Fe_{1-x}S$, which is a metal deficient iron sulphide. When alloyed with chromium a two-layered scale is formed which consists of a mixed inner layer of $Fe_{1-x}S$ plus a sulpho-spinel $FeCr_2S_4$, and an outer layer of $Fe_{1-x}S$. With increase in Cr there is a change in the inner layer towards single phase $FeCr_2S_4$, which is more stable and protective [10, 11]. Other steps [12, 13] identified for the sulphidation mechanism include:

1. Adsorption of the sulphur compounds on the scale surface.
2. Catalysed decomposition of the sulphur compounds and inclusion of sulphur in the $Fe_{1-x}S$ scale which forms additional cation vacancies and electron holes.
3. Diffusion of cation vacancies and electron holes to the $Fe_{1-x}S$/Fe interface.
4. Reaction at the $Fe_{1-x}S$/Fe interface whereby Fe "oxidizes" into the scale and reduces the concentration of cation vacancies and electron holes.

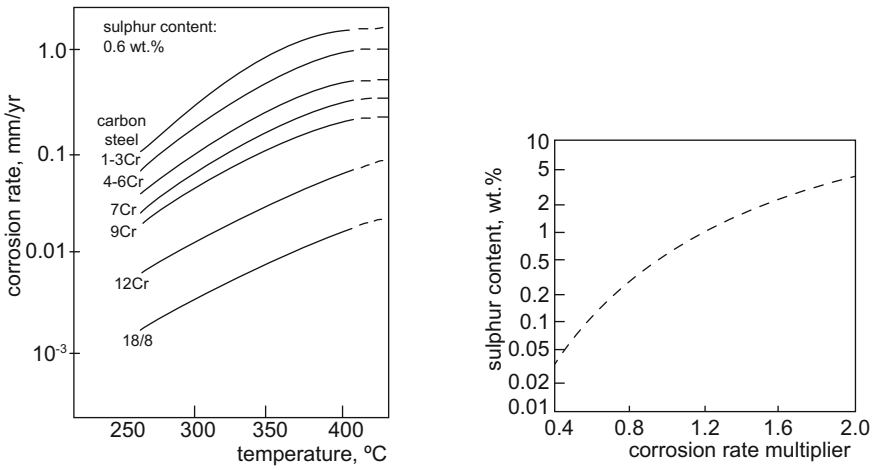


Fig. 10.2 Modified McConomy curves showing effect of sulphur in crude on high temperature attack of various alloys along with multiplier factor above 0.6%S [9]

In H_2-free environments steps (1) or (2) is the rate-limiting step [13, 14]. The role of chromium is believed to be related to poisoning of catalytic decomposition of sulphur compounds and reducing the diffusion of various species through the scale.

10.3.2 High-Temperature Naphthenic Acid Attack

10.3.2.1 Naphthenic Acid

Naphthenic acid (NAP) is a generic name used generally for all the organic acids present in crude oils having the chemical formula $R(CH_2)_nCOOH$, where R is a cyclopentane ring and is typically greater than 12. Naphthenic acid attacks iron to form Fe-naphthenate and in the process releases hydrogen. The reaction, which takes place in the absence of water, can be stated as:

$$\mathrm{Fe} + 2\,R\mathrm{COOH} = \mathrm{Fe}(R\mathrm{COO})_2 + 2\mathrm{H}^+ \tag{10.3.1}$$

$$2\mathrm{H}^+ + 2\mathrm{H}^+ = \mathrm{H}_2 \tag{10.3.2}$$

A part of hydrogen atoms also diffuses through the metal and recombines at outer wall. This flux of H_2 can be measured and used for monitoring corrosion rate. Acidity of crude due to naphthenic acid is commonly stated as TAN (total acid number) measured as mg of KOH/gm oil. The ASTM method normally used for analysis also includes other acids like phenol, CO_2, sulphide, etc. in crude. There

are also other methods which have been developed by oil companies themselves or companies dealing with chemicals to measure acidity which truly reflect the naphthenic acid content.

As a rule of thumb, crudes having TAN of more than 0.5 and cuts with a TAN higher than 1.5 are considered to be corrosive [15, 16]. Many crude oil produced in different fields in USA (California), Venezuela, Russia, India and China contains high naphthenic acid. Recently high levels of naphthenic acid have also been found in North Sea, West Africa, Mexico and offshore Brazil. Normally processing of such crudes for many years were avoided except where its dedicated supply was available and the refinery MOC was designed to process these crudes. However, in the present scenario of high demand sometimes there is no choice and a refiner has to process any crude available in the market which in the industry is known as "opportunity crude". Most the refineries are designed to process high-sulphur crude, and as high TAN crude is processed only occasionally in these refineries, special precautions are to be taken so that the existing MOC of the different units is not adversely affected. In addition to high TAN crude, calcium naphthenates containing crudes are also being recently marketed. Such crudes, in addition to creating processing problems, also increase high-temperature naphthenic acid attack. In addition to high-temperature attack, any low molecular weight organic acid produced during heating, adversely affect overhead corrosion in distillation column.

10.3.2.2 Control of Naphthenic Acid Corrosion (NAC)

Factors which control naphthenic acid corrosion can be broadly stated as:

- Neutralization number (TAN)
- Temperature of operation
- Velocity and turbulence
- Physical state (vapour or liquid)

The boiling points of NAP are dependent on molecular weight so its quantity varies in different distillates/fractions of the crude. A large number of acids can exist spanning over a wide boiling range and though heavier fractions would have high TAN it is not necessary that TAN of different distillates would be proportional to the naphthenic content of the crude as would be evident from Table 10.2 which gives the characteristics of some naphthenic acid crudes [17].

The types of acids present have also a large role to play. Tests carried out under velocity and vacuum conditions with addition of different types of known

Table 10.2 Distribution of naphthenic acid in various distillates

Crude oil	Crude TAN	Naphtha	Kero	LGO	LVGO	HVGO
Alba	1.42	0.0	0.1	0.8	1.9	2.2
Duri	1.27	0.13	0.8	2.5	2.7	1.8
Heidrum	2.6	0.03	0.19	3.9	4.2	3.5

naphthenic acid compounds showed that lower molecular weight compounds are more corrosive than higher molecular ones [18]. As naphthenic acid is a mixture of compounds of different molecular weights having different boiling points, the attack predominantly takes place in the temperature range of 200–400 °C, with the maximum effect in the gas oil range. No corrosion damage is usually found at temperatures above 400 °C, most probably because of the decomposition of naphthenic acids. Velocity plays a large role in increasing naphthenic acid corrosion and high wall shear stress. There is minor erosion effect on corrosion if velocity is between 1.2 and 6.5 ft/s (0.36–2 m/s). In heater the feed temperature increases from inlet to out let end and so does the extent of vapourization, depending on crude characteristics. Accordingly, the velocity also progressively increases reaching near sonic velocities at the outlet end. Naphthenic acids having boiling temperature up to the furnace outlet temperature also vapourizes. The higher linear velocity of hydrocarbon + naphthenic acid has corrosion/erosion effect leading to increased corrosion rates. Thus, heater tubes (especially those at outlet end), transfer line, elbows, tees, pumps and also the flash zone of crude column suffer heavy corrosion. HVGO and LVGO draw off pumps are also affected under some conditions. Table 10.3 shows the effect of linear velocity on naphthenic acid corrosion of carbon, alloy, and stainless steels at 360 °C [19]. As regards heater tubes, 5Cr–0.5Mo or 9Cr–1Mo can be used at the inlet ends where both temperature and velocities are not high (Table 10.3).

The physical state of acid, such as vapourization and condensing, also has an important role on corrosive effect. In addition to linear velocity/turbulence, higher rates of corrosion in heater tubes and transfer line are also related to the vapourization situation. Higher corrosion rates in the atmospheric and especially in vacuum tower, on the other hand, is related more to condensing situation than turbulence one. Attack by naphthenic acid has typical appearance having deep pits

Table 10.3 Influence of linear velocity on corrosion rate of various alloys

Material	TAN no. of crude	Linear velocity (mts/s)	Corrosion rate
Carbon steel	1.5	73	12 mm/year max at elbows
Carbon steel	1.5	26	0.6 mm/year at straight sections 6 mm/year at elbows
5Cr–0.5Mo steel	1.5	73	2 mm/year max at elbows
5Cr–0.5Mo steel	1.5	26	0.6 mm/year at straight sections and elbows
5Cr–0.5Mo steel	0.6	45	0.6 mm/year max at elbows
9Cr–1Mo steel	1.5	73	0.7 mm/year max at elbows
410SS	<1.5	<75	Light localized corrosion
316SS	1.5	Near sonic	Not detected



Fig. 10.3 Naphthenic acid attack on 5Cr. 5Mo heater tube

and grooves with smooth surface and no solid corrosion products are present. Nature of attack on 5Cr–0.5Mo heater tube bend processing naphthenic acid containing crude, investigated by the author is shown in Fig. 10.3.

10.3.2.3 Role of Sulphur in Naphthenic Acid Corrosion

Many types of crude containing naphthenic acid have very low sulphur content and in such cases high corrosion rate is encountered. However, if crude contains both sulphur and naphthenic acid, the extent of attack depends on the amount of sulphur and TAN of the feed. The combined corrosive effects of naphthenic acids and sulphur-containing compounds will have two additional reactions:

$$\mathrm{Fe} + \mathrm{H_2S} \Leftrightarrow \mathrm{FeS} + \mathrm{H_2} \tag{10.3.3}$$

$$\mathrm{Fe}(R\mathrm{COO})_2 + \mathrm{H_2S} \leftrightarrow \mathrm{FeS} + 2R\mathrm{COOH} \tag{10.3.4}$$

It will be evident that though Fe $(R\mathrm{COO})_2$ which is soluble in oil is swept away, it is possible that some of it can react with $\mathrm{H_2S}$ to regenerate naphthenic acid. In case of absence or low level of sulphur, the attack is high and predominantly controlled by naphthenic acid. On the other hand, if the sulphur content is very high, the presence of naphthenic acid will increase the rate of attack compared to the sulphur alone in the same concentration. Here the organic acids disrupt the sulphide film thereby promoting sulphide corrosion on alloys that would normally be expected to resist this form of attack. In case of intermediate level of sulphur, however, the naphthenic attack is inhibited because sulphide film formed offers some degree of protection [20]. This effect will be evident from Fig. 10.4 [21].

API 581 [22] has dealt with the role of sulphur on naphthenic acid attack on carbon steel and other alloys. To illustrate the effect a few of the data on 5Cr–0.5Mo (P5) given in Appendix G, Table G.19 of API 581 is shown in Table 10.4.

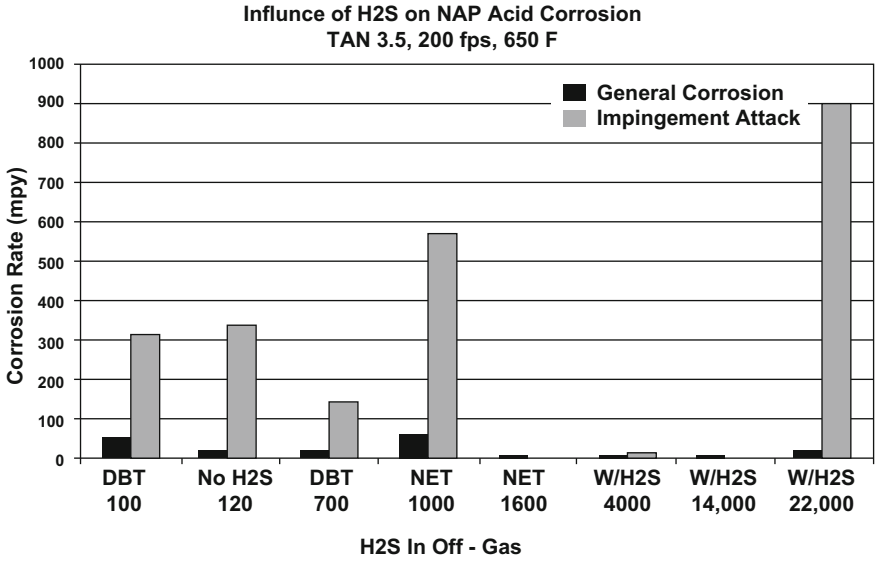


Fig. 10.4 The role of sulphur on NAP attack [21]. *Note* NET: 1,9–Nonanedithiol; DBT: Dibenzothiophene

Table 10.4 Effect of sulphur on NAP corrosion rate (mm/year) of P5

Sulphur (wt%)	TAN (mg/gm.)	Temp.°C 233–260	Temp.°C 289–315	Temp. °C 344–371	Temp.°C 372–400
≤ 0.2	0.31–1.0	3.0	6.0	10.0	15.0
≤ 0.2	0.31–1.0	3.0	6.0	10.0	15.0
≤ 0.2	2.1–4.0	15	30	45	50
0.20–0.60	2.1–4.0	6.0	10	20	30
1.1–2.0	2.1–4.0	8.0	10	25	35
2.1–3.0	2.1–4.0	15	30	40	45

10.4 Material Selection for Different Processing Units

Major refining processes can be divided into the following broad categories where the approach in material selection is similar:

Processing Medium: Hydrocarbon

- Distillation: (i) Atmospheric (ii) Vacuum.
- Thermal Cracking (i) Visbreaker (ii) Coking.
- Catalytic Cracking (i) FCC.

Processing Medium: Hydrocarbon + Hydrogen

- Catalytic Reforming

Processing Medium: Hydrocarbon + Hydrogen Sulphide + Hydrogen.

- (i) Hydro-treater (ii) Hydro-desulphurizer (iii) Hydrocracker.

10.4.1 Atmospheric Crude and Vacuum Distillation Units

Crude and vacuum units are the two sections which can be called the mother unit and produces maximum amounts of basic products like gasoline, kerosene, naphtha and light and heavy gas oils. In selection of the MOC of the two units we have to consider Fig. 10.5 which gives the simplified flow diagram of crude distillation unit (CDU) [23] in which three zones, high temperature (bold line), intermediate-temperature (dotted line) and low temperature (light line) have been marked. For selection of MOC for different equipment and piping we have to consider whether the unit has been designed for sulphur (low or high) containing or naphthenic acid containing crude.

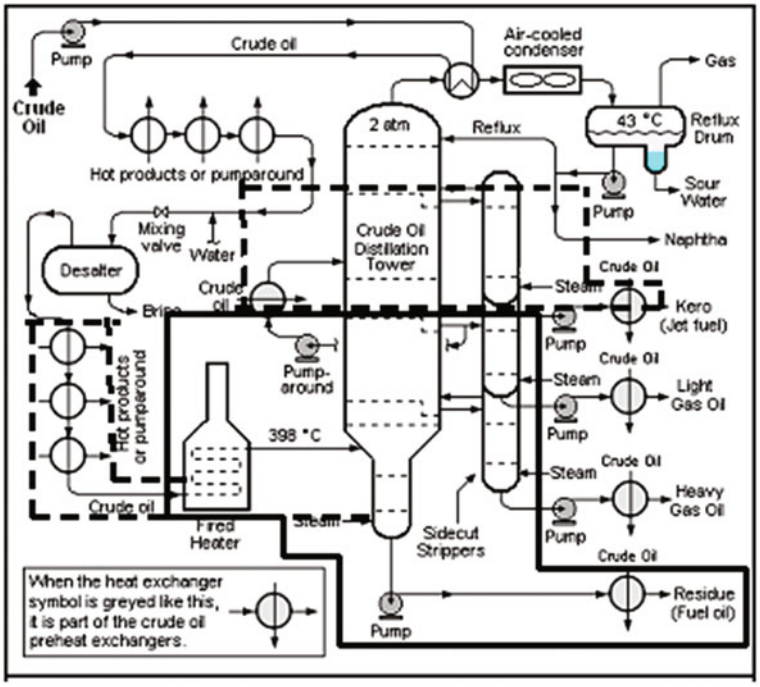


Fig. 10.5 Simplified flow diagram of crude oil distillation unit showing high-, intermediate- and low-temperature zones [23]

10.4.1.1 Low Sulphur Crude

Below 0.5% sulphur, the crude is considered sweet and in the absence of erosive action carbon steel has reasonably low rate of attack even up to 370 °C. In such cases the column, vessels, exchangers, and piping can be of carbon steel provided adequate precautions against erosion corrosion are taken by provision of SS 310 impingement plate at column inlet, use of long radius bends in piping and providing adequate corrosion allowance to attain the design life. Heater tubes and transfer lines from heater to column have multi-phase flow and therefore subjected to erosion corrosion action and it is advisable to upgrade their metallurgy to 5Cr–0.5Mo alloy. Two major components of any pump are casing and impeller. As the pumps are also exposed to erosion corrosion conditions, the MOC is to be carefully selected. The distillation column bottom pump handles bottom residue having temperature of ~380 °C so MOC would be all 5Cr–0.5Mo or 5Cr–0.5Mo casing and SS 310 stainless steel impeller. Pumps for HGO and diesel would be all 5Cr–0.5Mo. All other pumps in the unit would have carbon steel metallurgy.

10.4.1.2 High-Sulphur Crude

However, for processing high-sulphur crude it becomes necessary to consider change in metallurgy above 232 °C (450 °F) because of increased rate of sulphidation. As mentioned, the addition of chromium in steel increases its resistance to sulphur attack, and for material selection the modified MaConomy curve is used. While resistance to high-temperature sulphur attack increases with chromium content, historically 5Cr–0.5Mo steel has been the minimum specified metallurgy against sulphur attack. Rarely, lower alloying content MOC like 1.25Cr–0.05Mo or 2.25Cr–0.1.0Mo steels have been used. The author has, however, come across one case of 2.5Cr–0.5Mo tubes being used in some of the exchangers processing crude containing ~1% sulphur. With increase in temperature and sulphur content, alloys containing higher chromium are used.

Exchangers

As would be evident from Fig. 10.5, a number of exchangers are used to heat the feed going from the crude storage tank to desalter and finally to the fired heater. The feed is heated progressively by pump around from different section of the column and hot products from stabilizer and column bottoms. The material of construction of heat exchanger tubes depends on the sulphur content and maximum temperature of fluids on shell and tube sides. Depending on the source of hot product the crude may be on tube or shell side. If the hot product is on the shell side and above ~280 °C and shell side feed is below ~200 °C then the shell and tube (only from shell side) will have higher rate of sulphidation and therefore the MOC of both shell

and tube will be 5Cr–0.5Mo with shell having 3 mm CA (corrosion allowance). On the other hand, if feed on the tube side is above ~260 °C and shell side 350 °C, the tube will suffer high rate of sulphidation and the tube metallurgy may have to be further upgraded to 9Cr–1Mo to get good life. In another instance if the hot product is on tube side and cooler feed is on shell side (~240 °C) then tube side MOC would be 5Cr–0.5Mo and shell shall be of carbon steel with 3 mm CA. In other exchangers where temperatures on both shell and tube sides are moderate, all carbon steel exchangers are the recommended MOC. The fluids processed are heavy and therefor straight tube floating head exchangers are preferred for ease of cleaning during shut down. Similarly, heavy products with high viscosity are preferred on tube side. As regards the overhead coolers and condensers, U-tube bundle of proper MOC is selected with judicious use of corrosion control measures for both overhead stream and cooling water. In case of air coolers, normally metallurgy is carbon steel with suitable corrosion control measures.

Heater Tubes

Process heater and burner design has undergone large-scale modification since the last 50 years compared to the ones used earlier. The heaters have also become more compact with higher thermal efficiency but require greater control over operation. Heater has two sections, convection and radiant. From exchanger train the feed enters the convection section and depending on the nature of crude, at this stage, ~10% of the feed gets vapourized. As the feed moves through the convection and then radiant sections there is progressive rise in temperature and degree of vapourization. This results in increase in velocity leading to highly erosion corrosion conditions on the heater outlet tubes. Selection of alloys for heater tubes have to take these points into consideration and thus the MOC changes from convection section, where normally for inlet studded carbon steel tubes are used to increase heat transfer efficiency. A few of the rows downstream of carbon steel tubes are of studded 5Cr–0.5Mo metallurgy (higher corrosion allowance or higher thickness tubes can improve heat transfer due to convection type of heat transfer in this zone). The first one and two rows where the hot flue gases (~850 °C) enter the convection section are subjected to high heat flux and are known as shock tubes. In these two rows plane tubes of 5Cr–0.5Mo are used to avoid overheating and consequent damage to tube and chances of coking. Once the feed enters the radiant section, the tubes are exposed to high heat flux and minimum metallurgy historically has been 5Cr–0.5Mo. However, for better performance in the modern heaters some of the outlet tubes (~8 to 10) in different passes of the radiant section or all tubes in the radiant section are made of 9Cr–1Mo, which can be operated with a skin temperature of ~675 °C. For transfer line from heater outlet to the distillation column, 5Cr–0.5Mo or 9Cr–1Mo are specified. Use of 9Cr–1Mo ensures greater reliability with the present day practice of unit run lengths being increased to 3 years and above.

In case of vacuum unit, the hot atmospheric distillation column bottom residue directly goes to the heater where the feed is heated to ~400 °C; heater tube metallurgy is of 9Cr–1Mo. The transfer line is also of 9Cr–Mo. It is interesting to note for quite a number of years use of 7Cr–1Mo heater tubes was quite common but its use has been discontinued since the development of 9Cr–1Mo.

Atmospheric Distillation Column

The distillation column metallurgy depends on the sulphur content of the inlet feed and temperature in various zones. In a distillation column, temperature difference exists between the bottom and the top, which may vary from about 360 to 380 °C in bottom to as low as 110 °C at the top. The pressure at the top is near atmospheric. The temperature profile along the column vertical axis can be designated from bottom as high-, intermediate- and low-temperature zones. These zones are maintained by transfer of hot vapour moving up and cold reflux plus condensed fraction moving down. Because of this temperature gradient, condensation of different fractions, such as heavy gas oil, light gas oil (diesel), and kerosene occurs in the order of bottom to top, as shown in Fig. 10.5. From top of the column naphtha vapour and lighter hydrocarbon gases exit and go to condenser and the receiver from where part of the cold liquid is pumped back to the column top as reflux. Depending on process design, sometimes additional pump around are provided to withdraw the liquid from lower level and sent back at upper level after cooling so that design temperature profile is maintained. These fractions have different temperatures and sulphur content and, therefore, different degrees of corrosivity. In selecting the MOC these factors have to be kept in view.

The distillation column does not have a single metallurgy when high-sulphur crude is processed. Alloys like 5Cr–0.5Mo or 9Cr–1Mo, which possess good resistance to sulphur attack, cannot be used for tall distillation columns for their poor weldability and air hardening characteristics making fabrication difficult. As the design temperature is ~420 °C carbon steel can be used but it is not suitable against sulphur attack. By providing corrosion allowance (CA) of 3 mm or higher if necessary, its temperature limit of suitability can be raised to ~280 °C. Thus, in atmospheric distillation columns in high-temperature bottom section up to diesel draw off point is made of carbon steel cladded with SS 410, which has high resistant to sulphur attack. The MOC in the intermediate-temperature zone between SS 410 clad sections and top section till the level of 4th tray from top is of carbon steel with suitable CA. In the topmost section of column generally above 5th tray, aqueous acidic corrosion can occur and the metallurgy of this portion is selected accordingly. The MOC of this section has been discussed in detail under low-temperature corrosion. Thus, in case of main column, the metallurgy varies along the height of the column. For other columns like stabilizer and stripper columns of side cuts, where temperatures are in the intermediate range, carbon steel is used, independent of the sulphur content. The MOC of light gas oil stabilizer can be either carbon steel

with extra corrosion allowances or SS 410 clad carbon steel depending on severity of conditions. For HVGO, the MOC will be SS 410 clad carbon steel.

Column internals used earlier were of different types (bubble cap, half pipe sections, etc.) and MOC used were carbon steel or 5Cr–0.5Mo, but presently trays and valve system is used, the MOC of which is SS 405 or 410S in all columns, independent of sulphur content and temperature. This type of valve trays are found more economical in the long run because of improved performance compared to others.

Pumps and Valves

MOC of pump will be matching minimum the upstream columns and vessels but actual selection in critical cases may be fully or partly upgraded to higher metallurgy, especially components like pump impeller, or valve seats. For example, atmospheric and vacuum column bottom and HGO, HVGO stabilizer bottom pumps will be of all SS 410 metallurgy. On the other hand, pumps handling kerosene and naphtha pumps (hot or cold) will be of carbon steel. As highly erosion corrosion condition exists, the MOC may have to be upgraded. In case of diesel and LVGO, use of 5Cr–0.5Mo would give sufficiently good performance.

10.4.2 Processing High TAN Crude

Material selection for processing high total acid number (TAN) crude is to be examined from number of angles before final decision. The most important consideration is to know whether the refinery is to be designed on the basis of processing $\sim 100\%$ naphthenic acid crude or only to be processed occasionally as and when required. In case of the latter, it is more important to select one or other methods which would minimize the attack on 5Cr–0.5Mo or 9Cr–1Mo in a conventional refinery processing high-sulphur crude. The major objective here is to keep the damage within a limit which would not cause any major situation where the company has to go through large-scale repair and replacement. Here combination of various alternatives along with strict monitoring of damage in critical areas is to be tried.

10.4.2.1 Controlling Naphthenic Acid Corrosion by Material Upgradation

Materials Resistance to NAP

For long-term reliability, upgrading of MOC is the best solution in cases where only or for the major period high TAN crude will be processed. Alloys containing chromium which has high resistance to sulphur attack do not show the same degree

of protection against NAC. As a matter of fact, there is no substantial difference in corrosion rates between carbon steel and Cr–Mo alloys normally used in the processing of high-sulphur crudes. Even stainless steels Type 410 and Type 304 do not provide substantial benefits over carbon and Cr–Mo steels in naphthenic acid service, especially in areas or zones of high velocity (turbulence) and condensation/evaporation. Suitable material is austenitic stainless steels like 316L and 317L. The alloy used is dependent on the TAN and nature of service. Type 316L (with 2.5%Mo minimum) and 317L (3.5Mo minimum) are preferred, especially in case of heater tubes in the radiant section. In extreme cases 904L and 6XN can be used as alternate material.

Furnace Tubes and Transfer Lines

As discussed in case of the role of sulphur in crude, the temperature and degree of vapourization increase as the feed travels from inlet to outlet of the furnace. The fluid velocity increases and even small amounts of naphthenic acid in oil becomes very active and perceptible degree of NAC shall start and progressively increase to high rate by the time the feed exits the heater and enters the transfer line. If we consider the MOC, even conventional 5Cr–0.5Mo would start being affected at some stage in the radiant section. Thus the influence of temperature, velocity and degree of vapourization combined with process conditions like load, steam rate and turbulence would affect corrosivity. Under such multi-phase high velocity situation erosion corrosion would be operative and a change in MOC of tubes would become essential at some stage in the radiant section. The only minimum metallurgy for high resistance to NAC is SS 316L. Thus MOC of heater tubes and in processing of high-TAN crude would be as follows:

Convection section 5Cr–0.5Mo
Radiant Section—Initially 5Cr–0.5Mo/9Cr–1.0Mo, followed by SS 316L or 317L at the outlet end.

The changeover to 316L would depend on the TAN, nature and distribution of different naphthenic acid compounds, process parameters and vapourization characteristic of the crude or crude mix. The author had an opportunity to study the case of refinery heater tube MOC processing high TAN crude. For processing low sulphur heavier crude of 2.1 TAN, the heater in the radiant section was provided with tubes of 5Cr–0.5Mo metallurgy with the last five tubes at the outlet end being of 316L. The heater was in operation for 23 years without any reported failure of either 5Cr–0.5Mo or 316L tubes. Another unit using the same crude but blended with low sulphur low TAN crude in the ratio of 40:60 (Total TAN of $\sim$0.80) was originally provided with only 5Cr–0.5Mo tubes in the radiant section. However, blending with comparatively much lighter low TAN crude resulted in a much higher degree of vapourization at furnace outlet temperature of 350 °C. The subsequent increase in velocity led to replacement of last five tubes with 316L

metallurgy within a period of 2–4 years. Subsequently, some additional tubes had to be periodically replaced and presently after 23 years the furnace was still running with 11 tubes of 316L metallurgy. These two examples highlight how selection of MOC does not depend only on TAN but requires consideration of various factors which are not always possible to predict. The erosion corrosion conditions of furnace outlet continue downstream in transfer line, piping, pumps, thermo wells, etc. where 316L is to be selected.

Atmospheric and Vacuum Column

In the vacuum column, preferential vapourization and condensation of naphthenic acids increase TAN of condensates. There is less effect of velocity. Corrosion takes place only in the liquid phase. It can be considered to be condensate corrosion and is directly related to amount, molecular weight and boiling point of the naphthenic acid. Corrosion is severe at the condensing point corresponding to high TAN and temperature. Column shell up to LGO draw off is affected, with maximum effect above flash zone in HGO section. Generally, cladding of vacuum column is recommended when TAN is above 0.5 mg KOH/g and in atmospheric column when the TAN is above 1.0 mg KOH/g. Roll clad 316L plates are used, but when existing carbon steel column requires to be upgraded to process NAP containing crude, one has to resort to strip/sheet lining. The lining requires to be done carefully to avoid its detachment due to damage of weld.

Side-Cut Piping

In side-cut piping, normally much vapourization does not occur and velocity of fluid is lower. At many locations vapourization and medium fluid velocity exist. Some studies showed a possible inhibitive effect on NAC by sulphur compounds. As regards the side-cut piping and exchanger tubing, 5Cr–0.5Mo or 9Cr–1Mo MOC may give reasonable life in case TAN is not high (say up to 2.0 mg KOH/g) and temperature is <240 °C, otherwise 316L is to be used. In case downstream catalyst is likely to be poisoned by iron contamination, piping and exchangers are also made of 316L even if 5Cr–0.5Mo/9Cr–1Mo has good life.

Pumps and Valves

MOC of pump will be matching the upstream columns and vessels.

10.4.2.2 Other Methods for Controlling Naphthenic Acid Corrosion

Apart from change in MOC other methods which can be used to prevent/minimize NAC include the followings:

- Blending is more often used when using opportunity crude, whereby the naphthenic acid content of the feed is diluted suitably to well below 1.0 TAN by mixing high TAN crude with a low TAN one, thus reducing corrosion to an acceptable level. Blending of heavy and light crudes change shear stress parameters and this might also help in reducing corrosion. Similarly by blending with crude containing sulphur, it is possible to reduce the degree of naphthenic acid attack, as discussed earlier. However, there are no specific guidelines for these, as the characteristics of the crude vary and prediction is difficult.
- Neutralizing the acid by caustic, injected at inlet of the feed has been tried, but its feasibility will depend on the TAN which will determine the amount of caustic required for neutralization. Caustic injection is, however, required to be limited as too much sodium will increase the coking tendency in furnace tubes in downstream heaters of vacuum, coker and visbreaker and also affect efficiency of catalyst in FCC unit. The presence of caustic may also result in formation of scales and create operational problem in the exchanger train.
- Use of inhibitors to control naphthenic acid corrosion is being used presently by the oil industry. The method of protection is provided by producing a protective film on the metal surface. These are basically phosphorus based organic compounds (like esters) which form a stable passive layer of iron phosphate complex [24]. NALCO has also developed inhibitors against NAC which are based on phosphorous, sulphur and phosphorous + sulphur [25]. Use of inhibitors is a two-step process. First a stable passive film is formed for which higher doses of inhibitor are added. Once a stable film forms, inhibitor doses are reduced to a level where its main function is to repair any local damage of the film. Injection of corrosion inhibitors may also provide protection for specific fractions that are known to be particularly severe.
- The inhibitor used should not only be effective in the temperature range of 200–300 °C but the monitoring of corrosion rate needs to be adequate to check on the effectiveness of the treatment. In one instance, the corrosion rate of visbreaker column down comers (temperature in the area being $\sim$220 °C) was brought down by tenfold with the injection of a filming amine inhibitor. The monitoring in this case was done by use of hydrogen probe [26].

During the implementation of various methods discussed above it is necessary to monitor corrosion rate for which use of 'the electric field signature' technique is being used in the recent years. Here the electric field signature systems in atmospheric and vacuum unit furnace outlet bends and other high-turbulent areas like transfer lines are installed where the temperature is in the range of 200–400 °C. Data is collected manually or automatically using software. Figure 10.6 shows typical graph of all sensing pin pairs for online monitoring system in refinery [27]. GE has also developed Resistance Corrosion Monitoring (RCM) based on principle somewhat similar to traditional ER probes where corrosion is measured on the basis of change in electric resistance due to loss in thickness. Here also a grid or array of pins is welded directly on the component concerned. It is claimed that the instrument measures wall thickness to within 2% of total wall thickness [28].

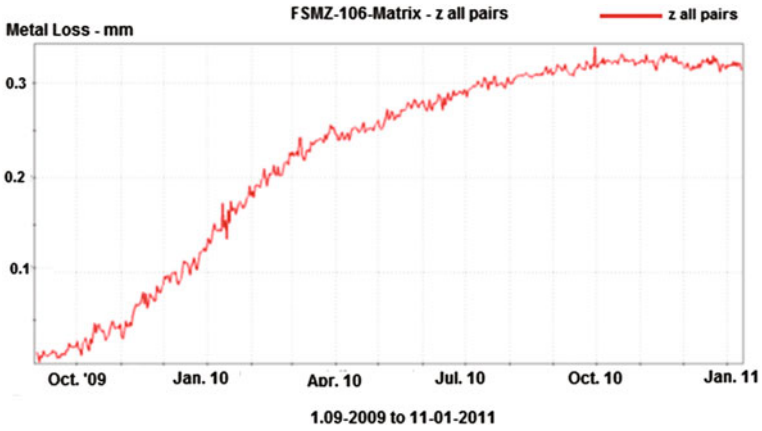


Fig. 10.6 Metal loss of all pairs but unfiltered with higher resolution to see daily changes in online monitoring system at Jamnagar refinery, India [27]

10.4.2.3 Summary of MOC

Table 10.5 summarizes the materials, by ways of some examples, which can be considered for the various equipment and piping for atmospheric and vacuum units processing of high sulphur and also high-TAN crudes. This table gives a general guideline and each case is to be analysed separately, depending on the nature of crude and process details. The material, as would be evident, can vary from carbon steel to the various grades of Fe–Cr alloys to stainless steels. It is known since 1966 [5] that carbon steel piping containing silicon content of less than 0.10 wt% can suffer sulphidation attack at accelerated rates of up to 16 times faster than carbon steel containing higher percentages of silicon. API RP 939-C gives a number of examples where the sulphidation failure occurred because of low silicon content [29]. A detailed analysis of the role of silicon content of steel is also given in the failure report of carbon steel LGO draw offline in Richmond refinery of Chevron [see Chap. 1]. Normally A 53 or A 106 carbon steel piping is used of which the former does not specify silicon content against minimum 0.1% specified in case of A 106. Refiners are generally specifying this requirement only since 1980s. API A570 recommends positive material identification (PMI) as a part of inspection procedure but normally used field-portable instruments cannot adequately identify silicon content. In view of the above, where there is any doubt, either chemical analysis by taking fine metal shavings or 100% thickness survey of each piping component should be conducted periodically to identify low silicon sections. However, there has been recent claim that Niton XL3t GOLDD + XRF analyser [30] allows for fast, accurate, and precise elemental analysis, including light metals like magnesium, aluminium, phosphorous, silicon and sulphur.

Table 10.5 Guideline for selection of MOC in crude and vacuum units for different process temperatures

Unit	Heater/transfer line	Column	Exchanger	Side stripper	Pump
Crude distillation processing high-sulphur crude	Convection—CS/5Cr0.5Mo Radiant—9Cr–1Mo Transfer line 9Cr–1Mo	Pre flash column—all CS Distillation column Bottom—SS 410 clad CS Top—Monel clad CS Intermediate—CS	*Tube (<180 °C) and shell (<250 °C)–T and TS–CS; shell–CS *Tube (>230 °C) and shell (<300 °C)–T and TS–5Cr–0.5Mo; shell CS + CA *Tube (>260 °C) and shell (>300 °C)–T and TS–5Cr–0.5Mo 9Cr1–0Mo; Shell 5Cr–0.5Mo + CA	HGO–410 clad CS LGO–CS + 3.0/4.5 mm CA Kero—CS + 3 mm CA	Column bottom and HGO—all SS410 LGO—all 5Cr–0.5 Mo Kero—all CS
Vacuum unit processing high-sulphur crude	Convection and radiant 9Cr–1Mo Transfer line 9Cr–1Mo	Column SS 410 clad CS Top-Monel clad CS (if required)	*Tube (>260 °C) and shell (>300 °C)–T and TS-5Cr–0.5Mo/9Cr1–0Mo; Shell 5Cr–0.5Mo + CA	HVGO–SS 410 clad CS LVGO–CS + 3.0/4.5 mm CA	Column bottom, HVGO–LGO—all SS 410
Crude distillation processing high TAN crude	Convection–CS/5Cr0.5Mo Radiant—5Cr–0.5Mo/316L/317L Transfer line 316L/317L	SS 316L clad carbon steel from bottom till ~220 °C (below Kero draw off)	*Tube (>230 °C) and shell (>300 °C)–T and TS–316L/shell–316L clad CS *Tube (<220 °C) and shell (<240 °C) tube 5Cr–0.5Mo 5Cr–0.5Mo + CA	HGO and LGO–SS 316L	Column bottom, HGO and LGO—all SS 316L

10.4.3 Visbreaker and Coking Units

10.4.3.1 Process Outline

Visbreaker and coking processes involve thermal cracking of heavy stock, normally columns bottoms. In case of visbreaker, the cracking condition is mild as the feed is heated up to 435–485 °C. The cracked products are distilled into various lighter fractions. During the process small amounts of carbon are formed, which is deposited mainly as coke on tube ID. Coke acts as an insulator resulting in rise in heater tube skin temperature. In addition, coke built up causes pressure drop. Depending on the rise in temperature and pressure drop, the operation is stopped for decoking. Earlier the coke used to be removed mechanically, but the present practice is to use steam/air decoking which does not require shutdown and opening of the tubes.

Delayed coking is also a thermal cracking process like visbreaker, but here the main objective is to convert low value bottom into higher value lighter products and also in the process to produce coke. The process, however, requires much severe cracking. Here the feed (vacuum residue + slop) along with fractionator bottom is heated in a furnace up to about 500 °C. This hot product goes into the coke drum (size—varying from 5 to 10 m in diameter and 18 to 30 m in height) where coke formation takes place slowly. The hot product is continuously routed into the coke drum till substantial solid coke level is build up in the coke drum. After the coke drum is filled with coke the hot product is diverted to the fresh coke drum and the filled coke drum is taken offline. The solid coke formed in the offline coke drum steamed to recover the hydrocarbon and then the coke is cooled by injecting water from the bottom and then cut with a water jet cutter from the chamber top. The pulverized solid pieces of coke are collected from the bottom flange of the coke chamber. The vapours from the coke chamber containing mixtures of lighter products go to the fractionator where lighter products are distilled into various fractions along with the original feed. A simplified flow diagram of the process is shown in Fig. 10.7 [31]. The process being a batch process, continuous operation is achieved by using two coke chambers. When coking is complete in one chamber, the same is isolated and the feed from the furnace is switched into the second chamber where coke formation continues. During this period the cutting of coke and initial preparation for taking the next batch of feed is completed. By this time the second chamber becomes ready for coke cutting and the feed from furnace is switched to first chamber. The cycle time is adjusted to maintain continuity of operation. Thus the coke chambers are subjected to cyclic changes in temperature.

10.4.3.2 Materials of Construction

The selection of material in both visbreaker and coking is based on the same consideration as for the distillation and vacuum unit. For heater tubes processing

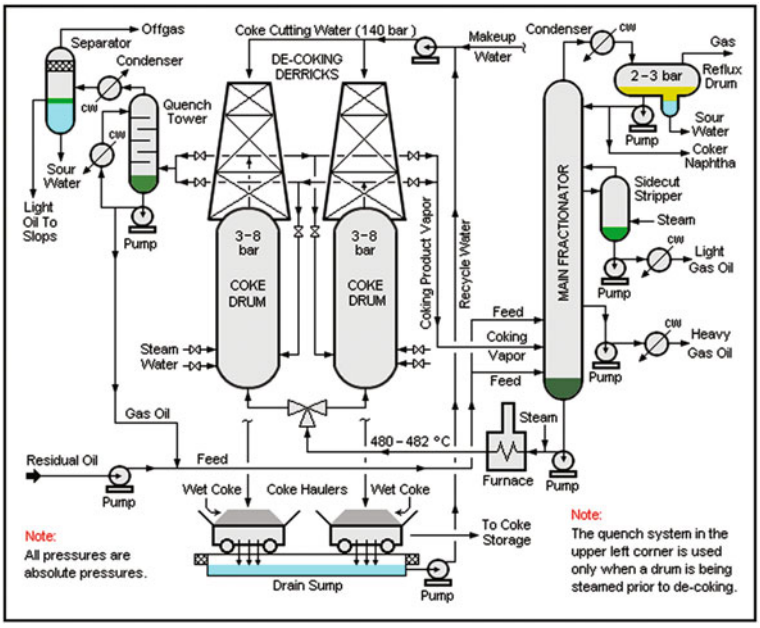


Fig. 10.7 Schematic flow diagram of delayed coking unit of oil refinery [31]

high-sulphur heavy stocks, where coking takes place, generally P 91, 9Cr–1Mo–V alloy, is specified to avoid failure due to overheating as coking raises the skin temperature due to its insulating effect. This alloy also possesses better resistance to sulphur corrosion, oxidation resistance, carburization resistance as well as creep strength. It is of interest to note that the coke layer formed also to some extent protects the tubes from sulphur attack. One major problem with these units is embrittlement due to internal carburization of the tubes, which is a slow process but over a long period sufficiently thick carburized layer is formed, resulting in brittle failure due to thermal shock. Also, the formation of chromium carbide reduces the amount of chromium retained in solid solution, thus reducing resistance to sulphur attack. Mostly, the section of the tube facing flame is affected. It is also well established that the life of these tubes are affected more by carburization than creep damage. Absence of NDE technique to measure the depth of carburization made prediction of degree of deterioration difficult. However, TOFD technique has been successfully used to measure the depth of carburization. It is claimed that minimum depth of 0.5 mm can be measured using this technique [32].

The transfer lines are of 5Cr–0.5Mo or 9Cr–1Mo depending respectively on low or high-sulphur content of the feed. The other lines are similarly of carbon steel or 5Cr–0.5Mo. On the basis of sulphur content and temperature, the metallurgy of the other equipment for high-sulphur feed is selected, which is summarized in Table 10.6.

Table 10.6 MOC of different equipment in visbreaker and coking units

Unit	Heater/transfer line	Column	Exchanger	Pump	Coke drum
Visbreaker	9CR–1Mo	SS 410 clad carbon steel	Tube and shell 5Cr–0.5Mo	SS410	
DCU	9Cr–1Mo	SS 410 clad carbon steel	Tube and shell 5Cr–0.5Mo	SS 410	CS/C–0.5Mo/1Cr–0.5Mo/2.25Cr–01Mo + SS 410 cladding

10.4.3.3 Specific Problems Experienced in Coking Units

Delayed coking is a batch process with duration of batch varying from 10 to 48 h. These cyclic changes in temperature cause changes in longitudinal and diametrical dimensions. Added to this is the stresses generated due to the quenching effect of cooling of coke which affect the stability of the coke drum. Thus irreversible damage, like bulging and cracking of circumferential weld limits the life of coke drum. In addition, other components of the coke drum and piping systems are also adversely affected. The situations conducive to commonly experienced damage are:

1. Fatigue-related failure occurs, especially in case of vapour lines that join the two reactors and skirt/drum joint.
2. It was believed for long that damage experienced in coke chamber is related to the quenching effect of large amount of water fed into the drum from bottom which generates hoop and axial stresses. However, it was proven only after Stress Engineering Services developed technique for direct measurement of stresses during the process of quenching. The method consists of fixing strain gauges at critical locations and measuring the stresses generated on coke chamber in a cycle from the starting of feed to water quenching. A plot of the stresses generated is shown in Fig. 10.8 [33]. Circumferential expansion and contraction of drum during heating and cooling cycle results in low cycle fatigue for which it is not designed.
3. This pioneering work not only confirms the important role of low cycle fatigue but also helps in predicting residual life and improvement in the coke chamber design.

Vapour Lines

Earlier failure of vapour lines was quite common as the understanding of piping stresses was in adequate and proper supports were not provided to take care of repeated cycles of expansion and contraction. With improved piping stress analysis, the situation has considerably improved and fewer problems are experienced.

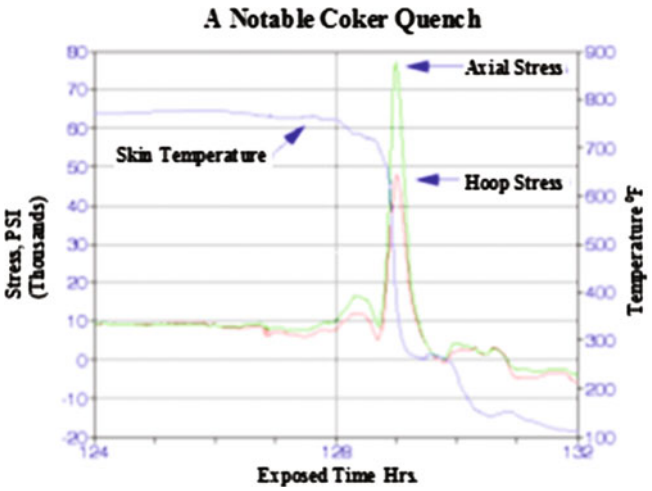


Fig. 10.8 Plot showing high stresses generated during the quench [33]

Bulging of Drums

Because the vessel operates under cyclic condition of severe heating and quenching, the resulting stress causes the drum to bulge. The base metal and weld have different strength, with normally welds having higher strength. During operation, the weld does not yield to the same extent as the base metal. Further, the difference in plate thickness between courses restricts the yielding of weld. The resulting stiffening of the weld gives rise to ballooning. The ballooning starts from the bottom course (about 40–50 ft from the bottom), which is subjected to highest quench rates and also has highest thickness, and then travel upwards as shown in Fig. 10.9. This leads to thinning of plate and circumferential cracking along the circumferential weld seam. It has been further confirmed using finite element analysis that the weld metal in the circumferential seams tends to have a stiffening effect which increases stress leading to distortion and cracking [34, 35].

It was also postulated quite early that increased severity of quenching results in higher temperature gradient which has a large role to play in weld cracking of coke drum. Based on the number of actual observations it was suggested by Well and Rapasky [36] that the cracking tendency of coke drum can be predicted from quenching rate used and this effect was expressed by a term "unit quench factor" (UQF). Based on plant survey data the following empirical relationship was arrived at:

$$\mathrm{UQF} = \frac{\mathrm{Water} - \mathrm{quenching\,time\ (minutes)}}{\mathrm{Coke\,capacity\ (tons)}}$$

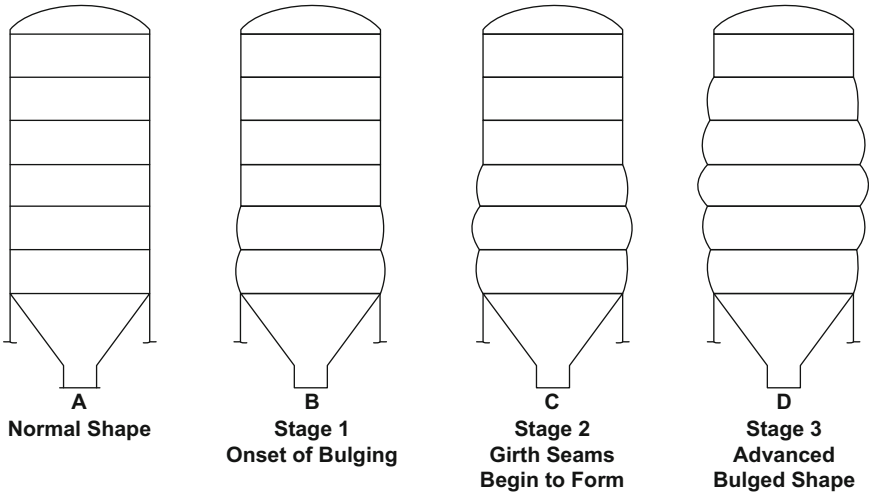


Fig. 10.9 Different stages in bulging during long-term operation

Bulging is maximum if UFQ is less than 0.5, is non-existent for UFQ of more than 0.8; and minimal when the UFQ is between 0.5 and 0.8. This would be evident from the field data given in Table 10.7. This relationship can be used as level 1 assessment of drum condition. Although the UQF takes into account the total time of water cooling, the initial cooling has serious impact on thermal stress. Therefore, slow opening of the deluge valve in the start of cooling operation reduces thermal stress and the resultant bulging of the coke drum and cracking of shell to skirt welding.

Table 10.7 Comparison of Quenching Methods on Coke Drum Bulging

Unit no	Water quenching time (min)	Coke capacity (Ton)	Unit quenching factor (min)	Relative severity of bulging/distortion
9	90	380	0.24	Severe
8	100	370	0.27	Severe
7	90	310	0.29	Severe
1	140	180	0.78	Negligible
5	135	180	0.80	Negligible
2	150	170	0.88	Absent
6	180	180	1.0	Absent

Coke Drum Life

Steps needed for the improvement of coke drum life and reliability has been an ongoing process for long. Participants have been operator, process designer, fabricators and industry organizations like API. Various modifications have been proposed and some of these have been implemented. The driving force behind this has been to increase coke drum reliability under shorter operational cycles to maximize production. Some of the modifications suggested are as follows:

- Decreasing the weld metal yields strength to be within a close percentage of base metal yields (i.e., 0%, +10%),
- Blend grinding of the weld profile,
- Specifying higher alloy like 2.25Cr–1Mo,
- Introducing more NDE and using more restrictive NDE acceptance criteria than the construction code requires,
- Maintaining a uniform shell thickness throughout the vessel,
- Specifying materials greater than 2″ in thickness.

M/S Chicago Bridge & Iron Company (CB&I) carried out a detailed study and concluded that the number of circumferential weld can be reduced and uniform thickness assured if "vertical seam" coke drum can be constructed with the long side orientated vertically as shown in Fig. 10.10 [37]. Based on the Vertical Plate Technology, which drastically reduces the number of circumferential welds, CB&I had between the year 2000 and 2008 completed 11 retrofit and six new coke drums. Importance of low cycle thermal fatigue was also suggested by some as the failure mechanism of coke drum cracking [38]. Studies conducted by process designer Foster Wheeler [39] have showed that useful drum life can be achieved by good

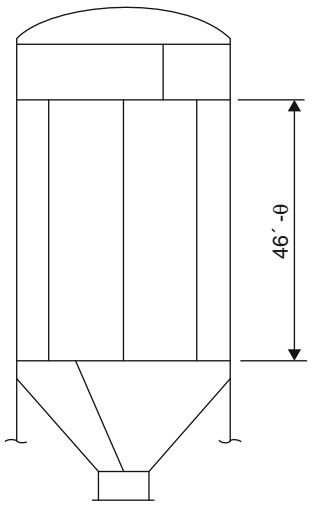


Fig. 10.10 Elimination of circumferential welds [37]

Table 10.8 Typical coke drum quench schedule

Duration (min)	Flow, GPM
30	275
30	625
30	775
30	925
75	975
100	1000

operation along with pre-emptive maintenance. A few specific operational recommendations mentioned include:

1. Use a quench schedule that is checked to meet requirements for minimum stress. Foster Wheeler suggests a stepped or ramped quench schedule that starts at low rates early in the quench operation and finishes at high quench flow rate as given in Table 10.8.
2. Alternate quench schedules, followed by some, using large water rates early in the quench and allowing pressures to run up to the relief valve set pressure, are detrimental to drum life regardless of the shell thickness, and should be avoided. 'Proofing', this is an operating procedure that blasts a large water flow into the drum to ensure that coke bed passageways are open, should be avoided, as this induces high stresses in coke drums."Proofing" can also create a safety issue by lifting the safety valve.
3. Always preheat with coke condensate to a minimum of 230 °C as measured at the drum inlet though the preferred preheat temperature is 345 °C (600 °F) or greater. Achieving this level of preheat in a low pressure coker operating on very short cycles (e.g. 14 h) can be difficult and modifications will be required to take care of this limitations.

Failure of Skirt and Skirt to Shell Weld

Conventional skirt to shell weld initially experienced a number of failures due to fatigue effect of cyclic heating and cooling. Cracking at the circumferential skirt to bottom head weld because of severe thermal gradients that exist between the shell and skirt is a matter of great concern. Here the skirt acts as a fin that enhances the thermal gradient that exists at the shell to skirt junction of a drum during a typical operating cycle. One corrective measure used is to provide key holes close to skirt to shell weld to improve flexibility of the skirt but over a period of time cracking is initiated at key holes and propagate up to the shell to skirt weld. Conventional design using a simple fillet weld also resulted in very large stress concentration factor at the inside crotch of the skirt to shell/cone attachment which led to operational fatigue cracking. To overcome this problem, designers came up with a modified weld system with an internal weld crotch radius of at least 0.5 in. (13 mm)

which significantly reduced the stress concentration factor of 5 by half. In case of a forged attachment the internal crotch radius can be increased to reduce further the internal stress concentration factor.

The basic approach was not to provide a continuous path for the growth of crack. Modifications like stepwise design were introduced but it did not help much. T-Rex skirt is considered as good design to minimize skirt problem [40]. The design avoids any sharp linear path for the crack to initiate and grow with time.

API Surveys

Till date four surveys on performance of coke drums have been carried out by API, i.e. during 1968, 1980, 1996 and 2013. The findings of these surveys are well documented and each survey has helped in the understanding the various aspects of coke drum damage and corrective actions which have been collated to issue a comprehensive API standard [41]. Based on the survey the various forms of damage identified were bulging, pitting in cladding, cracking in weld overlays, cracks in shell, nozzles and external attachments, cracks in skirt attachments. With inputs of various surveys and other studies number of modifications has been identified relating to the failures experienced in coke chamber. API 934G gives the various conclusions and considerations that affect the operation of coke drums and a few of these are stated below:

- Design: In design there are two approaches, reduction in distortion and prevention of cracking. For the former consider the role of fatigue as the equipment is subjected to cyclic loading during operation. This requires that commonly used MOC 1.25Cr–0.5Mo material will have to have higher minimum yield strength like 415 MPa (60,000 psi) instead of specified 310 MPa (45,000 psi) for class 2 grade. This will reduce the chances of distortion. On the other hand, for the second fracture ductility is more important. Use of higher strength material would lead to decrease in fracture ductility and thus increase the chances of cracking. For higher fracture ductility lower strength fine-grained carbon and C–0.5Mo steels with lower hardenability would be a better choice to avoid cracking but in this case distortion will be a problem.
- Materials: Change of MOC from carbon and C–0.5Mo to low alloy Cr–Mo steels has taken place over the years. Though 1.25Cr–0.5Mo is presently in greater use some designers have switched over to 2.25Cr–1Mo because it meets some of the requirements of higher yield strength of 415 MPa (60,000 psi), better toughness and crack arrest properties. Fine-grained C–0.5Mo is also being considered because of its good toughness, high-temperature ductility of HAZ and ease of welding requiring no PWHT.
- Thickness: Originally drum thickness calculation was based on pressure and weight consideration and therefore thickness in the upper section decreased with height. This led to concentration of stress at thickness transition interface which accelerated cracking process.

The standard covers various other aspects including damage of skirt, insulation, inspection, repair methods, etc.

Monitoring of Coker Drum Damage

This highlights the importance of regular monitoring of the condition of the drum because penetration of crack shall lead to leakage which cannot be easily detected as the vessel is insulated. There is a safety hazard as the leak may lead to local fire under the insulation, or at the ground level when the released product reaches the ground. Similarly, cracking of skirt can result in the instability of drum. Being a large vessel, inspection of coker drum has always been a matter of concern because of the amount of efforts required to remove insulation for measuring the extent of bulging or any other damage. Further, the circumferential crack can initiate on internal or external surface which would require installation of scaffolding inside and outside the drum. With the development of laser technique [42] profiling of internal surface of coke drums can be done in a short period for which an extended shutdown may not be necessary. It is a remote control system where the instrument is mounted to the drill used for coke cutting and then moved up and down the drum height. By this method it is also possible to detect the presence of any crack on ID or bulging of cladding.

10.4.4 Fluid Catalytic Cracking

10.4.4.1 Process Outline

In fluid catalytic cracking (FCC), heavy gas oil from the vacuum column is mixed with the hot catalyst in a reactor operating at about 480–580 °C and 1.5–2.0 kg/cm^2. The cracking of the large HC molecules occurs in the riser and the reactor. The cracked products exit from the top of the reactor. The catalyst which is covered with coke during the cracking process is taken out from bottom of the reactor to the regenerator. In the regenerator the coke is burnt (650–760 °C) and the regenerated catalyst, after being separated from gases in cyclones, is fed back to the reactor. A simplified flow diagram is shown in Fig. 10.11 [43]. The reactor and the regenerator are very large size vessels and the philosophy of material selection is similar to that discussed earlier, i.e. it is based on process temperature and sulphur content of the feed. There are many large diameter pipes (with slide valves) connecting the reactor and the regenerator through which the mixture of the feed and the catalyst flow. Under this condition, the equipment is also subjected to heavy erosive action by fast moving catalyst. The components in the regenerator circuit which are subjected to erosion corrosion, e.g. regenerator shell, piping, valves, cyclones, etc. are lined with erosion-resistant refractory. In some design even the reactor section is also refractory lined. Normally two layers of refractory,

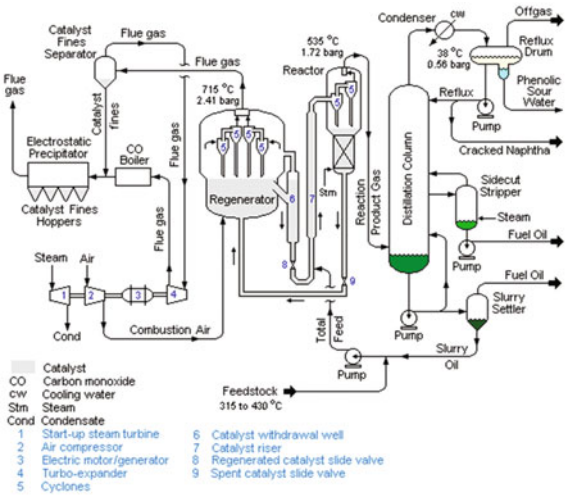


Fig. 10.11 Simplified process flow diagram of FCC unit [43]

erosion-resistant refractory over insulating refractory are provided. This lining system brings down the regenerator equipment and piping wall temperature to within elastic limit against an internal temperature of about 650–760 °C. The design temperature of this section is 350 °C and therefore carbon steel can be used as a material of construction. For cyclones SS 304H is used.

10.4.4.2 Material Selection

The reactor operates at a comparatively lower temperature and erosive action is not high, except for the bottom portion. Carbon steel with or without SS 410 cladding have been used successfully, but the present trend is to use 1.25Cr–0.5 Mo alloy because of its better high-temperature creep strength. All the internals, orifice chambers and high-temperature lines are made of SS 304H. During regeneration, poisonous CO is produced. Because of safety considerations, the present day practice is to burn the exit gases and produce steam in CO boiler. In case of any problem in CO boiler the exit gases are bypassed through bypass duct to chimney. The main and bypass ducts are also of SS 304H. There have been many instances of intergranular cracking at weld joints and also cases of bulging of orifice chamber, probably due to overheating and thermal stresses. The cracking has been attributed to sigma formation and polythionic acid SCC. It is claimed that introduction of nitrogen and ammonia purge at 93 °C (above dew point) during the shutdown minimize cracking incidence.

Expansion bellows (normally of large diameters) in the regenerated catalyst stand pipe are prone to failure due to a variety of reasons, e.g. CSCC, polythionic acid cracking, fatigue and embrittlement. The alloys which have been used for bellows are Inconel 625, Incoloy 800, Incoloy 801, SS 304 H, and Inconel 617.

However, none have been found to be fully successful though high nickel containing alloys give comparatively better life. To improve the reliability, double ply expansion bellows with full strength of each ply is used. In the event of failure of one layer, signal is received at control room and replacement of the complete bellow is planned in next shutdown. Till that time the plant operates on the second layer of the expansion bellow. Failure due to thermal fatigue of riser has also been reported.

10.4.4.3 Refractory Lining

One of the major problems in FCC is related to the integrity of the refractory lining. In regenerators, transfer lines, reactors, slide valves, etc. refractory linings are subjected to erosive action of the moving catalyst (velocities in transfer line can vary from 7.5 to 15 m/s) along with reducing and oxidizing actions in reformer and regenerator sections respectively. Depending on the component, the erosive action may be mild to very severe. It is not uncommon to see the transfer lines with patch plates at locations where the erosion is severe enough to erode the refractory and then puncture the metal. Types of refractory specified and their application are, therefore, to be given particular attention.

10.4.5 Catalytic Reforming Unit

10.4.5.1 Process Outline

Catalytic reforming process is specifically used to increase the octane number of gasoline, an essential requirement for increasing the efficiency of engines. It may be mentioned that earlier the common method used was the addition of lead compound to increase the octane number. These were known as leaded gasoline, but their use has been discontinued due to the poisonous nature of lead. The reforming process consists of reacting gasoline with hydrogen in the presence of platinum catalyst. The process is carried out at temperatures up to 560 °C. During reforming process H_2 is produced. However, the chloride in catalyst reduces due to the formation of HCl and the catalyst activity is reduced. The original process was known as semi-regeneration process, where the catalyst activity got restored periodically in situ in regeneration shutdowns. The reforming process is endothermic and the reaction is carried out at temperature of 500–520 °C at a pressure of about 30 kg/cm^2 in three or four reactors in series with intermediate heaters for reheating as shown in Fig. 10.12 [44]. In semi-regeneration process, periodic regeneration requirement used to affect the throughput adversely that led to the development of continuous regenerating reforming process. The modern continuous catalytic reformers use side-by-side (as in semi-regeneration process) or as-stacked reactors.

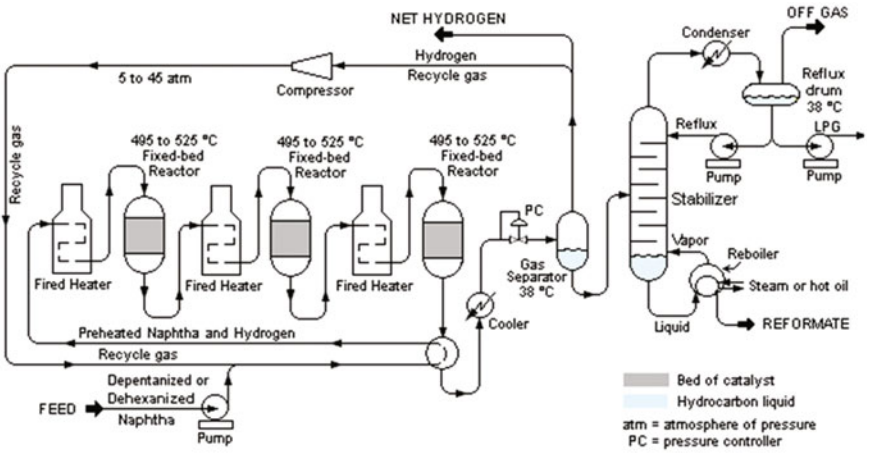


Fig. 10.12 Process flow diagram of a typical semi-regenerative catalytic reforming unit [44]

For continuous catalyst regeneration (CCR), the catalyst is continuously withdrawn from the reactor, regenerated and fed back to the reactor bed.

10.4.5.2 Selection of MOC

The material of construction used for high-temperature items, such as heater tubes, transfer line, reactor/effluent line, feed/effluent exchangers, are to be selected primarily for their resistance to hydrogen attack and operational temperature limitations of the alloys. The extent of hydrogen damage caused depends on temperature, hydrogen partial pressure and stability of carbide. Under the high-temperature operating conditions encountered in reforming, C–0.5Mo, 1Cr–0.5Mo and 1.25Cr–0.5Mo steels have been used in different sections of the semi-regenerative CRU. On the other hand in CCRU heaters, higher grades Cr–Mo alloys like P22, P5 and P91 are used because of their ability to withstand higher operating temperatures. If steels of specified composition are used with minimum lamination and maximum cleanliness, no major high-temperature hydrogen attack is experienced.

10.4.5.3 Problems Experienced in CCRU

Unlike semi-regeneration CRU, CCRU is operated at lower pressure but higher temperature of up to about 640 °C. Higher severity quite often leads to an increase in skin temperature to almost design value. To meet the requirements of higher temperatures, higher metallurgy like 2.25Cr–1Mo, 5Cr–0.5Mo and 9Cr–1.0Mo heater tubes are presently being used. Under the operating conditions, metal dusting/carburization of heater tubes occurs resulting in pitting/thinning of tubes.

It has been the experience that 9Cr–1.0Mo material is far more resistant to metal dusting than the 5Cr–0.5Mo, and particularly, 2.25Cr–1Mo. On the other hand, higher Cr–Mo alloys like 9Cr–1Mo would be more prone to carburization. Figure 10.13 shows carburization in a 9Cr–1.0Mo tube and near through wall cracking [45]. It is possible that at lower temperatures and in lower Cr–Mo alloys metal dusting is the primary cause of attack. At higher temperatures carburization becomes the dominant mode, especially in case of higher Cr–Mo alloys. In extreme cases, the carburized layer gets cracked and gets detached leading to tube thinning. It has been observed that the chemical used for chlorination has also a role in enhancing this type of damage. For example, in one refinery, the replacement of carbon tetrachloride (CTC—$CC1_4$) (because of its carcinogenic nature) with tri-chloroethane (TCE—$C_2H_3Cl_3$) as chloriding agent increased the severity of thinning of heater tube. The outlet end of 5Cr–0.5Mo heater tubes of charge heater showed through and through carburization (>1%C) combined with thinning. The problem was investigated and the observations could be explained on the basis of higher carbon potential of TCE (2.7 times) compared to that of CTC. This resulted in increased rate of carburization and subsequent thinning [46].

To avoid poisoning of catalyst the gasoline feed is desulphurized. However, it has been found that problems related to metal dusting and carburization has increased manifold after deep desulfurization (<3 PPM H_2S) of feed was started. To minimize the problem, the present practice is to add small amounts of sulphur in feed which get adsorbed on tube surface and inhibit carburization/metal dusting. During 2000 NPRA meeting (item C5.6-01: Catalytic Reformer) problems related to metal dusting and carburization were discussed and the general opinion was that the primary solution to this problem is burner management and control as these multi-cell furnaces are particularly prone to problems including flame flips. The type of fuel used, oil or gas, should also be given due concern to avoid overheating.

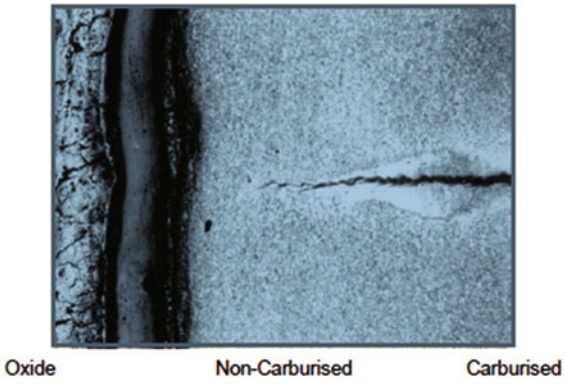


Fig. 10.13 Near through wall cracking in heavily carburised layer [45]

10.4.6 Hydro-desulphurizer and Hydrocracker Units

10.4.6.1 Process Outline

All petroleum fractions contain sulphur in small or large amounts, which is required to be removed for further use. Even small quantities of sulphur are not tolerated in some processes where it poisons the catalyst where the feed is first desulphurized as in case of hydrogen production, catalytic reformer and LAB production. For removal of sulphur, different fractions (diesel, kerosene, naphtha, HGO, etc.) are reacted with hydrogen at high temperature and pressure in the presence of a catalysts. These are patented processes and variously called as hydro-treaters, desulphurizers, hydrofining, etc. The other important process which is related to the use of hydrogen as one of the constituents of the feed is hydrocracking. Hydrocracking enables refineries to maximize middle distillates and simultaneously reduce the sulphur level in the products. All the processes are broadly similar and operate within the temperature range of 370–455 °C with the pressure varying between 28 kg/cm^2(400 psig) to 175 kg/cm^2 (2500 psig). In all these processes, sulphur is converted into hydrogen sulphide. In addition, any organic nitrogen and chlorine compounds present in the feed are converted into ammonia and hydrochloric acid, respectively, which also become part of the reactor products. Figure 10.14 shows simplified flow diagram of hydro-desulfurizer and hydrocracker [47].

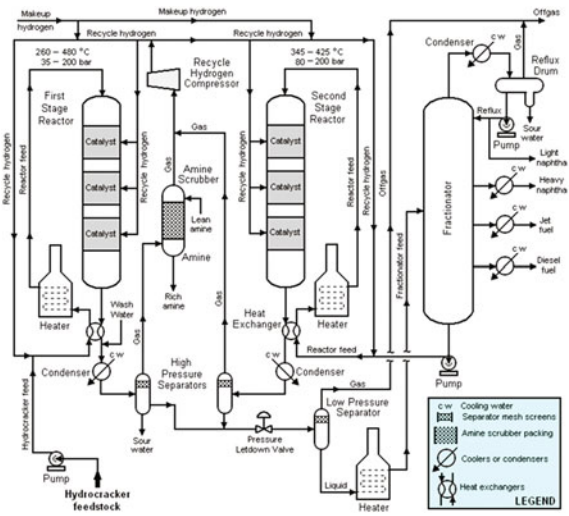


Fig. 10.14 Schematic process flow diagram of Hydrocracker unit [47]

10.4.6.2 Role of Hydrogen in High-Temperature Sulphur Attack

The nature and intensity of high-temperature attack in the presence of both hydrogen sulphide and hydrogen is quite different from that when either of the two is present alone. Here chromium does not have the expected beneficial effect [48]. Earlier it has been discussed as to how chromium helps in preventing high-temperature sulphur attack in the absence of hydrogen. One of the important points was the modification of sulphide scale when iron is alloyed with chromium. The modified scale makes diffusion of anion and action difficult. However, there is no change in the nature of sulphide scale in presence of hydrogen indicating that it does not play any role. However, this does not explain what role H_2 has in destroying protective properties of the scale. There are differences of opinion and various reasons suggested are as follows [48, 49]:

1. The absence of coke formation in lighter distillates resulting in formation of less protective scale.
2. Other less corrosive sulphur constituents getting converted into H_2S and higher H_2S makes the medium more corrosive.
3. H_2 promotes the decomposition of absorbed sulphur compounds and counteracts the influence of chromium.

Isocorrosion high-temperature sulphidation rates of carbon, iron-chromium and stainless steels were prepared by Couper and Gorman in naphtha and gas oil environment [49]. The intensity of hydrogen + hydrogen sulphide attack is dependent on hydrogen sulphide partial pressure, temperature, type of material and the product being treated. Various Couper–Gorman isocorrosion curves give corrosion rates for different temperatures, from 210 to 565 °C (400–1050 °F), and H_2S partial pressures in the process stream. Figure 10.15a–c give isocorrosion curves of carbon steel, 9Cr–1Mo and 18Cr–8Ni stainless steel respectively in gas oil diluents [50]. It would be evident that considerable improvement in corrosion rate is observed with increase in chromium content. The best performance is obtained in case of 18Cr–8Ni followed by 12%Cr steel. The industry in the initial stages of development of these processes used Cr–Mo steels thereby experiencing not only heavy loss of metal but also serious trouble due to fouling of equipment by loose sulphide scale carried along with the stream, leading to a pressure build-up in the reactor and the combined feed exchanger at reactor outlet, with subsequent decrease in throughput and increased maintenance.

10.4.6.3 MOC Used in Hydro-desulphurizer

Because of presence of hydrogen in the system, as mentioned earlier, the material selected should also be resistant to hydrogen attack at the operating temperature and hydrogen partial pressure. In hydro-desulphurizer, the operating pressure and consequently the hydrogen partial pressure increase with increase in severity of

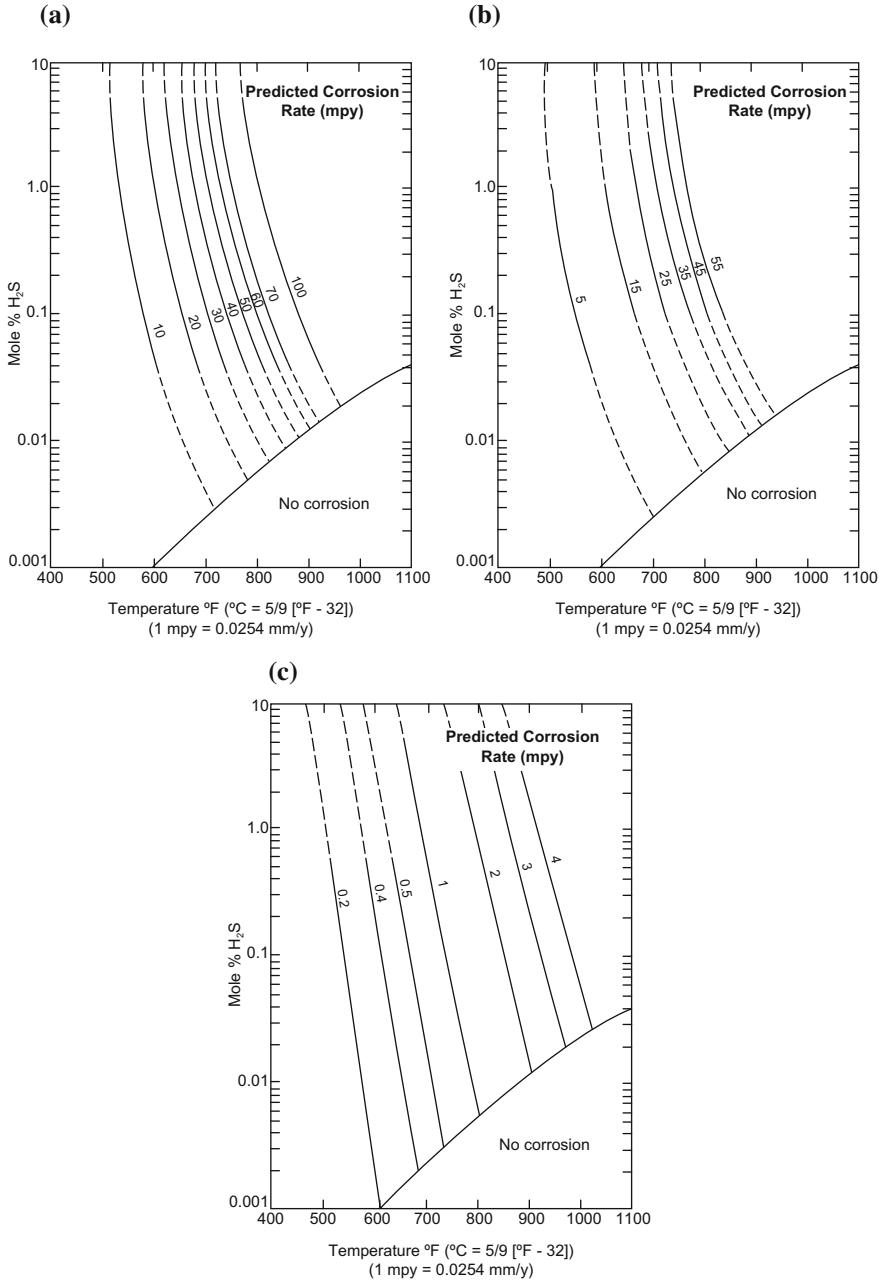


Fig. 10.15 **a** Isocorrosion curves of carbon steel in gas oil diluents [50]. **b** Isocorrosion curves of 9Cr–1Mo in gas oil diluents [50]. **c** Isocorrosion curves of 18Cr–8Ni stainless steel in gas oil diluents [50]

operation. If the conditions are moderate, heater tubes and transfer lines have earlier been made of 5Cr–0.5Mo/9Cr–1.0Mo steels, but with a limited life and high possibilities of fouling of reactor bed by sulphide scale. As the tube skin temperature and fluid velocities in the heater tubes are higher than that in the transfer line, the metallurgy of heater tube used presently is SS 321. In regards to the reactor effluent line having higher H_2S partial pressure and also a little higher temperature, the MOC is either solid or clad SS 321 line. Nowadays it is a common practice by many designers to specify heater tubes and piping of SS 321 even for naphtha unifier where the conditions are less serve. The reactor, being critical equipment, is made of clad SS 321. As hydrogen permeates through stainless steel, the base material is required to be resistant to high-temperature hydrogen attack with respect to the temperature and the hydrogen partial pressure. In selection of MOC for handling liquid hydrocarbon phase, it should be assumed that the hydrogen has effect of partial pressure similar to the gas with which the liquid is in equilibrium. In the train of feed/effluent heat exchangers used in hydrogen + hydrogen sulphide service, the materials of construction of different exchangers depend on the temperature and H_2S partial pressure on the shell and tubes side of individual exchangers. As an example, material selection diagram (MSD) of different equipment in simplified flow diagram of gas oil desulphurizer unit is given in Fig. 10.16 [6].

There are number of feed to reactor effluent exchangers in series (known as combined feed exchanger) where shell and tube side temperatures and H_2S partial pressure vary in different exchangers. The MOC of individual exchangers are therefore to be selected accordingly. For example, in the case of the first exchanger downstream of reactor where temperature on both tube and shell side are high along with higher H_2S partial pressure on shell side, based on the Couper–Gorman diagram MOC of recommended tube material can be SS 321 with shell of SS 321 clad 1.25Cr–Mo. As the temperature decreases, downstream exchangers would have progressively less alloyed material with the last one sometimes being of carbon steel.

10.4.6.4 MOC of Hydrocracker

In addition to the above requirements for desulphurizers, material selection in hydrocracker requires some special considerations. Because of the operating pressures of about 2500 psi, wall thickness required for pressure components are very high. Further, the 2.25Cr–1Mo used for reactor and related equipment is likely to develop temper embrittlement (see Chap. 8) at the operating temperatures, reducing the fracture toughness of the alloy. To minimize the susceptibility to temper embrittlement, level of impurities like P, Si, Mn, Sn, Sb, etc. in the base metal and weld is controlled to the minimum possible level. Cladding of reactor internal surface with austenitic stainless steel is used to protect the underlying steel from corrosive environments and also to avoid fouling and poisoning of catalyst by iron. In the case of hydrocracker, the recommended SS 18Cr–8Ni should have higher resistance to sensitization at high operating temperature (≥ 400 °C). Of the

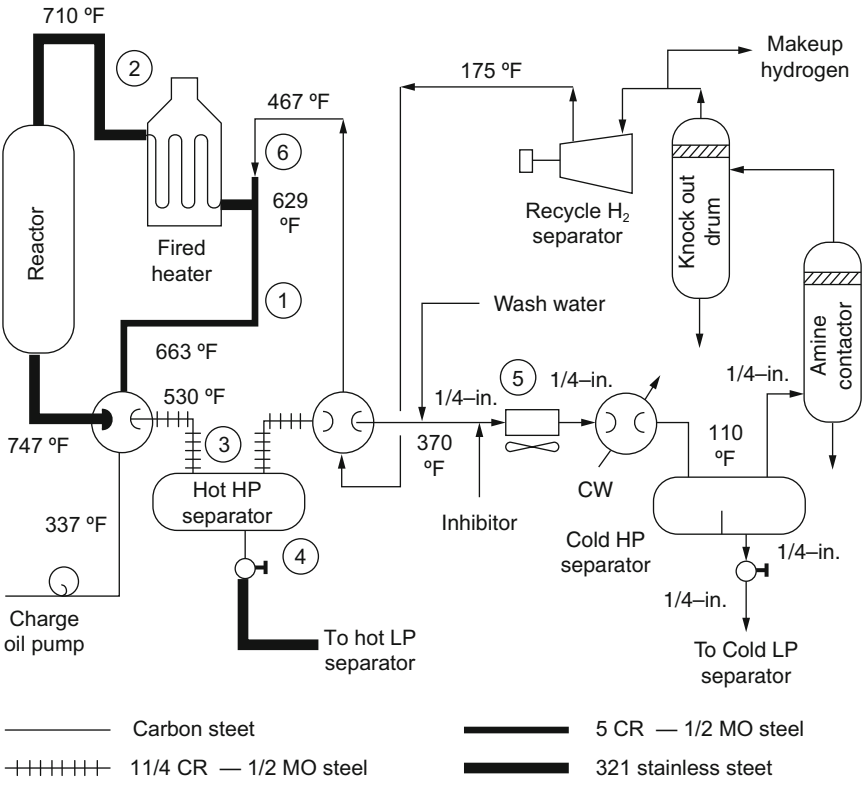


Fig. 10.16 Material selection diagram (MSD) for the high-pressure portion of a gas oil desulphurizer [6]. *Note* Pipe downstream of let-down valve of HP to LP line is of SS 321 instead of carbon steel to guard against erosion/corrosion by flashing H_2S containing liquid

various grades, Type 347 has much narrow temperature range of sensitization and also takes very long time to get sensitized compared to SS 321 or 304L [51]. In view of the above, Type 347 stainless steel is specified for hydrocracker equipment operating at high temperatures. This is also applicable for piping and other components in high-temperature high-pressure section of hydrocracker.

Advanced Cr–Mo–V Alloys for Hydrocracker

During the late 1980s, concentrated efforts were made to develop advanced 2.25Cr–1.0Mo and 3.0Cr–1.0Mo alloys containing vanadium. These had higher strength over the conventional alloys and were accepted as Code Case by ASME and subsequently included as a standard specification (Table 10.9). Details of required material properties and fabrication techniques for both the conventional and advanced steels were brought out as API 934A [52]. The standard specifies

Table 10.9 Base metal specifications

Steel		Conventional		Advanced		
Product form	ASME spec	Standard 2¼ Cr–1Mo	Standard 3Cr–1Mo	2¼ Cr–1Mo-1/4V[a]	3Cr–1Mo–1/4VTi-B A	3Cr–1Mo–1/4VCb–Ca[b]
Plate	SA 387	Grade 22, Class 2	Grade 21			
	SA 542		Class 2	Type D, Class 4a	Type C, Class 4A Grade 21V	Type E, Cl 4a, Grade 23V
	S 832			Grade 22V		
Forging	SA 182	Grade F22	Grade F 21	Grade F22V	Grade F3V	Grade F3VCb
	SA 336	Class 3 Grade	Grade	Grade F22V	Grade	Grade
	SA 508	F22, Class 3	F21, Class 3		F3V	F3VCb
	SA 541			Grade F22V	Grade F3V Grade F3V	Grade F3VCb Grade F3VCb
Pipe	SA 335	Grade P22	Grade21			
Pipe	SA 369	Grade FP22	Grade FP 21			

a. Covered by ASME *BPVC,* Section VIII, Division 2, Sect. 3.4
b. Covered in ASME Code Case 2151-1

stringent requirements on various aspects of material specification and fabrication procedure like:

- Immunity from temper embrittlement by controlling J and X-bar factors and performing step cooling test where necessary, control of impact values of plates and welding consumables respectively.
- Control of hardness before and after final PWHT.
- After welding hydrogen is to be removed before cooling using intermediate stress relieving (ISR) or dehydrogenation treatment (DHT).
- 100% ultrasonic scanning of plates and forgings in accordance with ASME SA 435/SA 578 (level C) and AM 203 for plates and forging respectively.
- Inspection of welds using DP and MPI followed by radiography. Ultrasonic testing is also permitted in lieu of radiography.
- Weld overlay will be inspected using ultrasonic in accordance with SA 578 Level C.

Advantages of Vanadium-Modified 2.25Cr–Mo Steel

The advantages of advanced 2.25Cr–1Mo–0.25V steel over the conventional 2.25Cr–1Mo can be stated as follows:

- Higher elevated temperature strength
- Lower susceptibility to temper embrittlement
- Less vulnerable to hydrogen embrittlement
- Less susceptible to hydrogen attack
- More resistant to weld overlay disbanding.

Equipment like hydrocracker or ammonia converter is designed as per ASME Section VIII Div. 2. Major changes have been made in the 2007 Edition of ASME Section VIII Div. 2 [53]. One of the important changes has been in the allowable (design) stress over that in the original edition. As per the new norms at 454 °C, a 33.3% increase in allowable stress over the conventional 2.25Cr–1Mo material is obtained in case of vanadium-modified steel which in turn leads to considerable decrease in wall thickness of pressure vessels operating at high pressures. The main driving force for increasing use of this alloy has therefore been its cost advantage, which has been well summarized by De Colellis et al. in [54]

> Thanks to all these benefits, reactors can be built lighter and, therefore, cheaper. For the reactor manufacturer, this translates into fewer and lighter movements in the factory, easier transportation, lighter loads on the roads and lighter lifting, which opens up crane availability and using a lighter crane while loading on a ship or during erection, which means less cost. The foundations where the reactor will sit can now afford to be lighter and shallower. Each of these activities provides cost benefits with a lighter weight reactor. The industry cannot deny these benefits as they give considerable economic advantage

However, the advanced steel do have some serious disadvantages, specially related to fabrication, such as, susceptibility to re-heat and weld cracking, requirements of close control over preheat, interpass and intermediate stress relief temperatures, difficulties in hardness and toughness control, etc. However, in spite of these the fabricators have been able to sort many of the problems and are more confident in the construction of V-modified steel vessels.

Hydrogen Embrittlement of Reactors

Care has to be taken in operation of reactor to minimize chances of hydrogen embrittlement. Bagdasarian et al. [55] have described studies conducted which highlight the role of both temper and hydrogen embrittlement After finding number of linear indications in welds of 2.25Cr–1Mo, six hydro-treating and hydrocracker reactors were retired in 1990 after 26 years of service, during which period it had undergone 50 thermal cycles (temperature falling below 121 °C). These were of first-generation alloys with J factor varying from 60 to 200. Detailed investigation was carried out to study various aspects of damage which occurred during service. One of the girth weld flaws of 15 mm was sectioned and examined in detail. The photomontage of the crack showed a 4 mm curved crack with blow holes (likely an original one) followed by the main crack with a step-like feature. From the

Table 10.10 Build-up of H_2 pressure in the steel matrix during rapid cooling

Phase	Temperature (°C)	H_2 pressure (atm)		
		2 ppm H	4 ppm H	8 ppm H
Γ	1400	0.058	0.23	0.90
Γ	1100	0.12	0.48	1.90
γ	900	0.23	0.92	3.70
α	900	0.58	2.33	9.30
α	700	1.83	7.30	29.2
α	500	10.4	41.6	166.5

fractograph the failure appeared to be a case of hydrogen induced cracking with each step of the crack corresponding to about one of the 50 thermal cycles that the reactor had undergone during its lifetime of 26 years, The effect of shutdowns on crack growth due to hydrogen embrittlement is now well known. The main reason is that when cooled from high temperature the soluble hydrogen from thick vessels cannot fully escape and cause pressure build up and cracking. Table 10.10 gives extents of hydrogen pressure build up which can occur in case no hydrogen diffuses out from steel containing 2, 4 and 8 ppm H [56].

Minimum Pressurization Temperature (MPT)

Tempter embrittlement as a metallurgical degradation has been discussed in Chap. 8. Keeping in view of its importance, close compositional control, i.e. lower Si and Mn and low level of P and tramp elements like Sn, As, Sb for both base metal and consumables is specified. Thus J factor and X-bar factor for base metal and consumable, respectively, are kept within limits. Further to avoid cracking due to temper embrittlement, the industry practice earlier had been that during start up the concerned equipment should not be pressurized beyond 25% of the rated values unless the temperature reaches above 150 °C. This is known as minimum pressurization temperature (MPT). This is to avoid failure due to temper embrittlement which occurs at temperatures of <120 °C. However, with continuous improvement in quality of steel, popularly known as fourth-generation steel (presently fifth-generation steel is also claimed to have been developed), it has been possible to reduce the J factor to a level where the chances of temper embrittlement is unlikely to occur. Consequently, there has been considerable reduction in MPT with reactors fabricated from alloy manufactured using modern steel making processes as shown in Fig. 10.17 [57]. According to API 571 [58] presently in temper embrittlement resistant steels the MPT is down to ~38 °C against generally 171 °C for the first-generation steel.

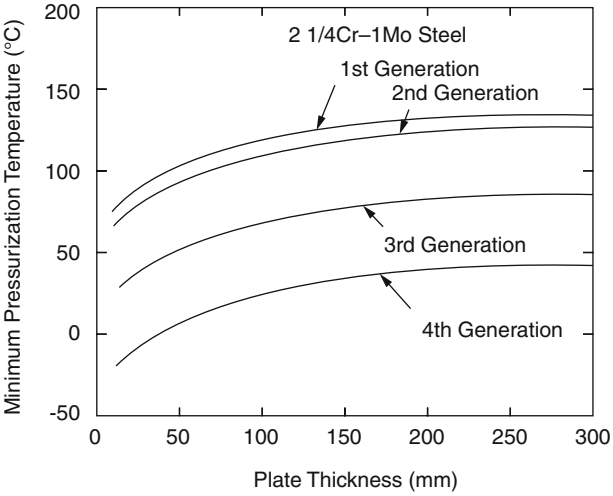


Fig. 10.17 Minimum pressurization temperature versus plate thickness in each generation [57]

10.5 Problems Related to Low-Temperature Service

10.5.1 Corrosive Constituents

At lower temperatures, in the areas where free water exists, corrosion due to electrochemical reaction is the most important damage mechanism. Hydrocarbons, whether in liquid or gaseous form, are non-corrosive but in cooler zones corrosion can occur where water condenses and the acidic or other corrosive constituents present gets dissolved in it. These corrosive constituents form either by decomposition of inorganic or organic compounds present in the crude or by reaction occurring during processing. The problem is, therefore, primarily confined to the overheads of distillation columns and reactor downstream product coolers. The corrosive species varies in different units depending on the characteristics of the feed and upstream operating parameters, but in most cases these are related to acidic corrosion. In a few cases of corrosion is by an alkaline species.

10.5.1.1 Acid Corrosion

The corrosion in overhead system is caused by:

- Hydrochloric acid, formed from hydrolysis of calcium and magnesium chlorides which is present in the water carried over along with the crude. This is the principal strong acid responsible for corrosion in crude unit overhead. Hydrochloric acid is also present downstream of hydro-processing reactors, where the organic chlorides present in the feed is converted into HCl.

- Hydrogen sulphide is the second significant corrosive agent which is formed by high-temperature decomposition of sulphur compounds in the feed. In processes like hydro-desulphurisation, hydro-treating and hydrocracking H_2S is also formed.
- Low molecular weight fatty acids with low boiling points are quite often found in the overheads while processing high TAN naphthenic acid crude.
- Carbon dioxide, though not common, can be found in the overhead of crude from CO_2 flooded fields and crudes that contains a high content of naphthenic acid [59].
- Sulphuric and sulphurous acids, formed by either oxidation of H_2S or direct condensation of SO_2 and SO_3 have also been found to have caused corrosion. The problem is more likely to occur in vacuum units where air/oxygen ingress from the atmosphere can happen [60].

10.5.1.2 Alkaline Corrosion

Ammonia is formed when the nitrogen compounds in the feed is converted into ammonia in processes using hydrogen. While ammonia is not corrosive, it combines with H_2S to form ammonium bi sulphide, which though an alkaline compound, is highly corrosive. The damaging effect of bisulfide is also experienced in the handling of sour water. Carbonate stress corrosion cracking and amine corrosion cracking also fall under this category.

10.5.2 Overhead Corrosion Control System in Different Units

The overhead system of any fractionator consists of column top, cooler/condenser, receiver and associated pumps and piping as shown in Fig. 10.18.

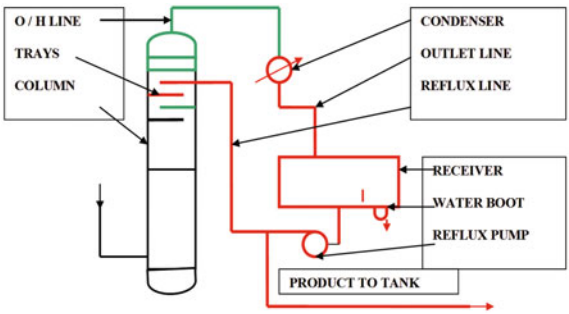


Fig. 10.18 Overhead system of crude distillation unit

10.5.2.1 Crude and Vacuum Unit

Crude and vacuum units are the mother units of any refinery and their operation is directly related to the profitability of the refineries. In oil refining industry, therefore, the problem of overhead corrosion of these two units gets maximum attention. NACE International Technical Committee report [61] has discussed various aspects of the problem in crude and vacuum units and suggested existing best practices to control overhead corrosion. This report should be consulted by refiners for controlling the overhead corrosion. Though it covers primarily crude distillation and vacuum units, the basic approach is applicable for fractionation columns. For other units, a broad outline of the problem and its remedial measures are described here.

Source of Hydrochloric Acid

Hydrochloric acid has a major role in the overhead corrosion of crude and vacuum units. The crude being processed contains some amounts of entrained water having high amounts of dissolved solids which is reflected in the crude analysis and reported as BS&W. The stability of these chlorides decreases at high temperature, and they hydrolyse on decomposition into hydrochloric acid. The reaction can be represented as

$$MCl_2 + H_2O \rightarrow MO + 2HCl \qquad (10.5.1)$$

where M is the alkaline metal.

Of the three chlorides, magnesium chloride has the least stability and sodium chloride the highest. Thus as the crude passes through the crude preheat exchanger train, first to decompose is $MgCl_2$, followed by $CaCl_2$. Table 10.11 gives the hydrolysis characteristics of the various chlorides [61].

Though NaCl has no role in contributing to the presence of HCl in the overhead, in crudes containing naphthenic acids possibilities of the hydrolysis of $MgCl_2$, $CaCl_2$ and even NaCl can increase. Source of hydrochloric acid, though not common, can also be what is known as non-extractable chlorides or organic chloride. Hydrochloric acid (HCl) formed is dry at this temperature and is, therefore, non-corrosive. Another source of chloride and other damaging constitutions can be related to the various oil field chemicals (OFC) which are being increasingly used [62]. As HCl passes through the heater and then to the column, it rises along

Table 10.11 Hydrolysis reactions

Reaction	Approximate starting temperature, °C (°F)	Approximate degree of Hydrolysis at 340 °C (650 °F)
$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$	120 (248)	90%
$CaCl_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HCl$	210 (410)	10%
$NaCl + H_2O \rightarrow NaOH + HCl$	<500 (<930)	2%

with the hydrocarbon vapour from the column bottom to the top. However, the rising vapour also contains some water, its source being the crude and the stripping steam used in the main and stabilizer columns. As the vapour is cooled, the water along with the hydrocarbon vapours condenses. The condensed water dissolves the HCl present in overhead vapour, making the water acidic. Thus, wherever acidic water condenses and collects in the overhead system, aqueous acidic corrosion takes place.

Source of Hydrogen Sulphide

Sulphur in the crude being processed is mainly present as organic sulphides with very small amounts of dissolved H_2S. The sulphur compounds partly get dissociated into H_2S at high temperatures during processing of crude and various distillates. Thus, various concentrations of H_2S are present in the gaseous phase along with HCl. H_2S, being a corrosive acidic gas, also attacks metal in areas where condensation of water takes place and accelerate overhead HCl corrosion, specially under low pH conditions. Though H_2S has much lesser impact on corrosion compared of HCl and organic acid, it does make the condensed water sour which in turn causes hydrogen-related damages like blistering, SSCC, and HIC.

Source of Organic Acids

Light organic acids are found in the overheads when naphthenic acid containing crude is processed. The problem has attained greater importance in the recent years because of considerable increase in processing high TAN crude. Sometimes acetic acid also comes from upstream well operation/processing or when added to desalter to improve performance and inhibit calcium naphthenate salt deposition [63].

Other Acids/Acidic Salts

Corrosion due to other acidic species like CO_2 and H_2SO_4 occurs in some specific cases only and does not fall under the category of general corrosion. Of greater concern is the solid acidic salt, ammonium chloride or amine chlorides, which are formed in the crude distillation overhead as a result of reaction between NH_3/amine and HCl. These salts form not only as a result of neutralization but can react in gaseous phase to form solid salt, which is dependent on temperature/partial pressure relationship for gaseous phase NH_3/HCl reaction. Depending on the operation, NH_4Cl deposit can form in overhead lines, coolers, and also in column top. When deposited in coolers (Fig. 10.19a) at locations having temperature above water dew point, the deposit is not washed away. Being hygroscopic, the salt absorbs water from vapour stream and the damp acidic salt cause heavy under-deposit corrosion (Fig. 10.19b).

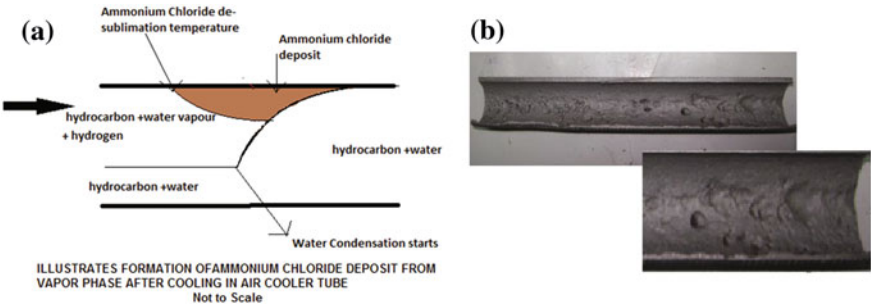


Fig. 10.19 **a** NH_4Cl deposit in air cooler tube. **b** Under-deposit corrosion in air cooler tube

Corrosion Control Measures

As discussed earlier, aqueous corrosion occurs only in areas where water is present in liquid phase. There are various methods by which this type of corrosion can be minimized and in actual situation more than one method has to be used to maximize the protective capability. The various measures which can be taken are (i) process changes (ii) injection of chemicals such as neutralizers and corrosion inhibitors, and (iii) materials upgradation.

Process Changes

The major approach in controlling corrosion due to HCl during atmospheric and vacuum distillation is to reduce its presence in the overhead. Reported targets mentioned are 10–25 ppm [64] in the overhead accumulator water to be achieved by taking the following steps:

* Reducing the amount of BS&W in crude with the help of desalter. By using double desalting, it is possible to reduce the chloride content to 90–95% of the original level and thus the corrosion rate to a very low level [65].
* As NaCl is stable at the operating temperature, dilute caustic is injected into the crude, downstream of desalter or sometimes downstream of exchanger train. The caustic either reacts with HCl to form NaCl or converts Mg and Ca chlorides to stable NaCl as shown below:

$$NaOH + HCl \rightarrow NaCl + H_2O \tag{10.5.2}$$

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + NaCl \tag{10.5.3}$$

$$CaCl_2 + 2NaOH \rightarrow Ca(OH)_2 + 2NaCl \tag{10.5.4}$$

The NaCl formed is sufficiently stable in the CDU preheat train and furnace. The following steps are needed to avoid problems with a caustic injection system:

* Quill design should ensure proper mixing oil and caustic to avoid caustic corrosion in the nearby carbon steel pipe. While fixing the quill to pipe it should be ensured that the quill opening facing the flow and caustic solution does not directly hit the pipe wall. The MOC of quill will preferably be Monel, though Alloy 825 can also be used.
* Put the crude on tube side of preheat exchangers to prevent caustic pockets around baffles and floating heads. Caustic strength should preferably be between 2 and 10% and, as far as possible, fresh caustic should be used to prepare the solution.
* For effective neutralization by caustic it should remain dispersed in the feed and, therefore, the caustic solution prior to injection should be thoroughly mixed with a slip stream of crude using a vortex mixture.
* Lower limit of chloride in the receiver is recommended to avoid over-feeding of caustic as excess sodium in distillation tower bottom shall lead to problem of coking in furnace tubes in downstream units like coker, visbreaker and FCC and also poisoning of catalyst. Best practice will be to add as much caustic as required to maintain sodium in reduced crude as maximum $\sim$25 ppm in downstream feed [66].

Corrosion occurs, wherever the acid condenses and the acidic water is carried. The amount of water in the column outlet vapour is quite small and its dew point, depending on the operating condition, it can be anywhere between 80 and 90 °C. Initially, small volume of water condenses as the dew point is reached. At this point, the metal surface is just wetted. Beyond this point, further cooling results in increase in the rate of condensation. The initial condensed water is rich in HCl (very low pH) because of high solubility of HCl in water. Further down, the pH of condensed water decreases because of decreasing amount of HCl in vapour and increased condensation of water. Thus, the pH of water at the first/initial condensation point is much lower compared to what we measure in the tail water (the point of pH control) as shown in Fig. 10.20 [61]. The former area, therefore, experiences the highest rate of corrosion.

Neutralization

1. In spite of process modification, the presence of acids in the overhead cannot be completely eliminated. Corrosion due to the remaining acidic species is to be controlled by neutralizing the overhead water to a near neutral pH range. Depending on operating conditions and metallurgy of the condenser tube (steel or copper alloys) typically, this pH range is normally maintained at 5.5–7.0. Adequate neutralization of HCl is critical to effectively elevate the water dew point region pH to as near to the accumulator water as possible.
2. The selection of a neutralizer is an important issue as it may cause more problems if not selected properly. Ammonia is often used for crude overhead pH

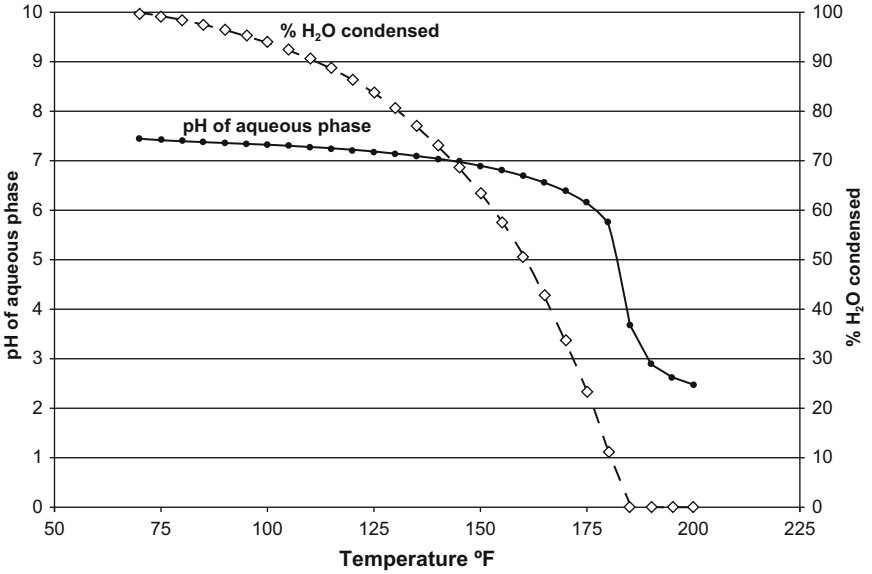


Fig. 10.20 pH versus temperature plot for simulated atmospheric tower overhead system [61]

control because of its low cost and fairly good neutralizing property. However, two major disadvantages are its inability to reliably control pH within the water dew point region (because of low solubility at high temperature) and undesirable characteristics of salt formed on neutralization.

3. A preferable alternative is the use of either an amine or mixture of amine + ammonia. It is typically added to the overhead vapour line to neutralize the various acid species and control accumulator pH within control range.
4. In short, it can be stated that selection criteria for the organic neutralizers includes their low salt deposition potential, condensation temperature being similar to initial water condensation temperature of the overhead vapour, pH buffering effect, low H_2S reactivity, relative volatility for distillation, etc. Each of these product capabilities varies in importance, depending upon the system application. The appropriate neutralizer can be selected based on the type and concentration of corroding chemicals present and neutralizer injection location. If the neutralizer is not selected appropriately, an amine chloride salt may actually form prior to the initial condensation point and cause under-deposit corrosion.
5. The neutralizer is typically added to the overhead vapour line to maintain accumulator pH within the control range. Addition of ammonia or neutralizer to the top reflux or base of the atmospheric column can cause fouling and corrosion to top trays, down comer, piping, etc. due to ammonium chloride or amine chloride formation.

Inhibition

In addition to neutralization, a suitable filming inhibitor is injected into the overhead system to form a monomolecular film on the metal surface which further helps in reducing corrosion. A continuous filming inhibitor injection is maintained to constantly replenish the film formation on the metal surfaces which is periodically destroyed from acidic attack.

Water Wash

The overall purpose of water washing can be described as (i) increase the dew point so that sufficient water is available at the inlet of cooler, (ii) scrub the vapour of any corrosive constituent, (iii) wash away the salt formed or already deposited, and (iv) dilute the acidic water. It is essential that water washing is properly planned and executed. Where chance of acidity is high, rigorous calculation should be made to find out minimum water injection rate required. According to NACE [61], calculation should be made assuming a worst-case scenario, of maximum overhead flow rate, minimum steam stripping, and minimum column overhead pressure. To this, additionally an excess of 10–25 vol.% should be added to account for process variability and to ensure that free water is available at the entry of the condenser even after the evaporation loss. Continuous injection is preferred over intermittent ones.

Wash water quality has an important bearing on the effectiveness of the system. Most important requirement is that the water should be free of oxygen which increases attack manifold. Water used can be recycled from overhead accumulator, stripped sour water (except that from FCCU and hydro-treater) or boiler feed water (oxygen free DM water) all of which are generally air-free. Fresh water, DM water, cooling water and process condensate should not be used. Water flow meter should form part of the system design, which quite often is not done. Water wash injection point is located, generally nearer to the tower outlet so that it can thoroughly get mixed with the vapour due to higher contact time. This also helps in scrubbing and ensuring elevation of dew pint at condenser inlet. On the other hand, in case of parallel condensers a better distribution can be achieved if injection points are at the inlets of each bank. Alternatively, the water injection can be split into two at both locations though it is highly costly.

Upgradation of MOC

Corrosion due to HCl also affects the top section of the distillation column in spite of the fact that top temperature is around 110 °C, much above the water dew point. This is because of the use of large volume of cold reflux pumped on the top tray which drastically reduces the temperature of liquid present in the top tray. Water condenses locally in spite of the fact that overhead vapour space temperature is 110 °C. Some amount of water is also carried to the column top along with the

reflux. The water collected on top tray, along with liquid hydrocarbon, flows down the trays, gets heated by the upcoming hot-HCl vapours and finally after a few trays vapourizes. The water absorbs HCl present in the rising vapours resulting in the corrosion of trays and valves and also of shell at the liquid line and above, in some cases. This effect of acidic water on corrosion on internals, shell and dome persists up to top 3–4 trays. As neutralization is not possible in this zone, the solution lies in the upgradation of metallurgy, Thus the top 3 or 4 trays and valves are replaced with Monel and top section of carbon steel column clad with Monel. Monel trays are attacked if pH of condensed water goes beyond 8.0. Care is, therefore, to be taken to avoid ingress of excess ammonia in the top section.

Thus overhead corrosion control becomes a matter of chloride management. However, we have also to consider the role of light organic acid in cases where high TAN crude is being processed. These acids also become a part of the acidity of the condensed water and have to be considered in planning the injection of neutralizer and inhibitors. These light organic acids have lower ionization characteristics compared to HCl and therefore have lower corrosivity. Therefore, in the presence of both hydrochloric and organic acids, equivalent factors as given in Table 10.12 [67] should be used to determine effective acid concentration.

In actual practice, proper control and monitoring (which can be done only with the receiver tail water) is not always possible and additional steps are to be taken. The additional protective measures are as follows:

1. Drain the water settled in the crude storage tank bottom as far as possible before sending to the unit.
2. Use continuous pH monitoring of receiver water (instrument is to be properly maintained and calibrated).
3. Analyse for iron, chloride, and H_2S content contents in receiver water, say twice a shift. The ideal level of chloride to be maintained in the receiver water is less than 20 ppm.
4. Ensure separation of water in the accumulator by providing separator plate and water boot. Drain the water regularly. Inadequate separation will result in corrosion of pump, reflux line, column top, storage tank bottoms and pipelines for transporting the product.

Table 10.12 Light organic acid corrosion equivalency factors

Type of acid	HCl equivalent factor
Formic	0.76
Acetic	0.61
Propionic	0.49
Methyl propionic	0.41
Butanoic	0.41
3-methyl butanoic	0.36
Pentanoic	0.36
Hexanoic	0.31
Heptanoic	0.28

5. Provide acid-resistant gunnite (cement) lining on accumulator bottom (3–9 O'clock position).
6. Upgrade metallurgy where necessary (mainly in case of condensers). Erosion corrosion of top tubes of overhead condenser is quite often experienced opposite the inlet flange. To prevent this type of damage, impingement plate on the top of bundle should be provided.

Vacuum Unit

Vacuum unit operates at high temperature (about 390–400 °C) under about 10–40 mm Hg vacuum, where the vacuum is created by number of ejectors connected to the tower top. The product from the top is light vacuum gas oil (LVGO) and from bottom heavy gas oil (HVGO). Because of high-temperature operation, acidic components like HCl, H_2S, light organic acids, CO_2 and SO_x are formed as a result of thermal cracking. Similarly, NH_3 is also formed as a result of cracking of organic nitrogen compound. The vacuum tower overhead system also produces a condensed water phase in which the acidic and basic compounds get dissolved which, in turn, cause corrosion. The species causing corrosion is more or less similar to the crude distillation unit and therefore strategies used are similar in both cases. In other words, neutralization and inhibitor addition are practiced but water wash is avoided because it can cause damage of equipment. The primary reasons are:

- Possible effect on depth of vacuum because of increase in vapour loading,
- Because the system operates under vacuum, the high velocity existing in the overhead can cause erosion corrosion.
- Moreover, salt accumulation is not experienced to a great extent in this unit.

10.5.2.2 Visbreaker and Coker Units

These units operate around temperatures of 460–520 °C, but depending on the product's demand and quality of feed fractionator top temperature and pressure are much higher than distillation unit, which raises the dew point of water. The major corrosive constituents in the overhead are thermally decomposed products. Mostly H_2S and NH_3 are formed, depending on the nature of crude, resulting in NH_4HS (alkaline) corrosion. There have been instances of heavy overhead corrosion due to acidic condition which occurred due to hydrolysable chloride entering the system along with slop (quite often added as 10–15% of feed) or feed contained high TAN bottoms. Normally, overhead corrosion is not a very serious problem in these two units and depending on the situation, combination of various steps described in case of crude and vacuum units (neutralization, water washing and inhibitor injection) are to be adopted.

10.5.2.3 Fluid Catalytic Cracking (FCC) Unit

Because of heavy fraction being processed and use of catalyst H_2S, ammonia and cyanide are main radicals formed during the process. Further, for regeneration the catalyst is burnt resulting in the formation of CO_2 and CO. The major problem experienced in the fractionator section of FCC is SSCC, the intensity of which is exaggerated due to the presence of cyanide which further promotes diffusion of hydrogen is steel in sour system. In FCC, NH_4HS concentrations are usually less than 2 wt% but high velocities and/or the presence of cyanides can remove protective iron sulphide scales. Blistering of carbon steel is also experienced in case the steel is not clean.

Carbonate Stress Corrosion Cracking

The other frequent occurrence in FCC is carbonate stress corrosion cracking. The main reason is the presence of carbonate/bicarbonate in the process fluid along with ammonia, and H_2S and that is why this type of damage is also called *alkaline carbonate stress corrosion cracking* (ACSCC). API 581 [68] has defined the conditions leading to ACSCC as:

- >50 ppm H_2S in the liquid water phase or pH of 7.6 or greater
- Non-stressed relieved carbon steel weld
- pH >9.0 and carbonate concentration >100 ppm
- pH 8.0 to 9.0 and carbonate concentration >400 ppm

Industry survey carried out by NACE in 2006 [69] throws light on the various aspects of the present state of understanding of this problem with respect to H_2S, carbonate concentration and possible role of cyanide [69]. One of the important observations has been that cracking is more frequent in non-stress relieved and improperly stressed relieved equipment in overhead systems, like condenser, receiver, compressor K.O drums, etc. Proper PWHT is necessary to reduce the stress below the threshold stress for cracking in this environment. Periodic monitoring of the feed and the carbonate concentration and mainly pH is necessary to minimize carbonate cracking. Control of weld hardness against carbonate cracking is also necessary which is included in NACE RP 0472-95 [70].

10.5.2.4 Catalytic Reformer

In catalytic reformer, corrosion downstream of reactor is mainly associated with HCl, formed as a result of chlorination of the catalyst, below the dew point of water. The solution lies in injecting sodium carbonate to neutralize the acid. Caustic is not recommended. In case of austenitic steel, chloride stress corrosion cracking can also be expected. These problems are more in the recycle hydrogen circuit.

10.5.2.5 Hydro-desulphurizer and Hydrocracker

In these processes, as discussed earlier, the catalysing reaction converts compounds of sulphur, nitrogen and chloride into H_2S, NH_3 and HCl, respectively. When the treated feed comes out of the reactor, depending on their partial pressure these react individually and with each other to form different compounds which are corrosive. For example, ammonia and HCl would form NH_4Cl while NH_3 and H_2S would from ammonium bisulfide (NH_4HS). Both of these salts sublimate and are also hygroscopic and, therefore, can form solid deposits resulting in under-deposit corrosion as in case of NH_4Cl deposit (Fig. 10.22a, b). In the presence of NH_3 + H_2S the corrosion is related basically to NH_4HS concentration. Though an alkaline salt, ammonium bisulphide is highly corrosive. First industrial survey showed that corrosion of carbon steel is negligible when the NH_4HS concentration was ≤ 2 wt% and the velocity ≤ 20 ft/s (6.1 m/s). It also indicated severe corrosion in the event of the NH_4HS concentration going above 3–4 wt% [71].

Air coolers are preferred in these units and under most of the conditions carbon steel is the specified material, with corrosion controlled by addition of inhibitors, neutralizer and water washing. In case of water washing, quality of water is important which should have maximum 50 ppb oxygen, 50 pm chloride and over 7.5 pH. In hydrocracker processing high-sulphur feed, corrosive conditions are most severe. Because NH_4HS solidifies below certain temperature (depending on pressure) temperature control is also important to avoid choking of tube. It is quite often necessary, therefore, to upgrade the metallurgy of coolers, depending on the percentage of bisulfide and velocity. Based on the guidelines of OSHA [72] and various information collected from literature and discussion at Refinery Conferences, the corrosion control measures can be stated as follows:

1. The design of air cooler bank inlet and outlet piping arrangement plays an important role in the corrosion of tubes. There are three designs, viz. (i) non-asymmetrical inlet and outlet (Fig. 10.21a) [72], (ii) symmetrical inlet but non-asymmetrical outlet, and (iii) symmetrical inlet and outlet (Fig. 10.21b). The last one is the preferred arrangement where every split is symmetrical to every other ensuring same resistance to flow in each path. In such cases uniform flow in all banks is ensured which is a very important requirement where bisulphide is present. However, where symmetrical flow may not be absolutely necessary and in such cases non symmetrical design can be used which has the advantage of minimizing structural height, number of bends required, etc. which has the advantage of reduced cost.
2. Bisulphide can also lead to alkaline stress corrosion cracking, and PWHT to relieve the welding stress is required as a preventive measure. This is included in NACE RP 0472 [70].
3. Corrosion has also been found to be very severe at dead ends. As far as possible, dead ends should be avoided during design itself and for carbon steel the velocity and bisulphide should be restricted to 10–20 ft/s and 8.0%, respectively. As the severity (velocity and bisulphide concentration) increase, material

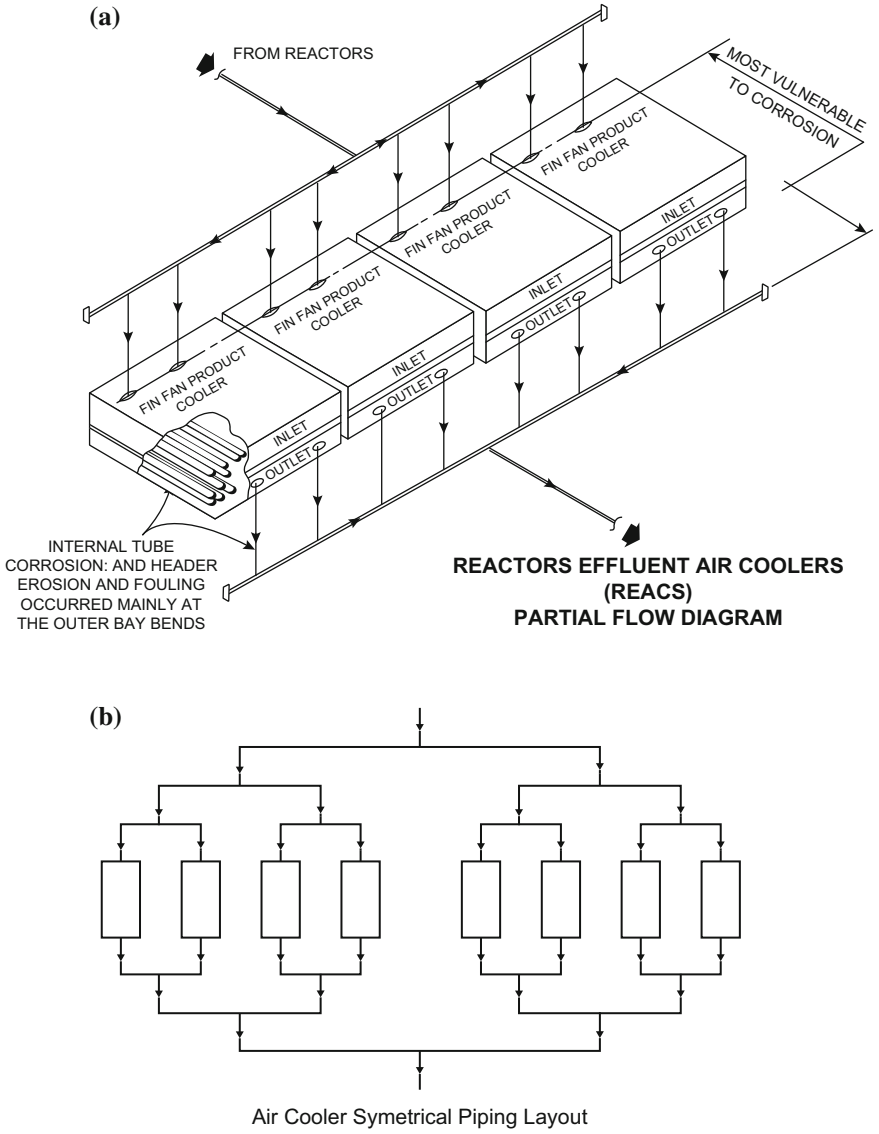


Fig. 10.21 **a** Air cooler with unsymmetrical layout [72]. **b** Air cooler with symmetrical

upgradation becomes necessary. Table 10.13 summarizes the use of various alloys for air cooler under different operating conditions.

4. Material selection for sour water system including REAC, discussed above, has been based on plant experience and somewhat on rule of thumb approach. On the basis of extensive laboratory studies carried out as a part of Joint Industrial Project, Honeywell [73] has developed a program (Predict—SW 3.0), which

Table 10.13 MOC of air coolers for hydro-desulphurizer and hydrocracker

Material	Bisulphide (%)	Velocity (ft/s)	Remarks
Carbon steel	2–3	<30	
Carbon steel	3–8	15–25	With ferrules at inlet
DSS	10–12	>25	
Incoloy 625	20–25	>25	

claims to be giving correct solution under conditions where dominated regime is H_2S, NH_3, or cyanide. The program predicts corrosion rates based on process flow induced shear stress, NH_4HS, and other process conditions. They have also developed isocorrosion curves for different materials which then form the basis of material selection. API RP 932B, first published in 2004 [74] provides guidance to engineering and plant personnel on equipment and piping design, material selection, fabrication, operation, and inspection practices to manage corrosion and fouling in the wet sections of hydro-processing reactor effluent (REAC) system.

Polythionic Acid Cracking

Because of their resistance to $H_2S + H_2$ attack at high temperatures, austenitic stainless steel is extensively used in hydrogen-related processes where presence of H_2S leads to polythionic acid cracking during shutdown. Polythionic acid (PTA), ($H_2S_XO_6$) is a complex acid formed by the reaction of sulphide of metals with water and oxygen during shutdown when the system is cooled and oxygen and moisture enter the system. The cracking is intergranular and occurs more readily in sensitized stainless steels. Sensitization of various alloys is time and temperature dependent. Normally for general corrosion resistance purposes, low and stabilized grades are selected to prevent sensitization of HAZ during the time taken for completing the welding process. However, all these grades do get sensitized when held/operated for long periods in the high-temperature sensitization zone. As the operating temperatures of hydro-desulphurizer and hydrocracker are high, before specifying a particular alloy it is essential to know the minimum temperature at which a particular alloy would likely to get sensitized over prolonged period of service. Temperature range of sensitization has been stated and the values in NACE RP 0170 [75] are given in Table 10.14.

Table 10.14 Sensitization range of different alloys against PTA SCC

Stainless steel grade	304/316	304L/316L	321/347	304H/316H	Alloy 825	Alloy 625
Sensitization range (°C)	370–815	400–815	400–815	370–815	650–760	650–1040

API 581 [76], on the other hand, has graded PTA SCC susceptibility as low, medium and high on the basis of two operating temperatures, at 425 °C (800 °F) or above 425 °C (800 °F) under three conditions of exposure (solution anneal, stabilized anneal before welding and both before and after welding). Of the various alloys, SS 347 and all austenitic steel overlays show least susceptibility when in two stabilized conditions. Superior performance of SS 347 over others is thus confirmed. Alloy 347AP (UNS S34751), developed by Sumitomo Metals [77] is claimed to have been used for a number of years in Japan as a substitute for SS 347. It is claimed that the alloy does not need post-weld stabilization anneal and neutralization treatment during shutdown against PTA SCC. It is a low carbon (0.02% max) low niobium nitrogen (0.06–0.10%) containing alloy having high resistance against PTA SCC. No cracking of sample was experienced in samples aged at 550 °C for 10,000 h when tested as per ASTM (G35) [78]. Because of low niobium, the alloy has also good weldability.

Prevention of PTA SCC

1. Use stabilized grades of austenitic stainless steel.
2. The material should be procured with stabilizing heat treatment and all welds should also be subjected to the same treatment to reduce the chances of in-service sensitization.
3. Implement NACE RP 0170 [75] recommended practice of nitrogen blanketing, nitrogen purging and soda ash neutralization.
4. Include all stainless equipment, piping and heaters (inside and outside) within the preventive procedure.
5. According to NACE, neutralization solution consisting of 2 wt% of Na_2CO_3 (though industry uses 1–5%) not only neutralizes the acid but also keep the equipment wetted with alkaline solution after the equipment is emptied thus helping in neutralizing any acid formed subsequently during the shutdown. However, when the plant is re-started possibilities of chloride SCC exists. The sources of chloride are the water, Na_2CO_3 and salt deposited in hydro-processing reactors. The recommended initial chloride level in case of former is 25 ppm against 250 ppm for the latter.
6. Addition of 0.4 wt% sodium nitrate ($NaNO_3$) is found to be effective in suppressing chloride SCC of austenitic stainless steel but care should be taken to avoid excessive addition which can cause cracking of carbon steel.

10.5.3 Low-Temperature Hydrogen Damage

10.5.3.1 Introduction

In the refining industry, the presence of H_2S is almost omnipresent, especially in the processing of high-sulphur crude. Though H_2S falls under acidic gases, its role is more in causing low-temperature hydrogen-related damage than acidic corrosion.

Hydrogen plays a large role in damaging metals and alloys, specially the ferritic steels. Two modes of attack takes place; high-temperature hydrogen attack (HTHA) and low-temperature hydrogen attack (LTHA). The mechanism of these damages has been discussed in Chaps. 8 and 9, respectively. The units in refinery where hydrogen-related damage is expected have been categorized in Table 10.15. Prevention against HTHA attack has been discussed earlier in this chapter. In this section role of H_2S, ("sour" condition) on hydrogen-related damage and preventive measures thereof under refinery conditions, and how it differs from the sour condition in the oil and gas industry (Chap. 9), have been discussed.

10.5.3.2 Damage in Wet H_2S Service in Refinery Service

The impact of hydrogen induced cracking was largely experienced by oil and gas exploration and production industry where frequent cracking of drilling rod, casing, surface equipment, etc. were experienced in the development of sour wells. Based on detail study and field experience it was established that cracking susceptibility increases with strength in the presence of aqueous H_2S. Various steps were taken to tackle this problem as discussed in Chap. 9, including finalization of NACE RP 0175, which was later combined with ISO 15156 as MR 0175/ISO 15156. NACE has reissued its separate Standard as MR0175-2009 [79]. Normally, hydrogen-related damage was not considered to be of great concern by the refining industry and there was no specific standard existed and when needed designers and operators used MR0175 as a guideline and these were popularly called "NACE grade steel".

Table 10.15 Hydrogen damage in refinery processes

Process	Damage
CRU	HTHA
NAPHTHA UNIFINER	HTHA
	LTHA
K-HDS	HTHA/LTHA
D-HDS	HTHA/LTHA
ARDS	HTHA/LTHA
H-OIL	HTHA/LTHA
HYDROCRACKER	HTHA/LTHA
HYDROGEN	HTHA
CDU	
VDU	
VBU processing high	
FCC sulphur crude	LTHA
GSU	
GTU	
LPG (storage)	

The ground situation was that low-temperature hydrogen-related damages in sour service were not considered to be of concern in the refinery industry. For minimizing chances of cracking of weld the general practice was to use carbon steels classified as P-1, Group 1 or 2 Grades. Later NACE RP 0472 [70] was issued limiting the hardness of completed weld to 200 BHN. However, subsequent to the failure of H_2S absorber of Union Oil Company in 1984 [80], detailed surveys were undertaken by different refineries which established that the problem is more widespread than thought earlier. This was made possible because the cracks could be identified more accurately with the introduction of WFMPI as the major NDT tool to detect fine cracks. NACE has discussed in detail the results of surveys carried out in 1990, where 1285 out of 4987 (26%) pressure vessels inspected were found to have developed cracks [81]. Results of one such study is given in Table 10.16 [82] where the inspection covered 100% of welds of 189 vessels. The inspection covered equipment exposed to (i) $H_2S > 50$ wppm + cyanides > 20 wppm, and (ii) wet $H_2S > 50$ wppm cyanide. It was evident from the inspection data that many of the cracks had initiated from small hard zones associated with weldments and the presence of cyanide in 60% of cracked vessels [82]. Subsequently, without fully defining the environment, the standard RP 0472 was revised in 1996 recommending guidelines to prevent cracking of weldments (weld, HAZ, and base metal) of carbon steel P-1, Group 1 or 2. As far as environment is concerned, it identified the role of hydrogen diffusing into metal but did not specifically define the concerned environment. The standard included SOHIC as one of the damaging mode. In addition, stress corrosion cracking due to carbonate,

Table 10.16 Inspection findings of weldment cracks

Item	Number
Vessels inspected	189
Cracks found	59
Cracks deeper than corrosion allowance	37
Crack depth (% watt thickness)	
<25	28
25–49	19
50–74	4
75–100	7
Crack length	
>2 in. (51 mm)	17
Longest: 4 ft (1.2 m)	
Location of cracks:	
In pressure and nozzle welds	33
In attachment welds	4
Vessels stress relieved and cracked	7
Stream composition for cracked vessels:	
H_2S quantity from 200 to 100,000 wppm	
Cyanide present in 60% of cracked vessels	

amine and caustic also formed part of this standard. In 2008, NACE changed RP 0472 to *specification* SP 0472. As a preventive measure greater emphasis was given to hardness control following a standard procedure for weld qualification test (Fig. 10.22a, b).

- Completed Weld—200 BHN
- Weld procedure qualification hardness across weld—248 HVN

According to NACE, lower hardness of 200 BHN against 22 HRC of NACE RP 0175 has been fixed considering non-homogeneity of weld and variations in testing of production weld.

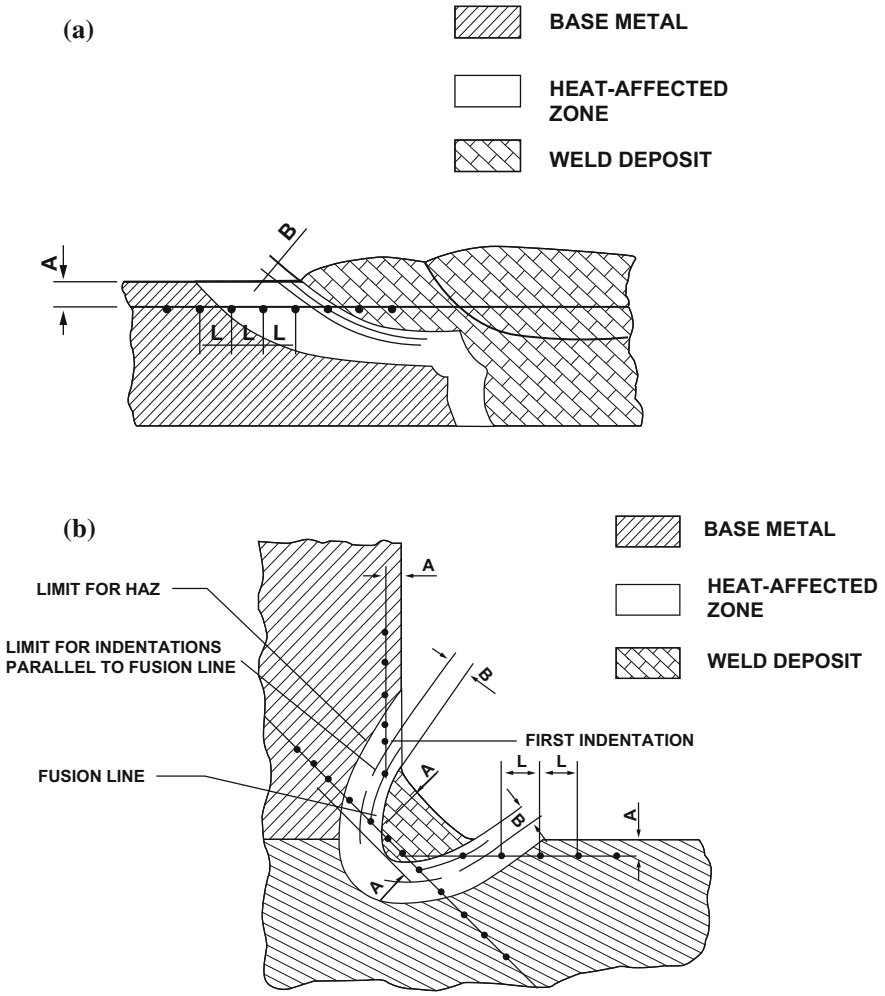


Fig. 10.22 **a** Hardness measurement during weld qualification test of butt weld [70]. **b** Hardness measurement during weld qualification test of fillet welds [70]

Major differences as far as refinery is concerned arose because of differences in materials used, greater emphasis on welding in refinery application and most importantly the definition of the sour environment. Considering these differences, NACE decided to prepare a standard which follows NACE MR 0175 but incorporates necessary changes related to refinery experience. A committee was formed in June 2000 as TG (Task Group) 231 which in 2003 prepared a new standard NACE MR 0103 [83] which defines material requirements for resistance to SSCC in sour petroleum refining and related processing environments containing H_2S either as a gas or dissolved in an aqueous (liquid water) phase with or without the presence of hydrocarbon.

Definition of Sour Service

MR0175:

When the partial pressure of H_2S in a wet (water as a liquid) gas phase of a gas, gas condensate, or crude oil system is equal to or exceeds 0.0003 MPa abs (0.05 psia).

MR 0103:

- >50 ppmw dissolved H_2S in the free water or
- A free water pH < 4 and some dissolved H_2S present (recognition that in low pH environments significant charging of materials with atomic hydrogen can take place independent of H_2S level), or
- A free water pH > 7.6 and >20 ppmw hydrogen cyanide (HCN) and some H_2S dissolved in the free water (recognition that at high pH the CN^- ion is stable and results in significant charging of ferritic materials by poisoning the formation of a protective iron sulphide scale), or
- >0.0003 MPa absolute (0.05 psia) partial pressure H_2S in a process with a gas phase.

It may be mentioned that the specification does not include other forms of hydrogen damage (blistering, HIC or SOHIC) except SSCC. In all these cases, it is recognized that under certain conditions hydrogen charging can take place even if these parameters like pH, H_2S/cyanide concentration, etc. are not fully met.

Prevention of SSCC in Refinery Sour Service

- It is the responsibility of the user to determine whether the process environment and operating conditions can cause SSCC.
- Cracking susceptibility increases with strength and as the latter is related to hardness, for quality control hardness is used and the specification mentions a maximum hardness permissible for different materials in this standard.

- Carbon steels listed as P-No. 1 Group 1 or 2 materials in Section IX of the ASME Boiler and Pressure Vessel Code are acceptable without imposing base metal hardness requirements. The only condition is that these should be in conventional heat-treated conditions and not cold-worked or cold-worked and process-annealed condition. Control of the HAZ and base metal hardness, and acceptance criteria, shall be in accordance with NACE Standard SP 0472-10 (earlier RP 0472).
- The weld and HAZ would conform to the hardness requirement, and the following methods can be used:

– Post-weld heat treatment
– Control of base metal chemistry to achieve the CE of 0.43 max along with limits on elements such as niobium, vanadium and boron. Unlike MR 0175, there is no restriction of 1% max nickel in MR 0103.

- Other carbon steels shall have a maximum hardness of 22 HRC (237 HBW).
- The acceptable maximum hardness of alloy steels under the ASME Boiler and Pressure Vessel Code Section IX P-Numbers having P-Nos. 3-11 are also included. Depending on P-numbers the maximum permitted hardness vary between 225 and 248 HBW. The standard thus covers max hardness requirements of base metal and weldments of various ferrous and nonferrous alloys, including austenitic stainless steel. Plates, pipes, bolting, valves, compressors, etc. are also included in the standard. The standard also gives a list of some typical refinery equipment susceptible to SCCC.

The guidelines and material requirements of NACE MR 0103 and NACE SP 0472 are presently being used by many end users and engineering contractors to specify materials for sour service in refineries. It may be mentioned that resistance to HIC does not form part of this standard. In case HIC resistance is required, it is to be intimated by the user. The selection of carbon steel material for all types of possible low-temperature hydrogen damage, such as, SSCC, HIC, SOHIC and blistering would depend on degree of sourness of the system, which has been divided into three categories in a separate report (8X-194) [84]. This technical committee report has provided an overview of the materials selection, fabrication, post-weld heat treatment (PWHT), inspection and testing practices for new equipment for use in wet hydrogen sulphide (H_2S) refinery service, which has been divided into three categories, viz. Category 1—low potential; Category 2—moderate potential; Category 3—severe potential. Along with MR 0103 and SP 0472, the report 8X-194 should preferably be used as a guideline by material manufacturers, fabricators, and users in the design and fabrication of new equipment used in wet H_2S refinery services. Similarly, plant personnel should follow the NACE Standard SP0296 to establish the condition and repair of equipment in sour service.

Bush et al. [85] have summarized the salient features of NACE MR 0103.

10.5.3.3 Cracking of LPG Sphere

On large-scale introduction of WFMPI for detection of cracks, by late 1970s reports of cracking of LPG spheres started pouring in. Systematic inspection was started which related the cracking to either H_2S or amine or both. As discussed, cracking susceptibility in wet H_2S is much higher in lighter products. Before marketing LPG is sweetened (freed of H_2S) for which either the gas is treated with amine or caustic (Merox process). Quite often due to operational upsets, slippage of H_2S and/or carryover of amine take place making the sphere liable to cracking. In this regard, many of the multinational companies carried out inspection of LPG spheres in their refineries worldwide. The results of survey by Exxon in 1980s throw interesting light on this subject [86]. Out of the 140 spheres, 49 were found to have severe cracking and required repair. Mainly field welds, both pressure containing and attachment welds, had suffered cracking. The MOC was carbon steel of both lower ($\leq$482 MPa/70 ksi) and higher (>482 MPa/70 ksi) strengths, and not subjected to PWHT in most of the cases. The conclusions from the Exxon survey in 1980s are given in Table 10.17.

It is obvious that as expected higher strength and non-stress relieved spheres were more prone to cracking, because of higher susceptibility under these conditions. Similar studies carried out by another company (Caltex) on several LPG installations showed that cracking was found in approximately one-third of the storage vessels [87]. However, of greater interest was the higher incidence of cracking in Europe and Middle East compared to USA, as experienced in Exxon study (Fig. 10.23). The authors of the paper have attributed this to use of higher strength (>72 ksi) steel used in these regions to reduce thickness which in some cases also help in avoiding PWHT.

There is another important point which requires to be considered is the relevant mechanical properties and design codes used in different regions. Steels used in Europe and Japan have generally higher tensile strength and especially yield strength compared to those used in USA. Further, the design stress as per relevant pressure vessel codes in these two regions are much higher compared to ASME Section 8, Div.1. As a result, the spheres are subjected to much higher stress. Cracking susceptibility increases with applied stress (Fig. 10.24) and, therefore, chances of crack developing in the presence of wet H_2S or amine will be more in case of spheres in Europe and Far East compared to that in USA. This would be further confirmed from the report that JIS-SPV50Q, a Japanese Q/T high strength

Table 10.17 Susceptibility to cracking of LPG sphere

MOC condition	No. inspected	Tensile strength	No. cracked
Tensile strength	20	$\leq$482 MPa (70 ksi)	3 (15%)
	18	>482 MPa (70 ksi)	13 (72%)
PWHT		Yes/No	
	22	Yes	3 (14%)
	44	No	22 (50%)

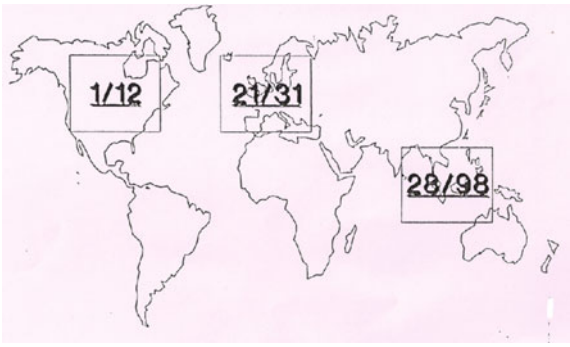


Fig. 10.23 Incidences of cracking of LPG sphere in USA, Europe and Far East [86]

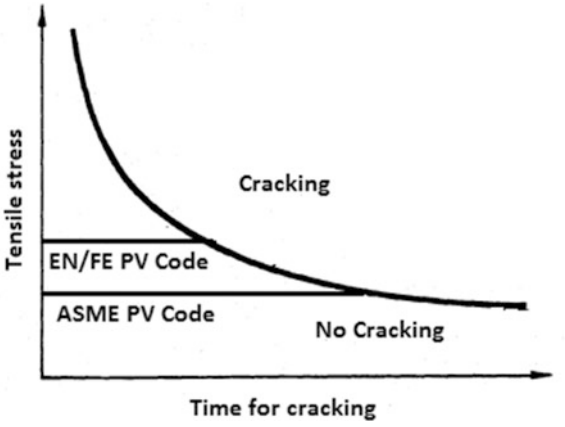


Fig. 10.24 Cracking susceptibility also affected by the design stress used for LPG sphere

steel used in Far East for the construction of LPG sphere, suffered from SSCC and HIC in wet H_2S condition. Generally, post-weld heat treatment is not performed after welding of SPV50Q (considered as P-1 material) and welding residual stresses remain high [88]. Such failures have also been experienced in ammonia Horton spheres constructed with in high strength steels.

The experience has been that the failure frequency and intensity is higher in the refinery storage than marketing storage spheres. This obviously is due to greater possibilities of H_2S slipping into the storage sphere along with the LPG. H_2S going further downstream is less probable.

10.5.3.4 Blistering

Blistering occurs due to accumulation of molecular hydrogen collected at laminations, inclusions and defects in the plate. In old refineries of 1950s and earlier, blistering had been a common defect since the steel in those days were normally not clean, had a lot of inclusions of different types and contained higher sulphur.

However, such problems have become less common with advances in steel making process, resulting in increased cleanliness with low sulphur. However, blistering can occur in cleaner steels also, as observed in case of a caustic wash vessel used for removal of H_2S in LPG produced in FCC. 80% of one of the plate of the vessel was found to have developed blisters of varying sizes. Some of the blisters had bulged to the extent to have developed crown crack [89]. The plate conformed to ASTM A516 with normal banded ferrite/pearlite microstructure but did not show any lamination due to slag or MnS which could have caused blistering. SEM examination showed the blister surface to have ductile/brittle fracture mode. From the study it was concluded that:

- Shortcomings in the operation resulted in the improper removal of H_2S in the reactor vessel, leading to the ingress of H_2S in the caustic wash vessel which made the environment sour.
- Blistering was due to the presence of midwall lamination formed due to shrinkage cavities/pores formed during continuous casting of the steel slab, which did not get metallurgically bonded during rolling, and formed partially bonded laminations in the plate.

10.5.4 Pyrophoric Iron Sulphides

In refinery operation, instances of formation of pyrophoric iron have been found in vessels, storage tanks, hydro-treater reactors, gas pipelines and other equipment processing sulphur-containing crude or sour gas. Pyrophoric iron is formed [90, 91] when hydrogen sulphide reacts with iron or iron oxide (iron scale) in absence of air to form iron sulphide by the following reactions in oxygen free atmosphere:

$$Fe + H_2S \rightarrow FeS + H_2 \tag{10.5.5}$$

$$Fe_2O_3 + 3H_2S \rightarrow FeS + 3H_2O + S \tag{10.5.6}$$

The sulphide formed remains dormant but when the equipment is opened for maintenance, inspection, dumping of spent catalyst, etc. the iron sulphide comes in contact with oxygen initiating following reactions which are highly endothermic:

$$4FeS + 3O_2 \rightarrow 2Fe_2O_3 + 4S + \text{Heat} \tag{10.5.7}$$

$$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2 + \text{Heat} \tag{10.5.8}$$

If the sulphide is dry, the heat produced by reaction can be sufficiently high to ignite the sulphide causing spontaneous fire because individual crystals of pyrophoric iron sulphides are extremely fine having an enormous surface area-to-volume ratio.

General precautions to avoid pyrophoric iron fires are as follows:

- The scraps and debris collected from cleaning of filters in naphtha/crude service must be kept wet and disposed of underground.
- Tanks, reactors, columns, and exchangers in high-sulphur feed service must be kept properly blanketed with N_2 during idle periods.
- All equipment and structured packing must be properly water washed and kept wet when exposed to the atmosphere. The author has witnessed a case where one side of packed column started glowing in spite of the fact that the column had been thoroughly washed to wet sulphide scale. Later investigation showed that there was channelling of wash water due to some disturbance in packing which left a portion of it non-wetted. The ignition of dry pyrophoric iron on opening caused overheating.
- In processes where catalyst handling is required, warm iron sulphide will ignite spontaneously and any coke and hydrocarbon present will catch fire. To avoid such a situation the catalyst before dumping must be stripped of all hydrocarbons, cooled to about 50 °C and wetted with water.
- Normally spent catalyst is sent for regeneration. In such a case, special precautions are required for handling. The best practice is to dump these into drums filled with inert gas and containing an internal liner.

10.5.5 Corrosion in Ethanol Service

10.5.5.1 General Corrosion in Ethanol Service

There has been increasing use of gasoline blended with ethanol, which falls under renewable fuel category. USA and Brazil are pioneer in this approach to reduce dependence on crude oil. The blending is done in various amounts like 5, 10 and 25% with balance as gasoline and designated with prefix of E, such as E10 and E25. In USA, it is common to add ethanol up to 10% (E10) and Brazil 25% (E25). Ethanol like methanol can cause corrosion if contaminated with water, acids or salts. Ethanol containing small amounts of water does show acidity due to the presence of some carbon dioxide which is a product of fermentation reaction. The acidity observed is also due to contaminates like acetic and lactic acids formed during fermentation. To distinguish between pH of ethanol from that of water, the latter is termed as pH_e, with neutrality in pHe being near 9.5 compared to 7.0 in aqueous solution. The corrosivity of the fuel is further increased if it is contaminated with chloride or sulphate. ASTM D 6423 gives procedure for the determination of pHe. Different forms of corrosion like galvanic, stress corrosion cracking, erosion corrosion, etc. can occur in ethanol solutions. Corrosion is managed by using blend of chemical additives (normally used with gasoline and diesel) + amine to neutralize the acid. Because of affinity of ethanol to water, its storage in tanks

which are open to atmosphere should be avoided. Water in small amounts (0.1–0.2%) has a passivating effect on ethanol systems, but in larger concentrations it enables other corrosion mechanisms to operate. Thus, ethanol characteristics like pH, water content and conductivity should be regularly monitored to ensure its quality [92].

10.5.5.2 Stress Corrosion of Carbon Steel in Ethanol Service

Though not very frequent, there have been reports of stress corrosion cracking of steel storage tanks and associated piping used in fuel ethanol service, which requires serious attention. The American Petroleum Institute commissioned survey in 2004 recorded instances of two dozen cases of cracking and leakage primarily in storage and handling of equipment in the distribution system for fuel ethanol. However, there were no reported cases at ethanol manufacturing facilities, or in E10 grade gasoline blends. The API study also included review of the various laboratory studies on SCC in methanol and ethanol. It was established that the cracks are intergranular and there is a critical amount of water that produces SCC in steel with less than 0.05 volume percent to just below 1% water by volume [93]. A summary of API Technical Report 939 D was presented at Corrosion 2004 Conference [94].

API 939 E gives details inspection, guidelines for construction, repair and steps necessary for prevention of corrosion in fuel ethanol service [95]. Most of the non-metallic elastomers, plastic, etc. are non-compatibility in ethanol. Another objection to the use of ethanol-blended gasoline has come from The National Marine Manufacturers Association (NMMA) of USA opposing the use of marine fuels that contain greater than 10% ethanol content by volume in recreational boat because of adverse effect on aluminium and fibreglass tanks used in boats.

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Chapter 11
Material Selection and Performance in Fertilizer Industry

Abstract Fertilizer plant has three basic units, viz. hydrogen, ammonia and urea. Hydrogen is produced by reforming at high temperatures in catalyst packed reformer tubes. Reformed gas after secondary reformer is cooled and hydrogen separated from CO_2. Then ammonia is produced by reacting hydrogen with nitrogen under high temperature and pressure. The materials used at high temperatures are subjected to oxidation, high-temperature hydrogen attack, temper embrittlement and nitriding. The corrosion in hydrogen plant in low-temperature section is due to CO_2. Urea is manufactured by reacting CO_2 and NH_3 at high pressure and the intermediate chemical formed carbamate is highly corrosive and the stripper section requires the maximum attention. The chapter describes the problems in different units and how over the years collaboration between process licensors and alloy developers has helped in developing new alloys for hydrogen reformer, resistance to metal dusting and carbamate corrosion.

Keywords Hydrogen production · Metal dusting · Ammonia synthesis · Waste heat boilers · Urea production

11.1 Introduction

Urea is produced by reaction of ammonia and CO_2. Hence, production of ammonia is the first step in the production of urea. Ammonia is also used in the production of other complex fertilizers. Anhydrous ammonia is produced by combining nitrogen and hydrogen in a molar ratio of 1:3 at high pressure and temperatures in the presence of a catalyst. While nitrogen is derived from the air, the source of hydrogen in all the present-day processes is hydrocarbon feed stock. The two major processes used to produce hydrogen are catalytic steam reforming and partial oxidation, where feed stock is naphtha/natural gas and fuel oil respectively. Except for some of the older plants and those using fuel oils as feedstock, all hydrogen plants are based on steam–naphtha or steam–gas reforming process. In the selection of material for various sections of the plant, one has to take into account their behaviour in the presence of

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hydrogen, carbon dioxide, carbonate, etc. under different pressure and temperature conditions. High-temperature strength and creep properties are also important for some of the components exposed to higher temperatures. While in ammonia production major damaging effect is related to hydrogen attack and temper embrittlement, carbamate corrosion plays an important role in the production of urea.

11.2 Hydrogen Production

11.2.1 Process Outline

A typical block diagram for ammonia production, using the catalytic steam reforming process for first production of hydrogen followed by ammonia, is shown in Fig. 11.1 [1]. The basic steps consist of (1) desulfurization of feed, (2) steam methane reforming, (3) carbon monoxide shift conversion, (4) carbon dioxide removal, (5) methanation and finally (6) ammonia synthesis. The reforming part for production of ammonia consists of primary and secondary reformers where the reformed gas from primary reformer is burnt in secondary reformer in the presence of catalyst to get H_2 + N_2 in proportion required for production of ammonia.

The general steam methane reactions can be expressed as

$$C_nH_{2n+2} + nH_2O = nCO + (2n+1)H_2 \tag{11.2.1}$$

$$CO + H_2O = CO_2 + H_2. \tag{11.2.2}$$

The reforming reaction is favoured by low pressure and high temperature. The lower the residual methane content desired, the higher would be the operating

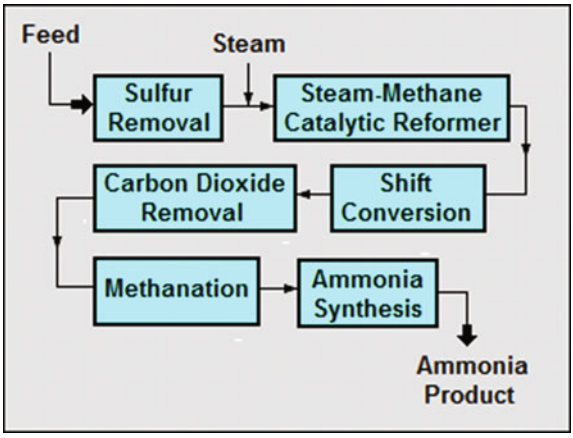


Fig. 11.1 Simplified block diagram of hydrogen and ammonia production [1]

temperature. Similarly, the higher is the operating pressure, the higher will be the required temperature. The present trend is towards higher operating pressure and higher hydrogen purities, increasing the severity of environment and thus imposing greater demands on the materials of construction. Hydrogen is also produced in refineries to be used in hydro-treating and hydrocracker. The process used is broadly similar to that stated above except for the absence of the secondary reforming.

11.2.2 High-Temperature Section

11.2.2.1 Primary Reformer

Primary reformer section of hydrogen plant consists of rows of vertical reformer tubes, collecting header and transfer line to the secondary reformer. Upstream of it the feed is desulfurized and fed at the top of the tubes at ~500 °C along with steam at 30–40 kg/cm^2. The reformed gas is collected in headers at the bottom form where it goes to the secondary reformer via a transfer line. The reformed gas outlet temperature is ~700 °C and the tube wall metal temperature is around 900 °C (designed for 925 °C) and therefore hydrogen attack, creep and oxidation resistance are the dominant factors in material selection. The main damage mechanism in case of reformer tubes is the creep process, which occurs under the influence of temperature of and stresses due to internal pressure and thermal stresses across the tube wall. For such operating conditions, high-alloy austenitic stainless steels are the only candidate materials. Earlier, when pressure and temperature were lower, wrought alloys (Type 310) were used, but in the 1960s a cast version of 25Cr–20Ni (HK-40) was introduced because of its much better high-temperature creep properties compared to the wrought grade. While this served well, a number of deficiencies were soon noticed. At the design temperature of 925 °C, the life of the tube was found to be very much dependent on proper control of skin temperature of tube during operation.

Figure 11.2 [2] shows how deviations from the design temperature and pressure can reduce or increase the operating life. In case of HK-40 alloy, a rise in 50 °C over design temperature can cause creep rupture in about 1½ years, which is nearly one-tenth compared to 11 years under the design conditions. The figure also shows that the effect of increase stress has less damaging effect (~one-third of design life for 100 psi increase) compared to temperature (6 kg/cm^2). Similarly, a decrease in temperature and pressure over the design values will increase the useful life. In spite of care in operation, failures can still occur due to localized overheating because of catalyst degeneration and excessive radiant heat form the furnace walls. In addition to creep damage, the high-temperature alloys also suffer from drop in ductility due to in-service precipitation of secondary chromium carbides prior to their coarsening. Formation of sigma phase further deteriorates the properties. The embrittlement

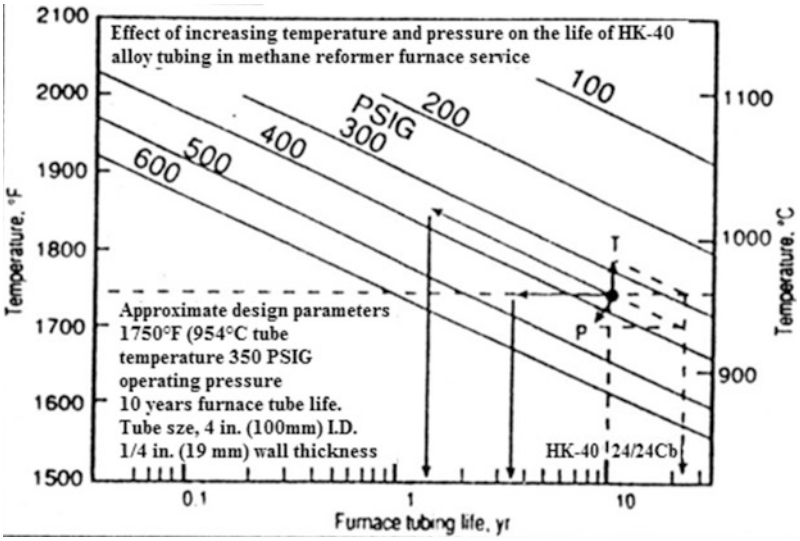


Fig. 11.2 Effect of deviations from design conditions on life of reformer tube [2]

results in cracking due to thermal fatigue and thermal shocks because the components are subjected to multiple (quite often undefined) stresses during start-ups and shutdowns. Unlike creep cracks, which are longitudinal, the brittle failures are circumferential. In addition, the embitterment adversely affects the weldability of the aged alloy, making any repair work very difficult. In this respect the performance of HK-40 was found to be very poor.

Search for new alloys having better properties compared to HK-40 started in late 1960s. The objective was to develop alloys having better resistance to oxidation (by this time ethylene cracker process, operating at much higher temperature was commercialized), better creep strength and resistance to coarsening of carbide precipitate. The studies resulted in the development of two alloys, viz. 24Cr24Ni1.5Nb (IN519) and 25Cr35Ni1.5Nb (HP-Mod). Of these two alloys, the largest use was of HP-Mod. Niobium is stronger carbide former than chromium. Nb-carbide precipitates are finely dispersed and do not coarsen easily. HP-Mod was first introduced commercially in 1975 by Manoir Industries, France with the proprietary name of Manurite 36X (25Cr/35Ni/1.5Nb/1.5Si). Since then a number of manufacturers of reformer tubes worldwide have started production of this alloy. Continued development has shown that much improved properties can be obtained if stronger carbide forming elements Ti, Zr, W, and rare earth elements are added to HP-Mod alloy as these alloying elements have synergetic effect. Because the amount used is very small, the alloys were named micro-alloy (HP-MA). Thus, a number of alloys are available today to choose from. The nominal composition of some important alloys is given in Table 11.1 [3].

Table 11.1 Heat resistance alloys used in hydrogen production

Alloy designations		Chemical composition, %								Stress to produce rupture in 1,00,000 h. (MPa)		
ACl, others	Cr/Ni, others	C	Si	Mn	Cr	Ni	Cb	W	Other	760 °C	870 °C	982 °C
HK-40	25/20	0.40	1.50	1.50	25	20	–	–	–	32.0	15.5	6.0
IN-519	25/20 Cb	0.35	1.50	1.50	24	24	1.5	–	–	45.1	21.0	8.0
HP-Mod.	25/35 Cb	0.40	1.50	1.50	25	35	1.5	–	–	45.1	25.2	10.0
HP-MA	25/35 WCb	0.45	1.50	0.70	25	35	Present	Present	–	–	24.1	9.1
Transfer lines and manifolds												
800H – Cast	20/32 Cb	0.10	1.50	1.50	20	32	1.0	–	–	35.1	15.1	4.7
– Forged	20/32	0.10	1.00	1.00	20	32	–	–	Al + Ti 0.7	29.0	11.0	3.4

Historically the various alloys are in use (or used) since the following years:

HK-40 (used since early 1960s)
In 519 (used since early 1970s)
HP-Mod (used since mid-1970s)
HP-MA (used since early 1980s).

Today the HP-MA has replaced HP-Mod as the most popular alloy for reformer and also cracker tubes, both for new plants and as replacement in existing plants. Manoir Industries have recently announced development and marketing of a new alloy XMR^{TM} for reformer tubes [4]. This alloy is claimed to have 15% higher rupture strength than HP-MA in the 950–1000 °C range. Both the HP-Mod and HP-MA are still proprietary alloys, with chemical composition (and so the properties) varying from manufacturer to manufacturer. Thus, unlike a single-standard creep rupture curve for HK-40 in API RP530, no such curves have yet been standardized for HP-Mod and HP-MA grades, and design is done on the basis of creep data supplied by the manufacturer.

Recent studies have indicated that the projected improved creep life of HP-Mod over HP-MA, as determined from LMP of original alloy, does not appear to be confirmed on the basis of tests on aged alloys as would be evident from Table 11.2 [5].

As would be evident from Fig. 11.3 the ductility of aged (service exposed) new alloys tends to be considerably greater than that of as-cast original material. The extent of change in elongation in case of HP50 varied from less than 10% (mostly 2–3%) in original condition to as high as 40% (typically around 25%) in service exposed condition. Similarly % reduction in area after service exposure increased to around 50% from original ~5% [6]. Thus from the point of view of creep HP-Mod grades of alloys withstand creep-induced dimensional change of 5–7% against 1–2% of HK 40.

The major flexibilities of the HP-Mod and HP-MA materials are as follows: (a) reduction in cost per foot of tubing due to the decrease in wall thickness, (b) better rate of heat transfer and lower thermal stresses due to lower temperature gradient across a thinner tube wall, (c) as replacement, the throughput can be increased due to higher I.D., (d) tubes can withstand greater temperature upsets during operations because of its 60 °C higher temperature capability compared to HK-40 and (e) the alloy can withstand a greater number of thermal cycle stresses associated with start-up and shutdown. Table 11.3 [3] compares the influence of tube material on minimum sound wall thickness (MSW) and other parameters for different alloys.

Table 11.2 Representative tube lives of aged material compared with as-cast material data

Alloy	Temperature, °C/°F	Stress, MPa (ksi)	Rupture time, h
HPNb HP Micro HPAged	900 (1652)	15 (2.2)	3×10^6 1×10^7 130,000

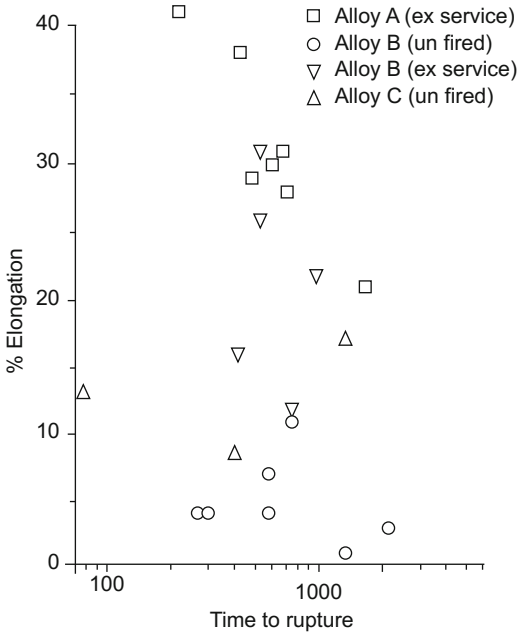


Fig. 11.3 Elongation of as-cast and aged HP grades of alloys [6]

Table 11.3 Influence of tube materials of MSW and other parameters

Case A	Sa (MPa)	MSW (mm)	ID (mm)	Catalyst volume	Tube weight (kg/m)
HK40	10.0	19.1	76.2	–	45.0
IN519	14.0	14.3	85.7	+27%	35.9
HP-Nb	19.0	10.9	92.5	+47%	28.3
HK-MA	17.6	11.7	91.0	+43%	29.7
HP-MA	22.0	9.5	95.3	+56%	25.1
Case B	Sa (Mpa)	MSW (mm)	Id (mm)	Catalyst volume	Tube weight (kg/m)
HK40	6.7	13.2	75.2	–	29.0
IN519	9.2	10.0	81.7	+18%	22.9
HP-Nb	12.5	7.5	86.5	+32%	17.7
HK-MA	12.4	7.6	86.4	+32%	17.7
HP-MA	14.8	6.5	88.7	+39%	15.5

Case A: Ammonia reformer: P = 4.0 MPa; T = 925 °C; and OD = 114.3 mm (4″)
Case B: Methanol reformer: P = 2.0 MPa; T = 975 °C; and OD = 101.6 mm (3.5″)

11.2.2.2 Pigtails and Collecting Headers

Because of high-temperature operation, it is necessary to provide a device to take care of stresses due to expansion and contraction of the tubes. Depending on whether the tubes are bottom or top supported, the pigtails connecting the reformer tube to outlet headers are looped or straight. The other main outlet components are manifold, T-pieces and cones.

Though the process-side temperature of reformer tubes and outlet components are same, the actual temperature of reformer tube is much higher because it operates on the principle of fired equipment involving transfer of heat from OD to ID. Thus the temperature difference between reformer tubes and header may be as high as 150–200 °C. The damage mechanism of outlet components including bottom pigtail (for bottom supported tubes) is generally less severe than that of reformer tubes because the outlet components are not subjected to thermal gradients across the tube wall due to the absence of firing conditions. The main damage mechanism is the hindered thermal expansion. The outlet system cannot expand (or shrink) freely. The tubes though fully supported are subjected to both expansion and rotating stresses. It is therefore not uncommon to find the bottom pigtails twisted when cut for replacement, due to permanent deformation. This also results in bowing, especially if there is restriction of free vertical expansion. These stresses also result in Low-Cycle Fatigue (LCF). Various factors affecting pigtail life are as follows:

- Relatively short pigtail designs combined with too many start-ups and shut-downs have caused failures due to thermal fatigue.
- Specification provides alloying element content to be within a range. If carbon titanium and aluminium are present at the extreme low end of Alloy 800HT specification, and if heat treatment is not proper, premature creep failure can occur.
- Solution annealing is preferable to mill annealing of cold-formed pigtail. Where this precaution is not taken, creep rupture failure (especially during replacement) at bend can occur.
- If a tube is run too hot for a long time with upset steam/feed ratio, carburization of pigtails occurs. While its normal performance may not be always affected due to carburization, reduced ductility does not permit its nipping when the corresponding tube requires to be isolated for operational reasons.
- Using design code API 530, along with design temperatures and internal pressures, a minimum tube thickness for 100,000 h life is specified. The H and HT grades of Alloy 800 have ASTM grain size No ≤ 5. Localized creep cracking has been noted in the outer surface of the bend. The pigtails are formed by cold bending during which the extent of deformation (stretching of metal) would decrease from outer to inner surface of the tube wall as shown in Fig. 11.4. During operation at high temperature recrystallization will result in fine grain (ASTM grain size No 7–8) on outer wall of bend and coarse grain (ASTM grain size number of ≤ 5) on inner side. As the fine grains lead to reduction in creep life, failure due to creep occurs on the bend portion [7–9].

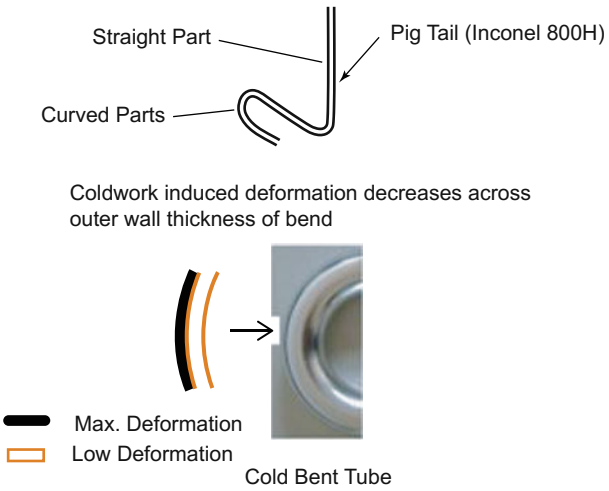


Fig. 11.4 Creep-induced failure of pigtail at bend

The same approach as that for reformer tubes is applicable for alloy selection for the outlet headers or manifold assembly and bottom pigtails, except that ductility is of primary importance followed by creep strength. High-temperature cast alloys used for reformer lack the necessary ductility because of high carbon content. The use of wrought alloys had been the preferred material in spite of their comparatively lower creep strength. For the manifolds, Incoloy 800H and later HT grade were developed. To get good creep strength of cast alloys combined with good ductility, the low carbon cast (or wrought) alloys based on 20Cr/32Ni composition, such as HP-Mod-LC and HPLC-MA, are also available. Here the adverse effect of low carbon on creep strength has been compensated by the addition of Nb, Ti and Zr in various proportions.

The outlet headers are connected to manifolds running side by side with the collecting header at the bottom of the furnace. The manifolds which collect the RG from different hot outlet headers were earlier made of high-temperature alloys, when the plant capacities were low. With increase in capacity the hot lines became unviable because of higher size and cost. This problem was overcome by the use of cold wall design. Here the large-diameter pipelines are designed for about 350 °C by internally lining the pipe with insulating refractory. As the high-velocity RG can cause erosive damage of the refractory, the refractory is provided on top with Incoloy 800H liner. The outlet headers are joined to the manifolds at suitable points.

The cost factor was also felt in the outlet header. The concept of cold wall design for reformer outlet header where the straight bottom pipes are used has also become popular. The reformed gas from tubes enters the header via a central gas pipe. The high-alloy reformer tube and the header are interconnected by means of an intermediate piece made of C–0.5Mo/1.25Cr–0.5Mo. The intermediate piece is kept

cool by an internal insulation made of special shaped firebricks. An expansion joint is provided between the reformer bottom and reformer tube for sealing the furnace at the point where the reformer tube passes through the bottom. There have been some instances of failure at DMW joint between C–0.5Mo and reformer tube stub end.

The introduction of cold wall design for reformer outlet components has resulted in increased use of top supported reformer tubes. In this case because of low feed inlet temperature ($\sim$520 °C), inlet pigtail tubes were earlier made of Cr-Mo steel. The joint between reformer tubes and alloy steel pigtails however suffered DMW cracking during long service. As a result presently stainless steel alloy grade 321 is specified for inlet pig tails.

11.2.2.3 Materials Specification for Primary Reformer Tubes

The major cause of failure in the high-temperature section of primary reforming is creep. To minimize this type of failure it is not only necessary to select a proper alloy and follow good furnace operation practices, but it is also necessary to ensure good quality of the material used. With modern AOD and VOD processes, it is now possible to attain the desired quality. It may be mentioned that most of the reformer alloys are not covered by any standard specification. User has to depend on the data provided by the manufacturers but some of the requirements should be clearly specified in any enquiry. The important requirements which need to be incorporated in the material specifications are as follows:

1. The trace elements, e.g. S, N, Al, Ti, Va, etc., should be maintained at low values; Ca, Se and Sn should be in ppm maximum and Pb and Te 20 ppm max.
2. To maintain the desired purity of the alloy, use of virgin raw material is preferred for manufacture of the alloy. Any scrap used should be either cropping or rejected casting of same or similar alloy made in own shop and pre-refined before adding to the final melt.
3. Metallurgical structure of final castings of reformer tubes has a major role. In reformer tubes creep damage is mostly confined between inner surface and midwall as would be evident from Fig. 11.5. Creep damage unlike vessels and heater and super heater tubes is not initiated on OD but from midwall. From midwall the crack propagates inward till ID and then travels back towards OD before failure. This nature of crack is believed to be due to maximum stress acting not on OD but on midwall as a result of hoop plus thermal stresses. Cast reformer tubes solidify and, depending on rate of cooling, a combination of dendritic (on OD) and equiaxed (on ID) grains forms. It has been observed that the creep crack is initiated near the interface of dendritic and equiaxed grains and, therefore, for reformer tubes a mix of columnar and equiaxed grains are preferred. There are differences in opinion and the recommended minimum equiaxed grain zone varies from 50% [10] to 0–20% [11]. Normally, one-third of internal wall with equiaxed grains is preferred (Fig. 11.6) [12].

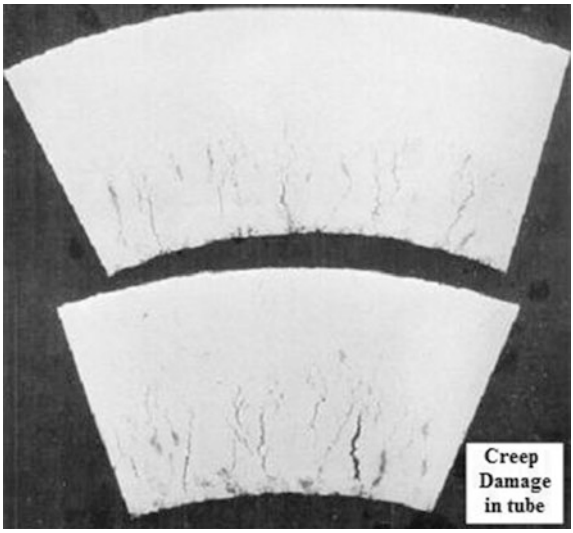


Fig. 11.5 Creep damage of reformer tubes

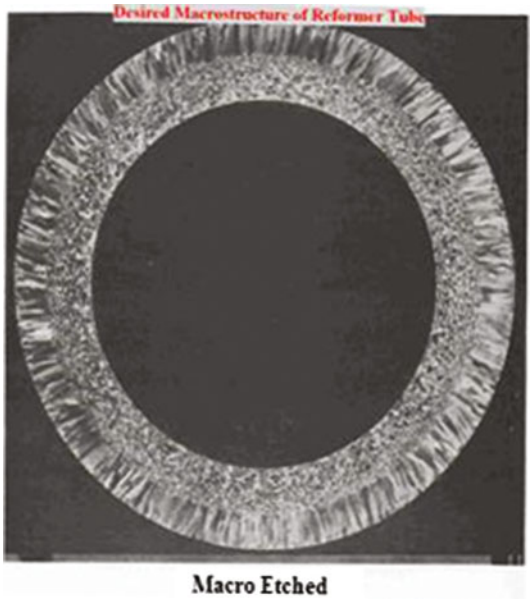


Fig. 11.6 Denditric and equiaxed grains in spun cast reformer tubes

4. Due to centrifugal force, suspended impurities, gas bubbles, etc. in the molten metal get concentrated in the ID, which is last to solidify. Depending on the diameter, tube thickness and other casting parameters, the porosity on the ID can be as much as 5 mm. To ensure sound metal at the ID surface internal machining (boring) is carried out [13].



Fig. 11.7 Creep and carburisation of fine-grained Alloy 800HT stub end of reformer tube

5. Another important requirement for high-temperature alloy is the grain size. These should have coarse grain, ASTM No 5 or lower. These requirements are also important for cast and wrought alloys, used for pigtails and manifold components. Deviations from this may cause damage due to lower creep life and also higher risk of carburization and metal dusting. Figure 11.7 shows Alloy 800HT stub ends of reformer tubes which bulged, cracked and got heavily carburised within 1–2 years of commissioning. The reason was found to be its fine grain size in the range of 7–8, which was off the specification [14].

11.2.2.4 Secondary Reformer

In the secondary reformer, the reformed gas is reacted with controlled amount of air above the catalyst bed where temperature may reach above 1250 °C. The hot gases pass through the catalyst bed. The reaction is endothermic and at the bottom of the bed temperature is around 800 °C. The reaction gun is of alloy 800H or 25/35 Nb and MOC of the catalyst bed support of HK40, SS 310 or refractory bricks. The shell is of carbon or Cr–Mo steel internally lined with dual hot/insulation refractory for protection and for reducing the shell wall temperature. The problem is mainly related to damage of refractory leading to hot spots. To monitor the temperature of outer shell (normally designed for ~350 °C) equipment and piping are coated with temperature-sensitive paint. On appearance of hot spot, cooling with water spray is done till during subsequent shutdown when the necessary repair is carried out. It may be kept in mind that continued operation for too long under this condition can result in HTHA of the shell.

11.2.3 Intermediate Temperature Section

After secondary reformer the reformed gas (RG) goes to the RG boiler where the gas is first cooled to about 450 °C. The cooled gas then goes to shift converters along with related coolers.

11.2.3.1 RG Boiler

- The major problems associated with RG Boiler are at the inlet and outlet portion due to damage of refractory and meal dusting, respectively. For prevention of high-temperature attack at inlet end of the boiler tubes, ferrules are used. The other major problem is related to waterside corrosion for which proper treatment of boiler feed water is essential. The different problems connected with RG boiler, including metal dusting, have been discussed later.

11.2.3.2 Shift Converter

- In the shift converters and the methenator the temperatures are lower, though above dew point of water. Here the major damaging effect is that of hydrogen attack. MOC is selected on the basis of Nelson Curve and consists of 1.0Cr/1.25Cr–0.5Mo, C–0.5Mo, and carbon steels in decreasing order of temperature. In new plants, 1Cr/1.25Cr–0.5Mo and carbon steel are used for vessels and piping exposed to hot CO + CO_2 + H_2 gas stream. However, type 304 is used for the wire mesh screen and gratings, grid sections, thermo wells, etc. because of the critical nature of these parts.
- In the exchanger trains downstream tube bundles of coolers, depending on tube wall temperature, are made of carbon steel or Type 304 where condensation of water is likely to occur. This is to take care of acidic corrosion due to CO_2.

11.2.3.3 Metal Dusting

Metal dusting is a catastrophic carburization process which results in the disintegration of iron, nickel and cobalt alloys. This phenomenon occurs at temperatures between 450 and 800 °C in a carbonaceous atmosphere as encountered when subjected to oxidation/reduction conditions of the process stream as in HC/steam reforming, coal gasification, synthetic gas production, etc. First descried in the late fifties, the process is still not fully understood. In hydrogen plants, the process equipment and piping between the RG boiler and the inlet of the high-temperature shift converter are most vulnerable, though this type of attack in reformer tubes and pigtails has also been reported.

Mechanism of Metal Dusting

It has been established that susceptibility to metal dusting is related to H_2/H_2O and CO/CO_2 ratios in the process stream. Here the carbon activity of the stream is of primary importance, which, in turn, is also related to its reducing potential. Modern hydrogen plant operates at higher pressure and temperatures in conjunction with lower steam to carbon ratios. The resulting high ratios of CO/CO_2 and low ratios of H_2/H_2O in reformed gas make metal dusting conditions more aggressive. The mechanism of metal dusting is not yet fully understood but can be broadly explained as follows:

1. Metal dusting is initiated in iron-based alloys at a point of breakdown in the protective oxide film when carbon activity is high. Carburization (Cr-carbides) occurs and the matrix gets saturated with carbon with the additional formation of metastable Fe_3C.
2. The condition at metal/gas interface at this stage changes with local drop in carbon activity. Once the activity reaches 1 and below, free carbon deposition formed by the reactions shown below occurs and free carbon filaments are deposited on the surface:

$$CO + H_2 = C + H_2O \text{ or} \tag{11.2.3}$$

$$2CO = C + CO_2. \tag{11.2.4}$$

3. The metastable cementite becomes unstable, and decomposes by react3.ion

$$Fe_3C = Fe + 3C. \tag{11.2.5}$$

   The reaction products (particles of carbon, carbides, oxides and metal) become loose, aided by internal stresses caused by the difference in thermal expansion between the carbides and the metal. The powdery loose particles (size ≈10 nm) are swept away by gas erosion, leaving behind a smooth depression on the meal surface. The above-stated mechanism appears to be generally true from the observation of the cross section of the depression formed [15]. The micro-section shows three distinct layers, i.e. first a light etching area on top, next a dark etching area and last a zone with carbide precipitation at grain boundaries. The most important observation is the hemispherical nature of the attacked area which confirms that carbon diffuses isotropically to form a hemispherical region.
4. In the case of nickel-base alloys no metastable carbide is formed and it is believed by many that the saturated matrix directly decomposes into meal particle and graphite. In this case disintegration produces larger metal particles ($\sim$100 nm) [16]. Thus iron-based alloys are more prone to metal dusting than nickel-base alloys, though latter are not immune. Figure 11.8 shows metal dusting attack on Alloy 800 in hydrogen reformer after >10 years of service [17].

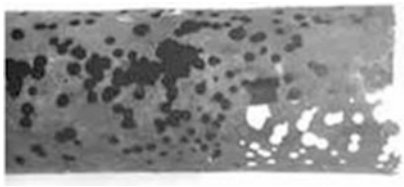


Fig. 11.8 Metal dusting of Alloy 800 from hydrogen reformer after <10 years [17]

Preventive Measures

The industry is facing quite a serious problem not only because the costly items are to be regularly replaced but the dust and pieces of alloys foul the downstream valves, piping and catalyst beds. Number of alloys like SS 310, Alloy 810H and Alloy 601 have been tried. The experience has not been satisfactory except that nickel-base alloys show comparatively better performance. There is, therefore, a great need for development of suitable materials resistant to metal dusting. Prevention or minimizing damage due to metal dusting can be attempted either by process modification or selection of more resistant alloys.

Process Modification

The process modification to suppress metal dusting tendency consists of either adding sulfur to the RG or reducing the CO/CO_2 ratio by adding extra CO_2 in the feed to the primary reformer. Both these are not feasible because the sulfur is poison for the catalyst and no additional CO_2 is available in a fertilizer plant. In the production of methanol excess CO_2 is available. In fertilizer plants where methanol is also produced, use of available excess CO_2 can help in reducing metal dusting. This has been successfully used in some plants.

Improved Alloy

Need for alloys having higher resistance to metal dusting are realized for long and considerable work has been done and are being done. Metal dusting degradation involves two steps, namely, the incubation and propagation. The approach, therefore, is basically to have an alloy which should be able to produce not only a highly protective oxide film but also has the capability to heal any damage of film even in the presence of low oxidizing potential. In addition, the alloy should form more stable carbides and the capacity of the base metal to get saturated with carbon should be low. Considering the experience that though not immune, nickel-base alloys perform better, most of the efforts have gone in the development of nickel-base alloys containing higher chromium and aluminium. Here the Cr_2O_3 film is reinforced by the addition of aluminium which forms highly adherent film of Al_2O_3. The suitability of such an alloy is proven from the performance of Alloy INCONEL® 693 (62Ni–29Cr–3.1Al and, small amounts of niobium, zirconium, titanium developed by Special Metal Corp [15]. This is considered to be the best of all presently available alloys. Use of aluminized (diffused aluminium coated) high-temperature alloys has shown good resistance but this material is primarily

suitable for small and medium diameter piping/tubing, fasteners, etc. but not or liner or thin-walled components.

Straight ferritic stainless steels (above 20%Cr) have good resistance to metal dusting but are embrittled due to ageing, and have poor weldability and low creep resistance. These, however, can be used as non-pressure parts like ferrules. Other methods like plasma-sprayed coating of zirconia (ZnO_2) and alumina (Al_2O) are reported to have been successfully tried.

11.2.4 Low-Temperature Section

11.2.4.1 Cooling of Reformed Gas Before Removal of CO_2

As the syngas leaving the shift converters is cooled, water saturated with carbon dioxide condenses out, forming carbonic acid. This condensate is extremely aggressive to carbon and low-alloy steels and has caused numerous corrosion problems. Corrosion rates have ranged from 50 to 700 mpy, depending on the temperature and pressure at which condensation takes place. Operating pressure has a major effect on corrosion severity because increasing pressure causes condensation of water at higher temperature and increases the amount of dissolved CO_2 in the condensate. Both of these factors increase corrosion rates. Depending on the need for resistance to high-temperature hydrogen attack, carbon steel or low-alloy steel are generally used for "hot" syngas piping above the water dew point. Once water starts to condense, stainless steel piping is required for corrosion resistance. Severe corrosion has occurred in dead legs of hot, low-alloy piping where local temperature has dropped below the dew point, allowing formation of carbonic acid. Addition of ammonia to the condensate has been found to be effective in keeping rates of attack within the accepted limit. In some plants, the secondary shift effluent is cooled by direct contact with a spray of recycled steam condensate in a section of the piping. Piping lengths of carbon steel immediately downstream of Type 304 spray nozzle are attacked severely by impinging water droplets containing dissolved CO_2. Such section of piping should be upgraded to Type 321 stainless steel.

Knockout pots to separate liquid droplets present in the wet syngas piping are lined or clad with austenitic stainless steel to provide protection against carbonic acid corrosion. The water drain line is also normally of stainless steel, although, if pressure is low enough, fibreglass pipe can also be used. For exchanger bundles copper alloys are not used in fertilizer plants because copper is attacked by ammonia. The material used is either carbon steel or austenitic and duplex stainless steels.

11.2.4.2 Carbon Dioxide Removal

For CO_2 removal, either alkanolamines, e.g. MEA, DEA, MDEA (methyl diethanol amine) or hot carbonate solutions, i.e. GV, GV+ glycine, Benfield and Catacarb systems are used. In the fertilizer industry both amine and carbonate systems are used for the removal of CO_2 from reformed gas. Amine system has been discussed in Chap. 8 used for the sweetening of gas.

Carbonate Process

The overall amine process being the same in both gas sweetening and CO_2 removal, the carbonate process, which is primarily used in fertilizer industry, has been discussed in this chapter. There are various patented carbonate processes like GV, Benfield, Catacarb, etc. Broadly the carbonate process consists of absorbing the CO_2 in potassium carbonate (K_2CO_3) solution. As a result of reaction, bicarbonate is formed:

$$K_2CO_3 + H_2O + CO_2 = 2KHCO_3. \tag{11.2.6}$$

For proper operation, the ratio of $2KHCO_3/K_2CO_3$ is kept around 0.3 and some chemicals are added to improve performance and also corrosion inhibition. In this process the reformer gas enters an absorber (pressure about 35 kg/cm^2 and temperature 40–50 °C) from the bottom and comes in contact in packed column with the carbonate/bicarbonate solution flowing from top. The CO_2-rich solution is then heated (about 110 °C) and transferred to the top of another column, known as regenerator, which operates at low pressure. Due to the reduction in pressure, the CO_2 flashes in the top section of the column. The liquid flows down and finally the CO_2-free solution (lean solution) comes out of the bottom and after cooling fed back to the absorber. Figure 9.20 in Chap. 9 gives the simplified diagram of the process.

Corrosion Control

The CO_2-loaded bicarbonate ion is corrosive and attacks the absorber and regenerator columns which are made of carbon steel. To inhibit corrosion, meta-vanadate salt is added to the solution which also acts as activator for CO_2 absorption. The inhibition effect can be described as follows.

Vanadium pentoxide (V^{5+}) is used as an inhibitor. The V^{5+} ion is reduced to V^{4+} and in the process releases oxygen which reacts with iron to form a thin and adherent film of magnetic iron oxide. For maintaining the efficiency of inhibition a certain ratio of V^{5+}/V^{4+} is to be ensured. In case the V^{5+} content goes down the minimum limit, oxidizer like potassium nitrate (KNO_2) is added to attain the ratio. In case of any neglect, corrosion increases and the damaged oxide layer gests peeled off in small flakes increasing the iron content of the recirculating solution and giving it a black colour. The integrity of the protective film is to be ensured all

the time. This integrity, in addition to the V^{5+}/V^{4+} ratio, is also sensitive to velocity. A velocity limit of 2 m/s is preferred. During operation, velocity-related failures are quite often encountered. Absorber and regenerators are packed columns. If packing is not proper and/or operational upset occurs, the shells of these columns are affected due to channelling of either gas or liquid between the shell and the bed resulting in grooving. The other easily affected component is the bottom gas distributor (Spurger) of the absorber, which generally is made of carbon steel. Due to velocity effect the holes get enlarged totally disturbing the flow which results in impingement on the shell and subsequent local thinning. This type of damage is commonly observed where the throughput is increased much beyond the design figure. To avoid these types of failures, there is a strong case for the industry and the designers to consider the use of clad stainless steel (Type 321 or 304L) columns for the absorbers (bottom) and regenerators (top), in vulnerable areas as above. Presently the general practice has become to use SS 321 cladded shell in the top section of regenerator. Internals like distribution pipe and tray are also made of stainless steel Type 321.

In case of new columns or in operating columns where any serious drop in V^{5+}/V^{4+} ratio occurs, or after shutdowns (short or long), the recommended start-up procedure is to be followed to build up the integrity of the protective film. In such cases, solution containing higher concentration of vanadium as V_2O_5 is circulated for a day or two before feeding the reformed gas.

11.3 Ammonia Synthesis

Synthesis of ammonia is carried out by subjecting the synthesis gases (hydrogen and nitrogen in the ratio of 3:1) at high pressure (2000–5000 psi) and temperatures (450–500 °C) in the presence of an iron oxide catalyst. From Fig. 10.1 it will be apparent that the unit operates at what can be called as intermediate temperature. The major problem at this operating temperature is primarily related to interaction of materials at high operating pressure with hydrogen and nitrogen in the system. As regards low temperature, the problems are less serious except the susceptibility of carbon and low-alloy steels to stress corrosion cracking in anhydrous ammonia.

11.3.1 Intermediate Temperature Section

The operating pressure and temperature in the high-pressure section is around 2500 psi and 420 °C, respectively. The material selection is primarily based on resistance to hydrogen attack for which API RP 941 is followed. Because of high pressure the thickness of equipment and piping is very high, where the operating temperature is above about 350 °C, metallurgical degradation can occur in Cr–Mo steels, especially in 2.25Cr/3.0Cr–1.0Mo.

Ammonia is produced in a single converter or in two in series. These are heavy-walled vessels (150–250 mm thick depending on size) where the catalyst is filled in a removable cartridge containing an integral tubular heat exchanger. In the first converter shell, the cold H_2 + N enter from bottom and passes between the reaction section second and the shell. This keeps the main shell wall cool and, therefore, there are no chances of hydrogen attack. MOC is carbon steel. On the other hand, the hot partially converted NH_3 + H_2 + N enter the second converter making it essential for the shell to be of 2.25Cr/3Cr–1Mo, either conventional or modified grades (similar to hydrocracker). The converter shell can be of layered or monowall design. The internals like catalyst basket inter-bed exchanges are made of SS or nickel alloys, especially keeping in mind the resistance to nitriding. The 2.25Cr/3.0Cr–1.0Mo alloys, especially the former, are susceptible to temper and hydrogen embrittlement. Further various components are also subjected to nitriding. Measures against such problem are described below.

11.3.1.1 Nitriding

Like carbon, nitrogen also forms interstitial solid solution in steel and other iron-based low- and high-alloy steels. The solubility of nitrogen is, however, less than that of carbon. Unlike carburization, nitriding occurs more readily at lower temperatures (450–550 °C) and in ferritic iron. Nitrogen forms nitrides of iron, chromium and titanium. Iron nitrite can be distinguished from its needle-shape morphology. The equipment and piping in high-pressure ammonia production section is, therefore, vulnerable to nitriding. Nitriding is diffusion controlled and thickness of the nitride layer follows parabolic law (initial high rate falls off with time). Nitrided layer is highly brittle and tends to peel off thus exposing fresh surface for further nitriding. In the presence of small quantities of strong nitride formers like Cr, Ti, etc., the nitriding rate of steel increases but decreases with increase in chromium content. For example,

- 2.25Cr1Mo has about 90 mil hard nitrided depth after 9 years when exposed at 484 °C in 16% ammonia.
- 5Cr0.5Mo developed 28 mil thick layer in 11% ammonia under the same condition.
- Type 347 SS produces about 7 mil thick bands in 9 years at 427 °C and 17.6% ammonia.

Thus overall rate is not only high in carbon and low-alloy steels but affect the long-term serviceability of thick-walled vessels and piping. On the other hand components like catalyst baskets, heat exchangers and other reactor internals, which are attacked from both sides and are made with thinner material, have shorter life as these disintegrate easily. To avoid this, the above items are made of 300 series stainless steels or nickel-base alloys like Inconel 600 which have much higher resistance to nitriding. Special precaution is to be taken while undertaking any

repair job on nitrided components. The nitride layer is very hard and is required to be first removed, especially prior to welding. Full removal of the affected layer should be ensured before welding. If the service involves high-temperature high-pressure hydrogen service, normal degassing procedure adopted in such cases will have to be followed.

11.3.1.2 Start-Up and Shutdown Procedures

During start-up and shutdown the converter is subjected to heating/cooling and pressurization/depressurization cycles. Unless these procedures are carried out in a planned manner the converter having monowall is likely to get damaged due to stresses generated and also due to the presence of dissolved hydrogen in the metal.

Heating Rate

- During the start-up initially a small layer of the shell on internal surface is heated by hot process gas and expands which in turn is resisted by cold outer layer. The level of internal stresses produced by this process depends on the rate of heating which may be too high in case of rapid heating. Uncontrolled heating also increases differential temperature across the shell and internals.
- Cooling during shutdown on the other hand creates temperature difference between outer and inner wall with the former being at higher temperature. Too sharp a difference between the two would again result in creating detrimental level of stress.

Pressurization Rate

- As the reactor is pressurized during start-up, the full thickness is not immediately pressurized uniformly but takes time to reach equilibrium. Within this period higher stresses build up in the inner layer which may be a cause of damage. By slow-controlled pressurization it is possible to minimize the time taken to reach equilibrium.
- In case of depressurisation during shutdown similar situation arises but in the opposite direction. In this case the inner layer tries to move inwards which is opposed by the outer layer which is still in strained condition. This results in buildup of stresses across the reactor wall.

Dehydrogenation

Ammonia converters operate at high temperature and high pressure and because of the presence of hydrogen the shell contains high amounts of dissolved hydrogen. As the solubility of hydrogen decreases with temperature and pressure the converter

is to be cooled and depressurized in controlled manner for dissolved hydrogen to diffuse out [18]. In case hydrogen does not fully diffuse out the hydrogen pressure will build up in the steel matrix. The above start-up/shutdown procedures are also applicable in cases of other processes operating under high-temperature high-pressure hydrogen service, such as, hydrodesulphurisers, hydrocracker, coal liquefaction (hydrogenation), etc.

11.3.2 Low-Temperature Section

While general corrosion of carbon steel in ammonia is low, it is susceptible to stress corrosion cracking in anhydrous ammonia. Once the ammonia gas is cooled, the equipment handling anhydrous ammonia becomes susceptible to SCC. For cracking the presence of oxygen in the medium is necessary. Thus, unless, the equipment is opened likelihood of any cracking to occur is negligible. This problem is of more concern in the storage of anhydrous ammonia. Prior to 1970s storage capacities of 500–3000 tonnes range were normally found to be sufficient and in such cases the ammonia was stored in spherical vessels (Horton spheres) under pressure. The pressure used varied from 12 to about 4 kg/cm^2, the storage temperature decreasing with increase in temperature. In modern large capacity plants, however, pressurized storage is not viable because of size and cost. Presently anhydrous ammonia is stored at atmospheric pressure at −33 °C in large size tanks.

11.3.2.1 Pressurized Storage

Companies using imported ammonia, like production of ammonium phosphate or nitrate, still use Horton sphere because their requirement is comparatively small. While general corrosion of carbon steel in anhydrous ammonia is low, it is susceptible to stress corrosion cracking in this service. In early 50s incidences of failure by SCC came to light with the introduction of high-strength steels to fabricate tanks for direct addition of anhydrous ammonia to soil. Even at this stage plant storage sphere was considered to be immune to SCC. During 1960s, spheres fabricated from high-strength steels were installed worldwide. Within a few years, a number of cases of failures were reported after WFMPI replaced the conventional DP for detection of crack. Worldwide concern because of these findings led to the introduction of detailed inspection and research programs, the findings of which are summarized below:

* The susceptibility to SCC increases with increase in yield strength of the steel.
* The incidence of failure decreases with decrease in pressure and temperature.
* Cracking susceptibility can be decreased/inhibited by addition of water (0.2% min), exclusion of oxygen (below 2 ppm) and PWHT of welds.

In 1982, a special conference on SCC of ammonia storage was organized for getting the industry feedback. The major recommendations to minimize cracking were as follows [19]:

* Use of steel with low Y.S. (preferably below 40,000 psi),
* Stress relieving of welds,
* Addition of 0.2w% water (stream condensate, deionized or distilled water) to inhibit cracking,
* Precaution in handling and transfer of ammonia by following procedures to minimize contamination of NH_3 with air.

11.3.2.2 Atmospheric Storage

The storage tanks are similar to normal atmospheric tanks with insulated single- or double-wall construction. For many years it was believed that SSC was unlikely to occur in low-temperature storage tank operating at −33 °C. However, there have been reports of stress corrosion cracking in some storage tanks operating at −33 °C. The cracks have been mainly detected in welds in the bottom zone (within the welds and perpendicular to the welds), bottom to wall joint, and at the clear areas.

Nature of Cracking

Based on experiences from the findings and extensive international research work, the main conclusions concerning SCC in ammonia tanks can be summarized as follows:

1. SCC is difficult to initiate at −33 °C. From the limited date available for cracking at −33 °C the time dependence is similar to pressurized storage but with reduced rate of 1/3rd of that at 18 °C (Fig. 11.9) [20].
2. SCC initiation required that the applied plus residual stress be above yield stress.
3. SCC initiation requires the presence of oxygen.
4. The presence of water inhibits the formation and growth of SCC.
5. Where SCC is found in low-temperature tank, the defects are in general very small (less than 2 mm deep) and transverse to the weld. However, a few exceptions with larger defects have also been reported.
6. Commissioning and, in particular, decommissioning are a critical period for the formation and growth of SCC.
7. Though there have been some indication about the prevention of SCC, this method and peening of welds are not considered effective.
8. Inspection of ammonia storage tank is required to be periodically done because of its toxic and hazardous nature. The European Fertilizer Manufacturing Association (EFMA) [21] report also gives the inspection schedule in different European countries.

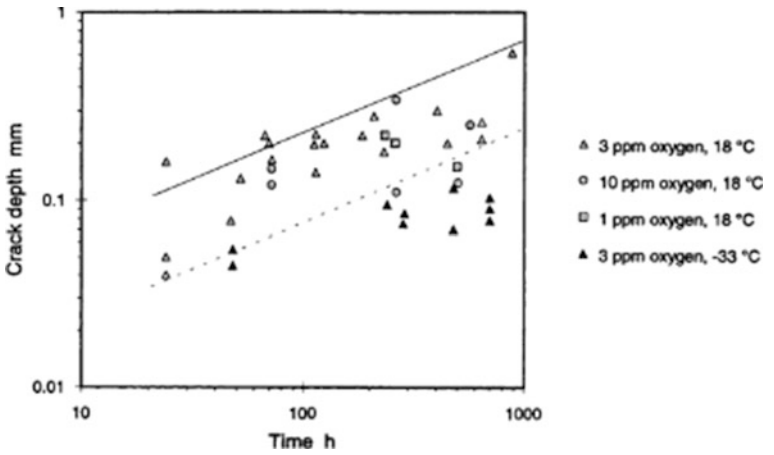


Fig. 11.9 Crack growth rate at atmospheric storage is one-third of pressurized storage at room temperature [20]

11.4 Waste Heat Boilers (WHB)

The major advances in the technology of hydrogen and ammonia production have been in the areas of improved catalyst, higher conversion efficiency and maximization of energy recovery. Because of requirement of steam as one of the feeds in the reforming process and its use in steam-driven pumps and compressors, generation of stream though WHB route is maximized. In WHB boiler the available extra heat energy is extracted as steam by exchanging with different process streams. The materials used and the problems associated with WHB are related to both process and waterside corrosion. The waterside problem is similar to that experienced in normal fired boilers. However, in the hot process fluid side the performance is dependent on the nature of the process fluid and operating temperatures and pressures.

The two important WHBs in a fertilizer unit are (i) downstream of the secondary reformer (known as R.G. boiler) and (ii) after ammonia synthesis reactor. Many units also include a super heater downstream of the R.G. boiler. There are two types of construction, horizontal and vertical. While the former design is used for the RG boiler, since the mid-1970, vertical boilers are being preferred downstream of ammonia synthesis reactor. The super heater is also of vertical design but with reformed gas on shell side. These boilers in most of the cases use natural circulation. Waste heat boilers are critical equipment because any damage to it would result in plant shutdown. However, their performance varies within wide limits. In addition to boiler water quality, which has significant role in any steam raising system, failures have been experienced due to a variety of mechanisms, including design deficiencies, manufacturing defects, failure of refractory, undue stresses and process upset conditions. Some of these problems are discussed next.

11.4.1 Reformed Gas Boiler

RG boilers, mostly of shell and tube design, where tubes are of C–0.5Mo and the tube sheets of Cr–Mo steel. Tube sheet and ducts are covered with refractory for protection against high RG temperature. The boiler has two chambers. Ferrules used at tube inlets are normally of Alloy 800H (replacing earlier used ceramic material which was brittle and liable to failure). This alloy has also been used for ferrules in the outlet and inlet tubes of the boiler. While its performance is generally satisfactory on inlet side, failure of ferrules in the outlet section has been quite serious due to metal dusting which has been discussed earlier. In case of RG boiler, the problems are also associated with performance of refractory linings of the ducts and the tube sheet. Performance of tubes, though generally satisfactory, is affected by the boiler water quality. Considering that the same BFW is used for all steam raising systems, including normally fired boilers in the plant, overall a good control on water quality is maintained. The problem of corrosion is also associated with design, with respect of flow rate and distribution of water from down comers along the length of shell, which is a long horizontal cylindrical vessel. Unlike normal industrial boiler, in case of WHB, the hot medium enters on one side and exit at the other end. The heat flux is accordingly maximum at the inlet end, just ahead of tube sheet/ferrule, and decreases towards the outlet end.

Steam is formed in a boiler or WHB by transfer of heat (heat flux) to the water flowing inside tube by process of forming steam bubbles on walls of the water tube. In simple term it can be stated that the nature and amount of steam formed depends on heat flux and rate of flow of water. Initially bubbles grow on tube wall and detach from the wall after reaching a critical size. The steam raised increases with increasing heat flux by the same process of nucleation. This process of steam formation is known as *nucleate boiling*. However, with increasing heat flux a stage reaches when large bubbles are formed rapidly resulting in the formation of steam blanket on tube wall. This stage of steam generation is termed as *deviation from nucleating boiling* (DNB) or *transition boiling, unstable film boiling,* and *partial film boiling*. The various boiling regimes are shown in Fig. 11.10 [22]. The steam blanket acts as thermal insulator resulting in over heating of water tube. This results in deposition of solids causing caustic or under deposit attack. In extreme cases tube rupture and hydrogen attack also occur.

To compensate the high heat flux at the inlet end of the WHB, the design should ensure that sufficient quantity of water from steam drum through down comer enters in this area. The major objective is to ensure nucleate boiling and avoid deviation from nuclear boiling. To ensure properly distributed flow, the number of nozzles is more on the inlet than the outlet end. If proper flow design is not maintained very early tube failure is experienced. The author has come across some instance where improper design led to failure of RG WHB in 2–3 years.

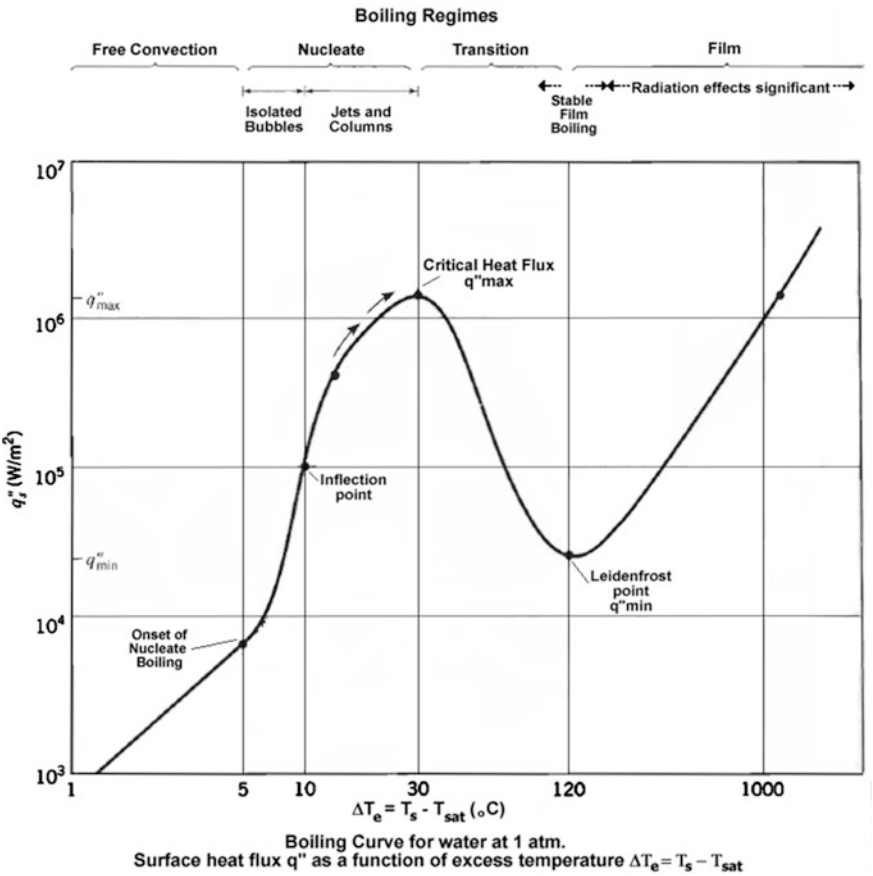


Fig. 11.10 Various regimes in raising of steam in boiler [22]

11.4.2 Vertical Waste Heat Boiler

The ammonia synthetic section normally uses vertical waste heat boilers (WHB) where water is on the shell side and the process gas on tube side which is of U-tube construction. Corrosion is primarily from the waterside and confined just above the tube sheet which is also the zone of high heat flux. Two types of design are common, one with water entering from periphery and in other from side. In both cases, the boiler feed water (BFW) enters the shell from its periphery and then spread inwards. Variation in water flow results in low flow and stagnant zones near the central area. Ideally boiling should start above the tube sheet which requires that minimum amount of BFW is made available throughout the cross section. However, as the flow varies across the cross section, boiling in low flow and stagnant areas reach DNB condition resulting in the tubes running hot. Formation of

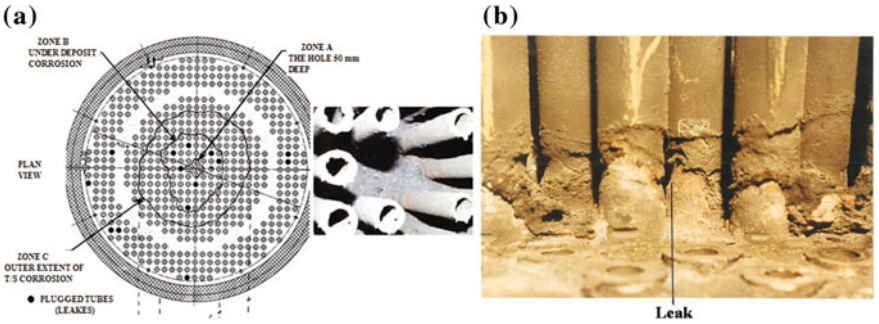


Fig. 11.11 **a** Flow of feed water entering from periphery creates low flow zones in central portion resulting in deposit formation. **b** Deposits formed result in UDC and subsequent leaks in the tubes

deposits followed by under deposit corrosion (UDC) results in leakage of tubes. The extent of corrosion in different zones in case where water enters from periphery and damage due to UDC is shown in Figs. 11.11a, b [23].

11.5 Production of Urea

Urea is produced by reacting ammonia with carbon dioxide under a pressure of 150–220 bar, in a reactor at temperatures in the range of 170–200 °C. The reaction consists of two steps; first, the formation of ammonium carbamate (NH_2COONH_4) followed by its decomposition into urea CO $(NH_2)_2$, which can be represented as

$$2NH_3 + CO_2 \leftrightarrow NH_2COONH \tag{11.5.1}$$

$$NH_2COONH_4 \leftrightarrow CO(NH_2)_2 + H2O. \tag{11.5.2}$$

The reaction is not complete, and unreacted carbamate, CO_2 and NH_3 are recycled in the system to increase the yield. Several developments in the process have taken place in stages to increase efficiency and to decrease energy consumption. The earliest urea plants operated on principle of depressurization and heating of reactor effluents. This was followed by "Total Recycle Process". Presently stripping process dominates the synthesis technology, which does not involve reduction of system pressure. Either CO_2 or NH_3 is used as stripping gas. The major licensers of stripping process are Saipem (earlier Snamprogetti) Stamicarbon, TEC-ACES (Toyo Engineering Company—Advance Process for Cost Energy Saving) and Urea Casale. Figure 11.12 [24] shows a simplified process diagram of high-pressure section of urea plant using Saipem technology. Materials of construction have been standardized by each of the licensers and hence, cannot

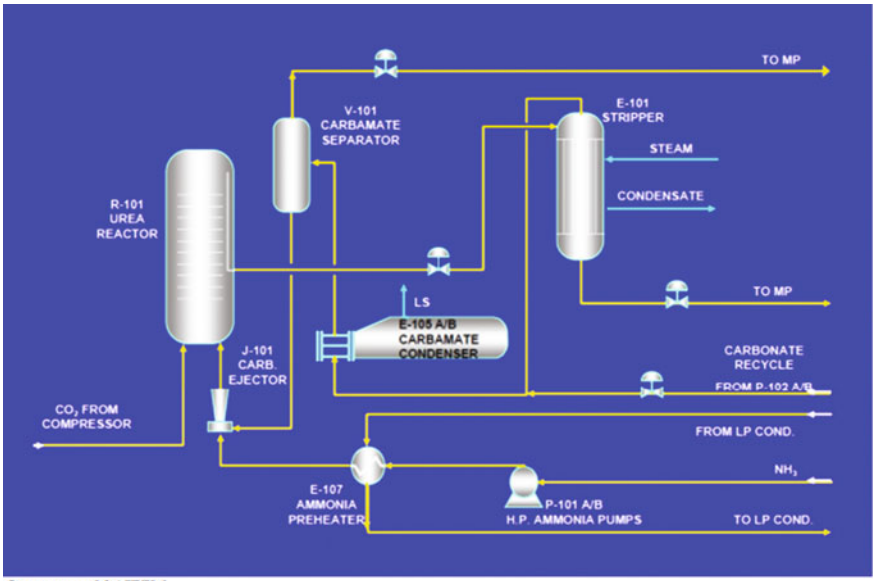


Fig. 11.12 Simplified flow sheet of HP section of Snamprogeti urea process

be generalized. However, a broad approach to material selection and their performance in urea synthesis has been discussed.

Ammonium carbamate, which is present both in the reactor and the decomposition stages, is highly corrosive and active corrosion rate of 316L can be as high as 50 mm/year [25]. Corrosivity of carbamate increases with temperature and is also affected by the ammonia/carbon dioxide ratio. Very few materials have adequate resistance to corrosion in such environment. In the early stages of process development with small size equipment, exotic and expensive materials were used, i.e. lining of reactors with silver, zirconium, etc. With increasing sizes of plants, the search for cheaper materials with good resistance to corrosion began. By the 1950s, it was established that austenitic stainless steel 316L has adequate resistance to corrosion, provided passivation is maintained by introducing oxygen (as air) in the system, originally patented by Stamicarbon [26] and now being universally used.

11.5.1 Conventional Alloys for Carbamate Service

Ordinary 316L alloy was the initial choice but it was soon found to be inadequate in this service due to the preferential attack of the ferrite and sigma present in small amounts. This led to the development of urea grade 316L UG with a low ferrite content attained by balance composition and maintaining a high level of purity. For many years, use of 316L UG along with injection of air remained the standard

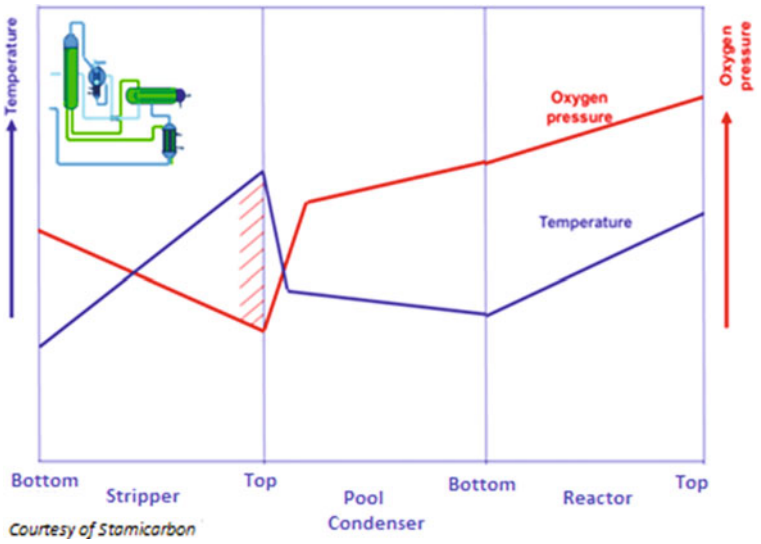


Fig. 11.13 Temperature and partial pressure of oxygen in the synthesis loop [27]

material for critical parts like reactor lining, carbamate condenser, and HP decomposer as no other better austenitic stainless steels were available. Under passive conditions corrosion rate of carbamate varies between 0.01 and 0.1 mm/year but under condensing condition (from NH_3–CO_2–H_2O vapour) the rate increases to 0.2 mm/year as in freshly formed condensate availability of oxygen is low. In practical situation this phenomenon causes accelerated corrosion in cold spots, especially in 316L UG steel.

In the synthesis loop corrosivity of ammonium carbamate varies with the severity becoming maximum in the stripper section. This is reflected in the variations in temperature and oxygen partial pressure where (Fig. 11.13) the lowest oxygen partial pressure and maximum temperature is located in the top of heat exchanger tubes of the HP stripper [27]. As regards stripper, the problem with 316L UG was found to be more serious where erosive conditions prevailed. Titanium which has a good passivation property and requires less passivation air gave better performance under these conditions and was accepted as MOC of stripper. TEC-ACES specified titanium even for lining other equipment like reactor in spite of its cost and difficulties in handling, especially maintenance welding.

Subsequent research carried out with the participation of the process licensers and alloy manufacturers led to the development of a new grade of alloy 2RE69™ by Sandvik having a balanced composition of Cr, Ni and Mo (25Cr–22Ni–2Mo). The main objective was to increase the passivation characteristic and stability of protective film by increasing the chromium content from 18 to 25%. Acceptability of stainless steel in urea service is assessed by Huey test (ASTM A-262-practice C) [28]. Acceptance criteria is 0.6 mm/year for 316L UG. For 25Cr–22Ni–2Mo the

Table 11.4 Effect of dissolved oxygen on corrosion rate of stainless steels in urea service

Oxygen ppm	Corrosion rate, mm/year	
	316L UG	25Cr–22Ni–2Mo
0.5	30–40 Active 1	10 Active 1
1.0	30–40 Active 1	10 Active 1
3.0	30–40 Active 1	0.03 Passive 2
5.0	0.12 Passive 2	0.03 Passive 2
7.3	0.12 Passive 2	0.03 Passive 2

Note 1 Active corrosion; *2* Steel is in passive state

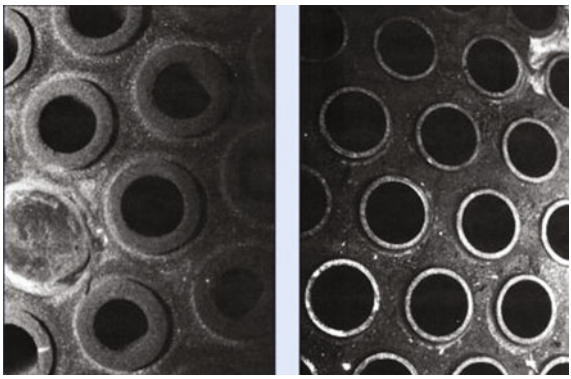


Fig. 11.14 Presence of uniform deposit on stripper tube sheet [30]

acceptance criteria are 0.27 mm/year for Stamicarbon and 0.3 mm/year for Saipem. Higher alloy, e.g. 25Cr–22Ni–2Mo, requires much lower level of oxygen than 316LUG as would be evident from Table 11.4 [29]. However, there is still requirement of good amount of oxygen in case of 25Cr–22Ni–2Mo though the additional advantage of the former alloy is that it can withstand upset conditions much better than the latter. The alloy further has better resistance to corrosion under condensing corrosion. Use of air, however, results in energy and yields losses because of the introduction of inerts (mainly nitrogen and also CO, H_2 and CH_4) in the system. Venting of inerts also results in loss of NH_3 and CO_2.

In general performance of 25Cr–22Ni–2Mo in Saipem urea plant during early 70s was found to be satisfactory even in a stripper (design life typically of more than 10 years) when the plant capacity was <1000 MTPD and reciprocating compressor for CO_2 and reciprocating pumps for NH_3 and carbamate were used. The reason for this was found to be the formation of a uniform protective layer of cracked oil (Fig. 11.14) which entered the system from the reciprocating compressor [30]. As the major erosion corrosion damage of tubes occurs in the top section, it was common practice to get a life of 10–15 years by reversing the stripper after 6–8 years. However, there is an instance where it is claimed that in a German plant two strippers with Sandvik 25Cr–22Ni–2Mo were replaced after 34 and 36 years [31].

11.5.2 Development of New Alloys

Increasing demand of urea since 80s led to increase in capacity to >1000 MTPD which in turn required replacement of reciprocating with centrifugal compressor and pumps. With resultant absence of oil ingress in the system the performance of 25Cr–22Ni–2Mo was not found to be adequate. While titanium Grade 3 was used as better material in stripper it was also not found to be completely immune to erosion if the plant was run above the design capacity, a practice which is followed by most of the plants. Large capacity also required greater reliability of equipment, along with reduction in cost of maintenance. Solution lied in development of better and cost-effective (based on life cycle cost) material(s) along with capability to withstand operation above design capacity [30].

11.5.2.1 Duplex Stainless Steel

The ferrite in 316L UG is limited to 1% because it has been found to adversely affect the performance of austenitic stainless steel in carbamate service. Ammonia like copper also attacks nickel but to a much lesser extent. The presence of nickel in austenitic stainless is considered to have some adverse effect on the performance of stainless steel in carbamate and one approach was to decrease nickel content and increase chromium content in stainless steel. This resulted in examining the suitability of duplex stainless steel (DSS) having high chromium content. The DP12™, (falling under 25Cr Super DSS grade) developed by M/S Sumitomo Metals, was first used in high-pressure urea synthesis section of TEC-ACES urea plants for some of the equipment like carbamate condenser and piping. For more severe operation in other equipment in synthesis section, TEC in collaboration with Sumitomo Metals later developed an improved version of DSS termed as DP28W™ having nominal composition of 28Cr–8Ni–Mo–W–N falling under the category of Hyper DSS [32–34].

Simultaneously, use of DSS was introduced by Stamicarbon who simultaneously developed a new grade of DSS jointly with Sandvik (Trade name Safurex®) [30, 33, 35]. DSS developed for carbamate service is easily passivated and therefore require less oxygen. It is claimed that passivation air can be drastically reduced in case duplex steel is used for all equipment and piping, one-fifth or less for DP28W™ [30] and 0% (0.04% normally maintained) in case of Safurex® [33, 35, 36]. According to Stamicarbon with HP stripper of Safurex® and HP carbamate condenser made of 25Cr–22Ni–2Mo, oxygen injection can be brought down from 0.6 to 0.3 vol.% [37]. In actual practice some operators using Safurex® have, however, reported deviations with respect to oxygen requirement claimed by licensor [38].

Corrosion resistance of Safurex® is not only determined by the ferrite content, but also on the ferrite/austenite microstructure, which consists of fully isolated austenite phases in the ferrite matrix. On the other hand, in fully austenitic materials

Table 11.5 Use of DP 28W^{TM} in TEC-ACES designed urea plants till 2008

Country	Plant	Equipment	Configuration	Number of products	Year
Indonesia	A	Stripper	Swirl tube	3100	2003
	B	Stripper	Swirl tube	3100	2005
	C	Stripper	Swirl tube	2434	2005
	D	Stripper	Swirl tube	2550	2005
China	E	Stripper	Swirl tube	10	2005
	F	Stripper	Swirl tube	3100	2005
Pakistan	G	Stripper	Swirl tube	200	2005
	H	Stripper	Swirl tube	1600	2008
Japan	I	Reactor	Lining plate, Forging	12 Mton	2006
Trinidad	J	Reactor	Lining plate, Forging	150 Mton	2007
		Stripper	Tube, pipe, plate, Forging		
		Condenser	Tube, pipe, plate, Forging		
Venezuela	K	Stripper	Tube, pipe, plate, Forging	135 Mton	2008
		Condenser	Tube, pipe, plate, Forging		

such as 316LUG or 25Cr–22Ni–2Mo a small amount of ferrite has a detrimental effect on the redox potential and thus on the corrosion resistance of the steel in carbamate solution. That is why an upper limit of 0.6 vol.% is specified. Safurex® was first introduced for fabrication of carbamate condenser and high-pressure scrubber. The highly corrosion-resistant properties of new range of super DSS have proven to be of quite advantage to increase the equipment life. Table 11.5 gives the use of DP28W^{TM} in equipment in TEC-ACES designed plant [39]. As a result of successful trials which proved the higher performance capability of Safurex® and DP28W^{TM} in carbamate solution, both Stemicarbon and TEC have recently built key parts of urea plant, such as strippers, high-pressure condensers, scrubbers, high-pressure piping and reactors using their respective patented alloys leading to considerable decrease in air injection.

The DSS used in urea plants is patented alloys and are supplied only to the units designed by respective process licensors. However, the overall advantages of these alloys are claimed to be as follows:

- Both DP28^{WTM} and Safurex® show high resistance to carbamate corrosion and so these alloys can also tolerate greater degree of disruption in air injection and longer period of holdup (blocking) in synthetic section. Electrochemical study on various grades of stainless steel with one-third requirement of air is plotted in Fig. 11.15. The result clearly shows that under very severe condition DP28W^{TM} compared to 304 or 316LUG gets quickly repassivated. The limit of 72 h normally set for conventional urea grade austenitic stainless steels can be increased because the oxygen requirement for passivation of DSS is very low.
- Tests carried by exposing the samples of DP28W^{TM} along with DP12 and 316L confirmed the high superiority of DP28W^{TM} over 316L UG. This would be evident from equivalent corrosion rates of the three alloys compared with DP12

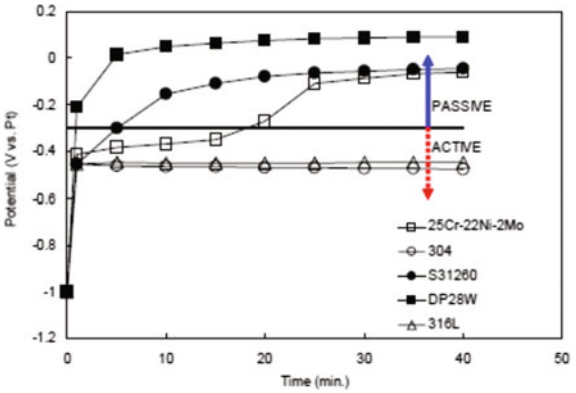


Fig. 11.15 Passivation of DP28W at low air concentration [34]

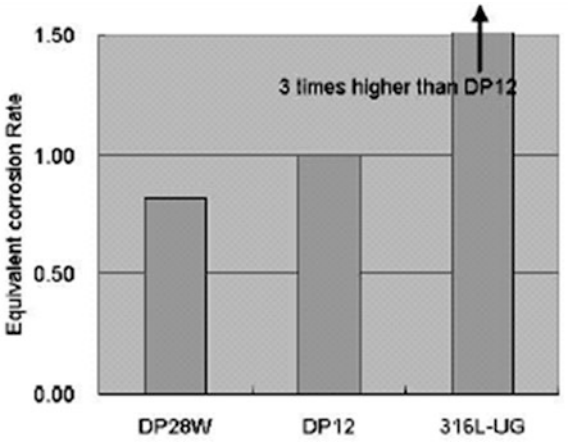


Fig. 11.16 Comparison of corrosion rate of DP28W with other stainless steels [32]

Table 11.6 Weight saving in HP stripper using Safurex®

Equipment	Weight saving (%)
Heat exchanger tubing	45.3
Top tube sheet	29.8
Bottom tube sheet	15.0
HP carbon steel top channel	3.3
HP carbon steel bottom channel	3.0
LP carbon steel channel	2.7
Liquid divider tubes	0.5
Shell side baffles	0.4

as shown in Fig. 11.16 [32]. The corrosion rate of DP28W™ was found to be more than one-third of 316L UG.

- Compared to 316L UG or 2RE69, the alloys have very high strength, which helps in reducing wall thickness/weight and therefore the material cost (Table 11.6) [27].

- These alloys are resistant to stress corrosion cracking.
- DSS also possess good weldability and formability.

It is claimed that HP stripper made of Safurex® has higher operating limits and turndown ratio. Because of excellent passivation properties the equipment can tolerate both too high and too low loads. In austenitic alloys, too high load can lead to flooding of the stripper tubes with consequent lack of passivation. At too low loads, on the other hand, stripper tubes are no longer sufficiently wetted by urea solution film and temperatures at the tube wall become too high, leading to the damage of the passive layer.

Improved Plant Safety with DSS

Another advantage claimed in use of DSS is connected with safety aspect. Small amounts of hydrogen as impurity are introduced along with carbon dioxide from hydrogen plant. Along with oxygen from passivation air and ammonia an explosive mixture of $NH_3 + O_2 + H_2$ with low auto-ignition temperature (AIT) can form in *inerts* released from plant. In case there is also ingress of any methane along with hydrogen there is further lowering of AIT [40]. For the above reason possibilities of explosion have always been a matter of concern in urea manufacturing. The steps required to avoid any mishaps are to keep these gas mixtures outside the explosion hazard zone. This can be done by either reducing hydrogen or oxygen or both. To minimize the chances of formation of explosive gas mixture and also amount of inert gas, a number of alternatives have been used/attempted as given below:

- Injections of pure oxygen, oxygen-enriched air and hydrogen peroxide have been attempted but not implemented because of various constraints.
- Reduction of hydrogen in carbon dioxide below 10 ppm by catalyst combustion helps in minimizing the chances of forming explosive mixture [40, 41]. However, this method not only involves extra capital cost but also has no effect in substantially reducing the production loss due to inert.
- However, where special grades of DSS (Safurex®/DP28W™) are used, the oxygen requirement for passivation is substantially reduced. This in turn reduces the ammonia and oxygen content of purge stream and shift it in the non-explosion limits of $NH_3 + O_2 + H_2$ mixture. According to Stamicarbon even at 0.3 vol. % of oxygen, composition of the HP purge stream would shift in the non-explosion limits of $NH_3 + O_2 + H_2$ mixture [37]. The use of Safurex®/DP28W™ thus has additional advantage of the cost-effective method to minimize the chances of explosion in urea plant.

11.5.2.2 Bi-metallic Stripper Tube

As discussed, the initial choice for the stripper tubes was titanium. However, to enable the tubes to be welded, the tube sheets had to be made of titanium clad carbon steel. Though titanium gives better service, its protective oxide layer is prone to long-term damage due to erosive action. Thus the stripper tubes had limited life of 10–15 years against 20–25 years for other high-pressure equipment. To take care of this deficiency, the approach of process licensors was different. While Stamicarbon and TEC developed duplex stainless steels Safurex® and DP28W™, respectively, Saipem selected zirconium which had proven good record in urea service up to 232 °C (CPI—Allied process), as replacement [42]. Excellent performance of zirconium is due to its easy passivation characteristics requiring no oxygen and extremely hard and durable oxide layer [43]. From cost consideration it was decided to use bi-metallic tube internally lined with zirconium.

Mechanically Bonded Tube

The tubes of the new stripper were bi-metallic with the outer tube of 25Cr–22Ni–2Mo and the inner tube made of zirconium [30, 33]. The inner zirconium layer has high corrosion/erosion resistance properties because of formation of hard oxide layer. The problem experienced with the bi-metallic tube was related to the manufacturing technique which consisted of expanding the zirconium tube inside 25Cr–22Ni–2Mo tube. This provided a mechanical instead of metallurgical bond which sometimes leaves a fine gap (crevice) between the two into which carbamate solution could penetrate. Deficiency of oxygen inside crevice results in tube end corrosion (Fig. 11.17) [30]. Alloy 25Cr–22Ni–2Mo cladding in channel section has also shown signs of corrosion due to oxygen deficiency and rise in process temperature (205–210 °C) beyond the desired outlet temperature limit of 204 °C [33]. In Saipem process oxygen (air) is injected at the bottom of reactor along with



Fig. 11.17 Corrosion of bottom tube end of mechanically bonded bi-metallic tube [30]

carbon dioxide against bottom of stripper in Stamicarbon process. To take care of corrosion in bottom channel additional passivation air is injected in the stripper bottom in Saipem designed plant if need arises.

Metallurgically Bonded Tube

To further improve the performance of bi-metallic tube ATI Wah Chang and Saipem jointly developed OmegaBond™ zirconium-lined titanium tube for urea stripper and confirmed its good performance by carrying out field trials for 3 years at Fauzi Fertiliser Company Ltd of Pakistan [43]. The production technique uses solid-state joining technology, which consists of hot extrusion of zirconium billet fitted inside a titanium billet to get good metallurgical bond. The extruded piece is then cold-pilgered to get final diameter and wall thickness [35, 42, 44, 45]. As the tubes are required to have Ti/Ti weld, use of 25Cr–22Ni–2Mo for tube sheet is not possible. The interior surface of lower and upper chambers is, therefore, explosively clad with titanium. Thus differential metal welding of tube-to-tube sheet is avoided [44]. As both titanium and zirconium get easily passivated, injection of air in the stripper is not necessary which has the additional advantage of

- Decrease in *inert* as a result of less air injected.
- Reduction in chances of explosive mixture formation.
- Capability to operate beyond the temperature limit of 204 °C.
- Increase in capacity of the plant which can be as high as 15%.

Subsequently two strippers one in GPIC, Bahrain and the second in Fauzi Fertiliser Company Ltd, Pakistan were fabricated using OmegaBond™ [43].

Zirconium Stripper Tube

To achieve high flexibility of operation and to maximize plant reliability with minimum maintenance Saipem has built stripper of the largest urea plant in the world using zirconium-lined steel and solid zirconium tubes for Profertil's urea plant in Argentina. It is claimed that the use of zirconium is not only reliable but the lowest life cycle cost [44].

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Chapter 12
Damage Assessment and Repair of Stationary Equipment

Abstract In an operating plant, the primary responsibility of maintaining the health of equipment rests with the inspection and maintenance personnel. This not only involves identification of damage but also carrying out repairs to restore the original code required parameters. For damage assessment, conventional and some special inspection techniques are used. To carry out quality job, concerned persons require the knowledge of inspection tools, code requirements and capabilities of performing in situ repair. As regards pressure vessels codes, there are variations in the requirements between ASME and EN codes. For repair jobs no separate codes were available till recently. Now the job can be executed as per ASME post-construction code PCC-2. PWHT is an integral part of any repair, but in field local PWHT is involved for which procedure used is different to ensure full stress relief. For post-repairs, hydrotest is carried out quite often and due precaution is needed in case of stainless steel equipment. Thus plant maintenance requires multidisciplinary knowledge. The chapter describes various aspects of plant maintenance including background knowledge required by concerned inspection, maintenance and other related persons. The special procedures to be used for in-plant maintenance and related jobs have been described.

Keywords Plant inspection · Pressure vessel code · Post-weld heat treatment · Inspection procedure · Repair welding · Hydrotesting

12.1 Importance of Plant Inspection

All equipment to a small or large extent undergoes damage over long period of service which adversely affects their reliability (*Note: In this chapter, unless specifically mentioned, the term equipment includes vessels, columns, reactor, piping, exchangers, tanks,* etc.). The nature of damage, depending on service conditions, can vary from simple thickness loss to pitting, cracking, surface and subsurface planer and volumetric attack, high-temperature attack, etc. Safe running of a plant therefore requires that integrity of equipment is ensured all the time so

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that fluids handled are contained within the vessel, piping, tanks, etc. Types of various damages and their mechanism have been discussed in earlier chapters. The API 571 [1] discusses the most likely damage mechanisms which can be experienced in the refining and other process industries. Some inspection can be carried online but many others require the plant to be shutdown. In any process or manufacturing industry there is a period when the plant is shutdown for some days to carry out what is known as "maintenance shutdown" which mainly consists of the following:

- Servicing and overhauling of rotating equipment
- Inspection of stationary equipment externally and internally of those which have been opened and permitted for safe entry
- Assess the extent and rate of damage and if any replacement or upgradation of MOC is required
- Carry out repair and replacement where needed
- Inspect condition of insulation and take corrective measures where necessary
- Cleaning of scale and deposits formed in heat exchangers
- To certify the statutory requirement of boiler and pressure vessel.

Such shutdowns in process industry were earlier carried out every year and so these were popularly known as annual shutdown. This approach to shutdown has now changed. The modern concept is to maximize production by increasing the period in between shutdown and minimize the shutdown period. This requires that the plant should operate uninterrupted without breakdown for long periods of 2–4 years which requires the inspection and maintenance practices to be of highest standard.

12.1.1 Inspection Tools and Techniques

The development of plant inspection system in the process industry has been closely related to the oil refining industry. A new area which started a little more than a century back, with simple tools like callipers, measuring scale, small magnifying glass and hammer, has grown today to a highly sophisticated area with the introduction of new techniques, advanced instrumentation, electronics and software making it possible to detect and map both the surface and volumetric defects using advanced techniques based on ultrasonic, eddy current, laser, magnetic properties, etc. It is also possible today to carry out condition monitoring of exchanger tubes, pipeline, tubular reactor or stripper. People connected with petrochemical industries are familiar with the various techniques available and the outline of some commonly used techniques has been given and some specific cases of damage assessment where both results and conclusions are to some extent subjective have been discussed.

Inspection forms an important part, both during fabrication and operation. During the lifetime of an equipment, periodic inspection is carried out to

- Detect type and extent of defect
- Measure thickness of components
- Measure dimensional changes
- Determine degree of metallurgical degradation
- Ensure that the defect is within code requirements/acceptable limits and would in no way impair the future usefulness of the component.

Depending on whether the defects are surface or subsurface, whether both internal and external faces can be reached, nature of defect and type of equipment and defects, various inspection techniques are used. The techniques include visual and non-destructing inspection. Considerable advancement in non-destructive examination (NDE) techniques has taken place and these are mostly based on

- Radiography
- Dye penetrant (normal and fluorescent)
- Ultrasonic-normal and automated
- Magnetic particle
- Eddy Current
- Acoustic Emission
- Field Microscopy
- Laser technology.

12.1.1.1 Radiography

Though radiography is primarily a tool used to ensure the quality of welds during fabrication and repair during plant inspection, its use as a tool for plant inspection is limited primarily for identifying subsurface defects, pitting and sometimes for determining loss in wall thickness. Use of image analyser gives a clear contour of the crack. With development of digital radiography detection of corrosion damage without removing the insulation has become possible.

12.1.1.2 Dye Penetrant (Normal or Fluorescent)

Dye penetrant (DP) is a sensitive non-destructive method of detecting defects, e.g. cracks, shrinkage porosity, etc. which are open up on the surface. There are two variants—normal and fluorescent. Of the two, the latter shows up fine defects more clearly and reveal fine cracks and especially suited for inspection of stainless steels. In case of fluorescent penetrant, viewing is done under the black light (ultraviolet). For DP good surface preparation is essential. To get reliable results it is essential that surface to be examined is prepared to a finish so that the indications are not masked.

Normally grinding as a means of surface preparation is used. In such cases use of heavy grinder should be avoided so that the opening of the defect on the surface is not closed due to smearing by deforming metal. In such cases the final surface preparation should be done by light grinding.

12.1.1.3 Wet Fluorescent Magnetic Particle Inspection (WFMPI)

WFMPI is the most sensitive method for detecting fine surface breaking cracks. This method has therefore replaced the liquid penetrant and dry or wet magnetic particle testing for ferritic steel as the most reliable tool for plant inspection. Surface preparation prior to testing is important and the best method is to abrasive blast the weld and adjacent base metal for a distance of 150 mm on both sides of the weld to a near-white finish in accordance with NACE NO2/SSPC-SP10. For WFMPI AC yoke instead of DC prod should be used. Testing equipment, levels of magnetizing fields, etc. should be monitored periodically. Procedure to check system performance and sensitivity is detailed in ASME SE 709 [2].

12.1.1.4 Ultrasonic Test (UT)

It is the most commonly used NDT for equipment in process industries for plant health check. Ultrasonic test is used for measuring thickness, location of internal defects and mapping of the crack. Other important use is in detecting internal defects like blisters, HIC, debonding of cladding, lamination, etc. With the help of advanced signal processing and imaging available from the μ+ (microplus) system, high-quality mapping of internal damage can be got, analysed with suitable softwares and recorded. Other important development in ultrasonic has been the technique which not only scans and stores quality of weld and the presence of cracks but also evaluates their length, height and position with high degree of accuracy (Fig. 12.1) [3]. Radiography was the only method approved by ASME for the inspection of welds and ultrasonic was not accepted. This resulted in long hours for inspection especially in case of heavy wall equipment. This also affected shutdown schedule when major repairs were involved. With the development of Time-of-Flight Diffraction (TOFD) technique it became possible to get fast, accurate and repeatable full volumetric inspection data recorded electronically. TOFD has now been included in ASME Section VIII as a method for the inspection of welds greater than 25 mm thick in lieu of radiography. Many other uses of TOFD have now been found for defect detection. Thus with use of B-scan, C-scan, TOFD, etc., it is possible to get good information on volumetric damage.

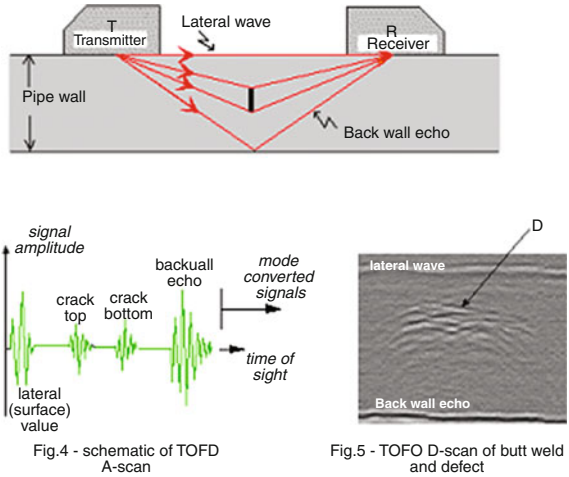


Fig. 12.1 TOFD technique for defect detection and mapping [3]

12.1.1.5 Acoustic Emission (AE)

Acoustic emission has become in the recent past an important NDE tool to establish integrity of equipment (Fig. 12.2). Whenever a metal deforms or crack propagates it emits sound waves. Using AE technique these sound waves are picked by probes placed on the equipment. Then after filtering out unwanted noises the data is analysed to get the necessary information [4]. In process industry this method has been used mainly to monitor growth of cracks (stress corrosion or hydrogen cracking) which can become unstable and grow under the influence of stress, leaks, etc. Thus on the basis of this type of testing and application of API 579-1/ASME FFS-1-Fitness-for Service it can be assessed as to what stage a crack is required to be removed thus extending operation of the equipment and avoid unscheduled shutdown.

Other NDE techniques are available for obtaining specific information. Some of these are eddy current for determining thinning, pitting, fatigue crack of tubing; magnetic permeability for deterioration of reformer and cracker tubes (austenitic) due to carburisation; tomography for internal fissures and defects, etc. Use of TOFD has also been successfully made to determine extent of carburization in ferritic heater tubes used in visbreaker and coker units in a refinery (Fig. 12.3) [5]. Various NDE methods are available and each of them gives some definite information but have certain limitations also. Therefore, in actual practice more than one technique may have to be used to get correct picture of the condition.

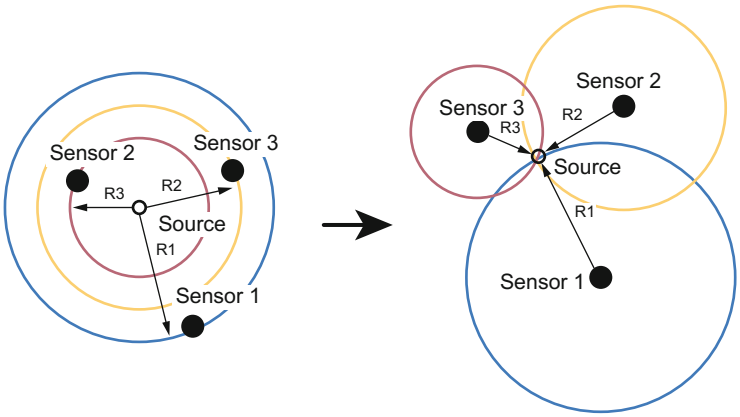


Fig. 12.2 Placing of AE sensors to locate the position and growth of a linear defect

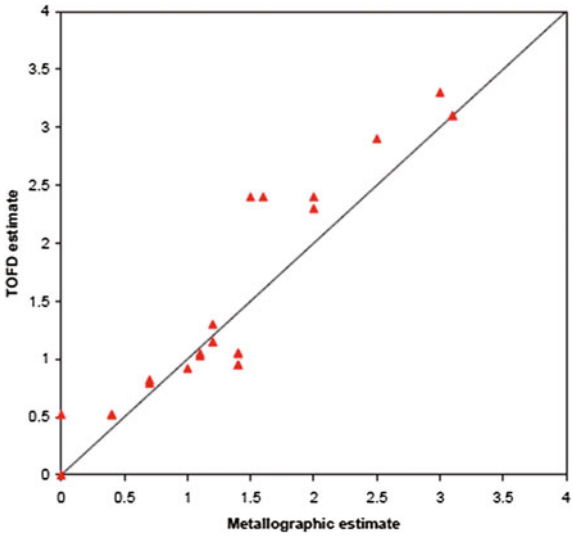


Fig. 12.3 Metallographic and TOFD measurements of carburization [5]

12.1.2 Inspection Planning

12.1.2.1 Conventional Inspection Practices

API 571 provides the inspection engineers an initial indication about the expected service-induced deterioration and failure modes. The in-plant equipment history combined with information obtained from API and other sources form the base for planning the inspection schedule. Two API recommended practices for pressure vessel, piping and tankages are API 510 [6], API 570 [7] and API 653 [8].

The API 570 classifies piping service class and gives details of corrosion monitoring locations (CML), inspection intervals, corrosion rate measurements, repair, etc. On the other hand API 510 deals with similar aspects of pressure vessels with greater emphasis on various other modes of deterioration to which equipments are subjected. Alternative rules for exploration and production (E & P) pressure vessels have now been included in API 510. All these standards give details of various aspects of inspection including recording of data in a format which can be easily retrieved for future use. While carrying out inspection of pressure vessels it is advisable to study the guidelines discussed for pressure vessels in API 572 [9]. In addition the inspection group should have all information about the plant layout along with fabrication drawings, material data sheet, equipment history records, P&ID and piping isometrics, etc.

12.1.2.2 Risk-Based Inspection

The cost of inspection is much higher today because of increasing use of advanced techniques combined with high manpower cost. This led to the demand by industry to develop a more cost-effective system without compromising the integrity of equipment and safety. Based on this requirement a new concept of planning inspection based on '*risk*' involved as a consequence of failure as the base and not time elapsed between two inspections as per conventional practice. In other words more attention is to be given to the equipment in a particular system whose failure can lead to release of containment that can cause fire, explosion, environmental damage and loss of life along with related direct and indirect cost. However, this alone is not sufficient to take a decision as there may be cases where consequence of failure may be high but the likelihood of failure may be significantly low. Thus the consequence of any failure is also to be related to the likelihood of failure to assess overall level of '*risk*' involved. This system was named as Risk-Based Inspection (RBI).

RBI defines risk as a product of the consequence and likelihood of failure which for a scenario (S) is stated as

$$\text{Risk}\, S = Cs \times Fs, \tag{12.1.1}$$

where

S scenario number,
Cs consequence = (area in ft^2 or \$) for scenario, s,
Fs failure frequency (per year for scenario, s).

The risk is determined as the sum of the risks for all scenarios pertaining to the items under consideration.

As damage mechanism is varied, the system has to be applied for each mechanism and quantify level of risk in case failure takes place. The final calculated risk for a plant item is a combination of the estimated likelihood of failures due to

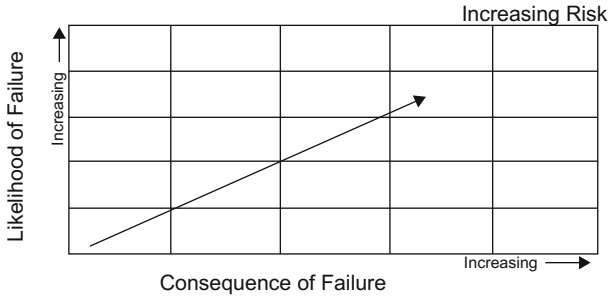


Fig. 12.4 Relation between risk and likelihood of failure vs. consequence of failure

different mechanisms and the consequence of that failure. Such an evaluation shows increasing '*risk*' when probability of failure is plotted against consequence of failure as shown in Fig. 12.4. If these results are plotted on a matrix, it is possible to get broad idea about the different degrees of '*risk*' involved, e.g. low, medium, high or very high, which in turn can be used to prioritize the extent and period of inspection.

The main advantages of RBI are as follows:

- More cost-effective alternative to traditional inspection.
- Better use of inspection resources by optimizing inspection cost versus '*Risk*' as shown in Fig. 12.5.
- Reduction in plant downtime.
- Decrease of risk and increased safety.
- Cost reduction of inspection and maintenance activities.
- Adherence to codes of compliance.

The RBI technology was developed by API, details of which are given in standards API 580/581 [10, 11]. These standards deal specifically with problems experienced in refining industry but the concept and procedure outlined have been

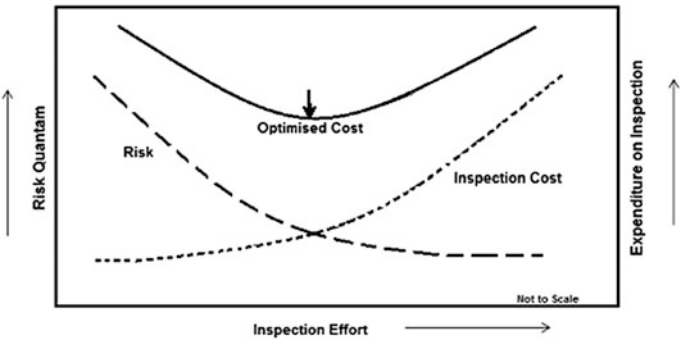


Fig. 12.5 Optimizing cost of inspection against the risk

used also in other industries by introducing specific situations pertaining to the particular industry. A fully integrated RBI system includes inspection activities, inspection data collection and updating and continuous improvement of the system. The RBI gives methodology for both qualitative and quantitative assessment of which the qualitative methodology can quickly identify the high-risk systems in various units. This can then be followed up by detailed analysis to quantify risk for each piece of equipment in high-risk areas. Softwares and agencies are available today who are experienced in its implementation by engaging a multidisciplinary team. API 580 supplements API 510, API 570 and API 653 and RBI approach has now been included, in these standards for the planning of inspection. Many large companies have also fine-tuned and developed in-house systems.

Using RBI optimization of inspection cost along with decrease risk and increased safety can be achieved. This has been concluded from various studies carried out in refinery, oil and gas [12, 13], fertilizer, petrochemical and power industries. To give couple of examples:

- In one fertilizer plant the inspection and associated maintenance cost savings were estimated at $237,500 for a Return on the Investment (ROI) of 5:1. The annualized savings were estimated at $47,500, which equated to a 5% reduction of their maintenance and inspection budget [14].
- Conoco's (Commerce City, Colorado) estimated inspection and maintenance-related expenditure of a little over $1 million for the 10-year plan period was reduced to just under $200,000 after RBI study [15].

12.2 Pressure Vessel Code

Basic objective of inspection, in addition to ensuring reliability, is to assure that the pressure vessel code-related parameters are restored where damage has occurred and any repair work has been done. While post-construction activities follow different guidelines the final corrective measures cannot be divorced from the code under which the equipment has been designed and fabricated. This requires that the maintenance, inspection and professionals looking after a particular job possess an overall knowledge of the Pressure Vessel Codes, Addenda and CodeCases. Some of the important aspects of pressure vessel codes, material requirements, design rules and heat treatments, along with repair related internationally accepted guidelines, are outlined next, for the details of which the readers should consult the original documents. The American practices have been discussed in detail but some aspects of European codes have also been given.

12.2.1 History of Pressure Vessel Code

With advancement of civilization the need for introduction of nonhuman forms of force to perform work led to the use of animals, wind, water and other natural forces. However, these forms had limitations in the quantum of power output which intensified the efforts to look at other alternatives and in era 1700 steam engine and boilers were invented. It was about 1800 that a steam engine that operated at a pressure of 65 psi was designed by Richard Trevithick with boiler and engine mounted together. This led subsequently to expansion in use of steam for various purposes like railways, automobile, power generation and later household and industrial uses. Additional improvements in water tube boilers were incorporated by George H. Babcock and Stephen Wilcox in 1875, which even today is considered as a major step in the development of boilers [16]. Similar developments took place in other countries in Europe and elsewhere. During the early years boilers operated at low pressure with saturated steam using softened water with pH controlled by addition of caustic. The boiler drums were of riveted construction which continued to be used till late 1929/early 1930s before welding became the accepted method of joining. During this period the design details of pressurized components were not that well understood and different criteria were used by different boiler manufacturers. Incidences of boiler explosion were quite common and the history reports number of serious boiler accidents with the rate of explosions and fatalities reaching one and two per day, respectively, in USA during early twentieth century [16–18].

12.2.2 American Codes

Realizing the need of scientific approach to the reliability of boiler, American Society of Mechanical Engineering (ASME) was formed in 1880 which was later followed by establishment of American Boiler Manufacture Association (ABMA). The activities of ASME were limited till the first Massachusetts Rules were approved in 1907, as a result of serious boiler failures including one at a shoe factory [16, 19]. Devastation of the plant which caused many fatalities is shown in Fig. 12.6 [20]. The major reasons for failures were deficiencies in mechanical design and safety devices along with caustic cracking. The boiler water entered the crevice formed between two riveted plates, got concentrated over time resulting in caustic cracking. Considering the demand for a code applicable in all states in USA, ASME in September 1911 appointed a committee for steam boilers and the code was published as ASME Section I, in 1915 (officially 1914 Ed) after public hearing for clearing doubts and opposition of boiler manufacturers [16, 21]. Material specification portion was published as Section II. Since publication of code for boiler a sharp decrease in failures has occurred [22].



Fig. 12.6 View of Grover Shoe Factory disaster, March 1905 [20]

12.2.3 Unfired Pressure Vessels Code

Code for boiler was fore runner for other codes developed by ASME. By 1920s the necessity of having a separate code for air tanks and pressure vessels was found necessary as use of boiler code for these items by some manufacturers did not prove successful. A separate code, code for Unfired Pressure Vessels, ASME Section VIII Div 1 was published in 1925. Subsequently number of codes was published and by 1930s this had grown to eight though many of these have been presently discontinued, modified or replaced with other codes. ASME Section VIII Div1 provides requirements for design, fabrication, inspection, testing and certification of fired or unfired pressure vessels, operating at pressures exceeding 15 psig. Subsequently in 1968 *Section VIII Division 2—Alternative Rules* was published introducing design by analysis methods with design stress higher than Div. 1. Further in Div 2 requirements on materials, design and non-destructive examination were more rigorous compared to Div1. These standards were further modified, Div.1 in 1999 and Division 2 after 2006, with design stresses higher than earlier Divisions. Key features of the changes in the two codes have been highlighted by LR Insurance Inc. [23]. Many of the critical equipment like high-pressure reactors, absorbers, equipment handling toxic fluid, etc. were earlier preferably constructed using Division 2 (Old).

Preparation of pressure vessel code requires multidisciplinary inputs for which Committees having members representing expertise in areas like mechanical, materials, structural, physics, chemistry and other disciplines are formed in addition to mechanical engineering. The members work voluntarily in the Committee. Of the various pressure vessel codes the ones important for process industry are Section VIII for unfired pressure vessels and related Sections like II (Materials), V (NDT Examination) and IX (Welding). Fired heaters and heat exchangers and waste heat boilers are covered by API and TEMA, respectively. It is accepted that by following the code it is possible to meet the minimum requirements to operate the pressure vessel in safe and reliable manner. The codes are used variously as a jurisdiction requirement or as a contractual requirement between the user and the fabricator. In almost all provinces of United States and also in Canada the various

sections of the Boiler and Pressure Vessel Code have been adopted by law. Furthermore, ASME PV codes are internationally accepted by many countries and companies [21].

12.2.4 Process Piping Code

The pressure piping code B31 was issued in 1935 as the American Tentative Standard Code for Pressure Piping, which was prepared with the participation of members from engineering societies, industries, government bureaus, institutions and trade associates. Later it was issued as petroleum refinery piping code as ASA B31.3-1959 by American Standards Association. This was finally accepted by ASME piping committee and issued in 1980 as ANSI/ASME B31.3, Chemical Plant and Petroleum Refinery Piping code. In 1996 its name was changed to ASME B31.3 Process Piping Code [22].

12.2.5 Pressure Vessel Code in United Kingdom

In the UK and other countries also incidences of boiler explosion were common and as per UK Board of Trade, 1871 boiler explosions with 732 fatalities were recorded over a 25-year period at the end of nineteenth Century. The first design rules "Tentative requirements for fusion welded pressure vessels" were issued by Lloyd's Register of Shipping in 1934. Initial specifications prepared by British Standard Institute (BSI) were conservative compared to that of ASME and API which adversely affected the export [24]. In the 1950s the BS 1500 was published followed by BS 1515 in 1965 which included a more detailed and advanced approach leading to higher allowable stresses, compared to both BS 1500 and ASME Section VIII Div1. The Standard BS 5500 which included both "Design by Rule" and "Design by Analysis" was issued in 1976.

12.2.6 European Pressure Vessel Codes

Like UK, different European countries had their own codes but presently all European Union countries have accepted a single standard EN 13445 as per the Pressure Equipment Directive (PED) (97/23/EC) adopted by the European Parliament and the European Council in May 1997. Initially the standard came into force on November 29, 1999, and from May 29, 2002 the Pressure Equipment Directive was obligatory throughout the European Union [25]. EN 13445—3 gives the rules to be used for design and calculation under internal and/or external pressure of pressure bearing components of pressure vessels. The standard gives

both "design by formulae" (DBF) and "design by analysis" (DBA Direct Route) wall thicknesses by the use of the finite element method to calculate the stresses, though in most of the cases the DBF method is generally followed, i.e. appropriate formulae are given in order to find stresses which have to be limited to safe values for non-cyclic loads, that is, full pressure cycles not exceeding 500. The safety factor used for ferritic steels in 13445 is similar to new ASME Division 2, which in case of DBA Direct Route is further reduced but still giving a margin of safety of 2 towards burst for vessels with moderate notch effect. This approach makes it possible to use high-yield-strength materials like thermo-mechanically rolled and quenched and tempered steels for pressure vessels.

12.2.7 Some Important Aspects of ASME and EN Codes

From the point of view of an inspection engineer, who looks after the health of equipment, it is essential to know some basic code-related guidelines like

- Material requirements
- Design aspects
- Heat treatment
- Repair related guidelines/ procedures (only included during last few years as code).

12.3 Material Requirements

12.3.1 Thickness

Thickness is an important factor not only with regards to the mechanical integrity and cost but also heat treatment requirements and some important mechanical properties like fracture toughness. For determination of thickness the three factors considered are design pressure, design temperature and the design or allowable stress (design margin on UTS and YS) employed in a particular code. Here design or allowable stress is the primary stress resulting from internal pressure which in no case must exceed.

The equation used for determining thickness is

$$t = \frac{PD}{2\mathrm{SE} - 1.2P}, \tag{12.3.1}$$

where

t thickness in mm (inches)
P design pressure in MPa (psi)

D diameter in mm (inches)
S allowable stress, MPa (psi)
E joint efficiency.

12.3.2 Allowable/Design Stress

During operation it is important that the code-determined minimum thickness is maintained throughout the working life. The primary criteria for thickness are the design or allowable stress for a particular material selected for fabrication. In selecting allowable stress, distinction is based on two criteria, that is, operation is below or above creep range. While in case of former it is the UTS and YS, and in case of latter it is creep rupture strength which need to be considered. It is important to keep in view that unlike elastic regime, the equipment operating in the creep region has limited life because of irreversible damage introduced during the creep process. Thus, the allowable stress/design margin philosophy employed by each of these codes has a significant impact on a vessel's ultimate cost.

12.3.3 Carbon and Low-Alloy Ferritic Steels

For ferritic steels, each of the codes establishes allowable stresses based on the minimum yield and ultimate tensile strength of a material. Table 12.1 illustrates the specific allowable stress for each code.

Table 12.1 Allowable stress basis for ferritic steels

Design code	Allowable stress
ASME Section VIII Division 1 (Pre 1999)[a] VIII Division 1 (1999)	$\frac{UTS}{4}$ and $\frac{YS_{0.2}}{1.5}$ whichever is less $\frac{UTS}{3.5}$ and $\frac{YS_{0.2}}{1.5}$ whichever is less
ASME Section VIII Division 2 (Pre 2007) VIII Division 2 (2007)[a]	$\frac{UTS}{3}$ and $\frac{YS_{0.2}}{1.5}$ which ever is less $\frac{UTS}{2.4}$ and $\frac{YS_{0.2}}{1.5}$ which ever is less
EN 13445	$\frac{UTS_{20}}{2.4}$ and $\frac{YS_{0.2}}{1.5}$ which ever is less

where
UTS Minimum ultimate tensile stress at design temperature
$YS_{0.2}$ Minimum 0.2% offset yield stress at design temperature
UTS_{20} Minimum ultimate tensile stress at 20 °C (68 °F)
[a]In 1998, Code Cases 2278 and 2290 for ASME Section VIII Division 1 allowed for alternative maximum allowable design stresses based on a factor of 3.5 under certain provisions instead of a factor of 4 used by the Code. These code cases were incorporated into the Code in 1999. The old ASME Div. 2 was replaced with new one in 2007 where the design factor was changed from 3.0 to 2.4, similar to EN 13445

It will be evident from Table 12.1 that though design margin for yield strength in all codes is same at 1.5, there are considerable differences in the values related to ultimate tensile strength, which progressively becomes smaller in the order of 4.0 to 3.5 to 3.0 to 2.4 for old and new ASME Section VIII Division 1 and Division 2. On the other hand EN 13445 has design margin of 2.4 but allows use of 1.875 for high-yield stress special material. Further, an important difference between ASME and EN 13445 is the tensile strength values taken to calculate allowable stress. While the former considers tensile strength at design temperatures, the latter uses only the ultimate tensile strength of the material at 20 °C (68 °F). These differences result in higher allowable stresses in the EN code and lowest in ASME Division 1. But it can also create a situation where allowable stress is based on yield stress in EN Code, whereas in ASME code at the same temperature, it is based on tensile strength [26].

12.3.4 Stainless Steels

In case of stainless steel also design stress is based on UTS and $YS_{0.2}$ but formula used to establish allowable stresses differs considerably in case of ASME and the EN code.

- In ASME (Div. 1 and 2) two cases are considered. In Case 1 two formulae based on UTS and $YS_{0.2}$ are used with factor of safety similar to that in case of ferritic steels given in Table 12.1. However, in Case 2 a new formula is included, that is, $0.9 \times YS_{0.2}$ in place of $\frac{YS_{0.2}}{1.5}$ along with that based on UTS; and lesser of the two is used to calculate thickness.
- As per ASME the higher stresses shown by Case 2 should be used only where slightly higher deformation is acceptable but not in cases of strain sensitive items like flange, etc.
- In EN 13445 the approach is different. The formula used is $\max\{\frac{SY_{1.0T}}{1.5}, \min\ \frac{SY_{1.0T}}{1.5}, \frac{UTS}{3}\}$ which leads to higher allowable stress. The main reason for this is that yield strength of stainless steels (EN 10028-7:2000) at 1.0% offset is 30 to 40% higher than that at 0.2% offset. Additionally, EN 13445 allowable stresses are a function of the greater of two values against lesser of two values in case of ASME.

Figures 12.7 and 12.8 compare the allowable stress as per ASME and EN code for carbon and stainless steel which confirms that for similar conditions equipment fabricated using EN code will have lower thickness compared to ASME Section VIII Div. 1 and 2 (Old) [26]. This advantage is temperature dependent and greater advantage is observed in case of alloy steels. In case of ASME Section VIII Div 2 2007 (New) the thickness will be similar to EN Code.

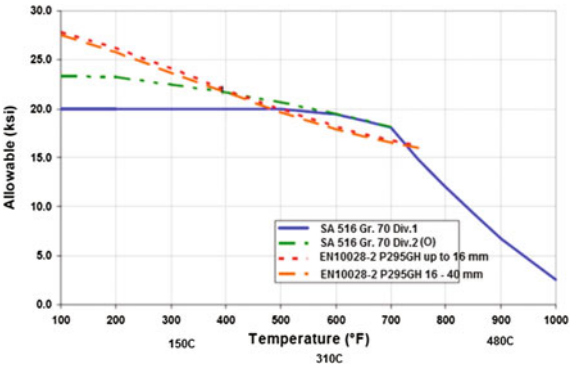


Fig. 12.7 Allowable stress versus temperature for carbon steel [26]

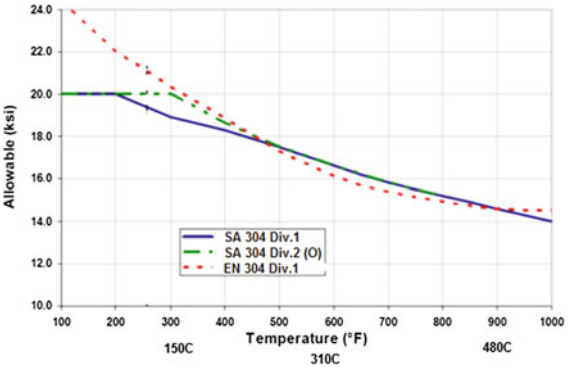


Fig. 12.8 Allowable stress versus temperature for stainless steel [26]

12.3.5 Cost and Preferences Related to ASME and EN Codes

The cost advantage of equipment fabricated using different codes and also the preferences were determined on the basis of enquiries to different owner/users, material suppliers and fabricators sent all over the world. The results obtained for different types and sizes of equipment from eight different countries, including three EC members were compared and found to be more or less similar (Fig. 12.9), except for 1.25Cr–0.5Mo reactor (where ASME Div 1 shows highest cost) in spite of thickness advantage. The main reasons for this were different levels of material specification and inspection requirements, stress and finite element analysis involved, fatigue analysis, etc. As regards preferences of the survey respondents, without exception, the respondents selected the ASME Section VIII, code as their first preference (Fig. 12.10), based on the frequency of use, overall economic advantages and familiarity with the ASME codes internationally [26]. Low preference of EN 13445 is probably because of the code being enacted only a few years

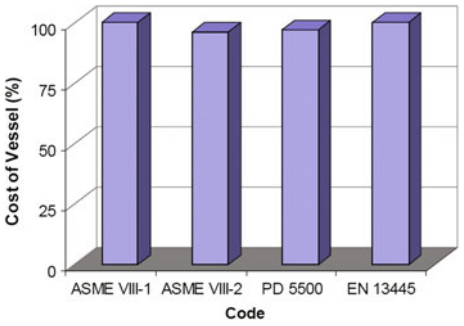


Fig. 12.9 Trayed column carbon steel with SS clading [26]

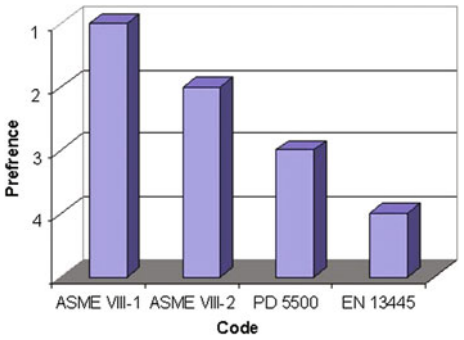


Fig. 12.10 Preference ranking of different codes [26]

back and adopted comparatively by few, and greater control required by fabricators during different stages of production. However, with Pressure Equipment Directive (PED) throughout European Union, more companies would follow this code in future.

12.4 Heat Treatment Requirements

12.4.1 Post-Weld Heat Treatment

In the construction of welded pressure vessels or piping of carbon and alloy steels like C–0.5Mo, 1.25Cr–0.5Mo, 2.25Cr–1Mo, 5Cr–0.5Mo and 9Cr–1Mo, PWHT is to be carried out under certain conditions. As discussed earlier the major consideration in conducting PWHT is to reduce welding stresses and increase the resistance to brittle fracture. In BS 7910 [27] a reduction in yield stress of the weld metal to the extent of 15 and 30% is assumed, respectively, for stresses transverse and parallel to the weld. In addition, PWHT softens/tempers hard structure (both weld and HAZ) susceptible to cracking, increases notch toughness, helps in preventing service-related cracking and also increases fatigue resistance. Universally all

pressure vessel codes specify PWHT beyond certain thickness which varies from 32 mm (1.25″) to 40 mm (1.57″), (1.5″ in case of ASME), for carbon steel and for alloy steels. The minimum thickness for PWHT is due to the greater rate of cooling with increase in thickness which not only increases the residual stress but also the chances of formation of hard structures like martensite and bainite, depending on steel composition. However, the reason why a particular thickness range has been selected is not clear. It is of interest that experiments carried out during mid-1970s showed that carbon-manganese steels develop residual stresses above the yield stress at a thickness of 35 mm thus confirming the code-specified minimum thickness [28].

For ferritic alloy steels, the thickness beyond which PWHT is mandatory which vary depending on P number of material as given in Table UCS 56 of ASME Section VIII Division 1. The requirement specified against composition of alloys is given as below:

- C–0.5Mo 1.25Cr–0.5Mo (mandatory for P3 Gr 1 & 2 above 13 mm (5/8″) and Gr 3 for all thicknesses).
- 2.25 Cr–0.5Mo (Mandatory up to and including $\geq$ 13 mm (5/8″) except where exempted up to 13 mm (5/8″) under certain conditions for pipe if diameter is <max. 100 mm (4″) and C $\leq$ 0.15%C).
- 5Cr–0.5Mo/9Cr–1Mo (mandatory for all thicknesses except where exempted up to 5/8″ under certain conditions for pipe if diameter is <max. 100 m (4″) and Cr and C content are max. 3 and 0.15%, respectively).
  Note: Consult UCS 56 Tables for detail.

To avoid PWHT strict conditions, as stated in codes, have to be met before post-weld heat treatment can be waived. It is clear therefore, that with alloy steels, the removal of residual stress is not the only consideration for the application of post-weld heat treatment.

Compared to pressure vessels, lower thicknesses for PWHT in case of piping take into account the acceptable hardenability. In case of pressure vessels, resulting hardenability of P1 materials after welding is acceptable up to $\leq$ 38 mm and in process piping $\leq$ 20 mm so that the resulting residual stress and hardness can come within the acceptable range. There is also the fact that piping is subjected to different types of stresses, other than the Hoop stress, because these are laid over long lengths with different isometric, which are quite often restrained and not fully aligned.

12.4.1.1 Post-Weld Heat Treatment Requirement in Some Other Industries

If we look at the PWHT done on welds other than for pressurized equipment like boilers and process-related equipment, the requirement of PWHT is not given the same importance in many industries. For example in offshore industry, PWHT

earlier was common but the same is not the case today. The DNV and the HSE Guidance Notes [30] requires PWHT for highly stressed nodal welds greater than 40 mm thick and other welds greater than 50 mm thick unless fracture mechanics calculations show that the joint possesses adequate toughness in the as-welded condition. The latest DNV Standard [31] specifies that PWHT will be applied in special areas where thickness exceeds 50 mm as per details in DNV-OS-C401 [32]. The standard further states that PWHT may be omitted if by fitness-of purpose analysis, satisfactory performance in as-welded condition is established against fracture and fatigue crack. This change in approach has been due to the development of various programs to establish fitness-for-service [27, 33, 34] based on fracture mechanics. PWHT is also not included in structural welding standard and for heavy machineries in mining industry [28]. Recent development in the application of ultrasonic peening has shown that by its application CTOD values, a measure of brittle fracture resistance, of weld and HAZ can be improved due to the reduction of tensile residual stresses and the introduction of compressive stresses. It is further claimed that by applying ultrasonic pinning after every weld pass thick welds can be relieved of stress [35].

12.4.1.2 Post-Weld Heat Treatment Temperature

Pressure vessels constructed as per any code, which was originally post-weld heat treated, generally require PWHT for any repair done on it during service. It is therefore necessary to examine the steps necessary to carry out the PWHT, both during fabrication, construction and service repairs. For PWHT heating and cooling rates along with normal holding/soak temperature and minimum time are specified for carbon and alloy steels. This aspect is covered in Table UCS 56 of ASME Section VIII Div. 1. Table 12.2 compares the recommended temperature for carbon steel and some commonly used Cr–Mo steels in ASME and some other codes [36].

From Table 12.2 it will be apparent that though ASME VIII specifies a minimum holding temperature and not a temperature range as in BS and EN specifications, it permits PWHT at temperatures up to 93 °C (200 °F) below specified minimum,

Table 12.2 PWHT temperatures in different pressure vessel specifications

Steel grade	BS EN 13445	ASME VIII	BS PD 5500
	Temp range °C	Normal holding temp	Temp range °C
C steel	550–600	593	580–620
C–0.5Mo	550–620	593	630–670
1Cr–0.5Mo	630–680	593	630–700
2.25Cr–1Mo	670–720	677	630–750
5Cr–0.5Mo	700–750	677	710–750
3.5Ni	530–580	593	580–620

provided holding time is correspondingly increased as per the Table UCS 56.1. The ASME code-specified temperature and time is primarily related to reduction of stresses and tendency to brittle facture. However, there are situations where service conditions can result in hydrogen-related failure which is controlled by tensile stress, hydrogen pick up from environment and a sensitive microstructure (related to higher hardness). In such cases the additional objective of PWHT is to temper the susceptible microstructure (by limiting hardness below specified minimum). Similarly where environmental-related stress corrosion can occur, the residual stress is to be reduced below the minimum applicable for the particular alloy environment system. This often requires the PWHT temperature to be raised above the minimum specified value. For quenched and tempered or normalized and tempered materials, however, the PWHT holding temperature shall be at least 15 °C (25 °F) below the original tempering temperature of the base metal except in cases where the fabricator demonstrates that required mechanical properties can be achieved only on use of higher PWHT temperature and holding time [37].

12.4.1.3 Post-Weld Heat Treatment Holding Time

ASME Section VIII US 56, Table gives holding time which increases in stages with nominal thickness range of ≤ 50 mm ($\leq 2''$), > 50 to 125 mm (>2″–5″) and >125 mm (>5″). The increase in time with thickness is applicable in EN13445 but the total time at different thicknesses is less than that of ASME VIII as shown in Figs. 12.11 and 12.12 for carbon steel and 2.25Cr–1Mo [26]. Thus shorter times of PWHT are an advantage in case of En Code, especially for equipment with higher thicknesses.

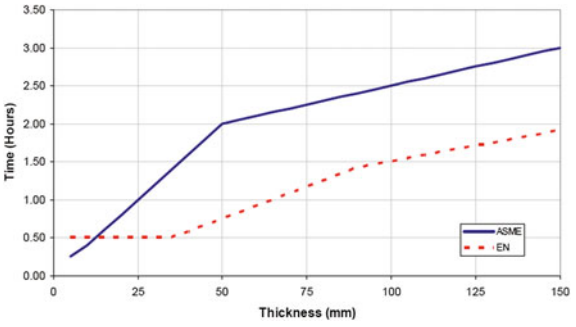


Fig. 12.11 Minimum PWHT times for carbon steel [26]

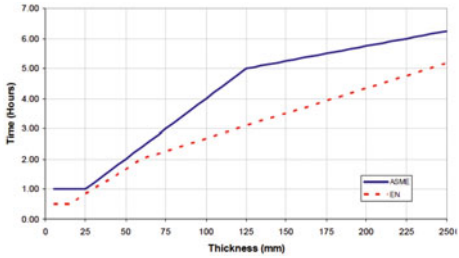


Fig. 12.12 Minimum PWHT times for 2 1/4Cr–1Mo [26]

12.4.1.4 Procedure for Post-Weld Heat Treatment

Shop Welding

The pressure vessel codes give details of procedure to be used during fabrication. ASME Section VIII Div.1, Part UW 40 discusses various methods by which PWHT can be conducted in accordance with the requirements given in the applicable Part in Subsection C. The methods commonly used by fabricators are as follows:

1. Carry out post-weld heat treatment by putting the whole vessel in a furnace.
2. Where the length of vessel is more than furnace length, the code permits completing the same in more than one heat. In such a case minimum overlap of 1.5 m (5 ft) is to be ensured. In case of piping the overlap shall be at least 300 mm (1 ft) [38]. In such a case the temperature gradient between the portion inside and outside the furnace is required to be controlled by insulating blankets as per the requirements of applicable codes.
3. In case where neither alternate 1 or 2 above is feasible, the PWHT can be carried out using multiple steps, such as heating of shell sections to PWHT temperature in more than one pieces and then joining these to make the completed vessel. This would then be followed by local PWHT of circumferential joints.
4. The procedure given above is also used often by the fabricators to carry the heat-treated equipment in parts to the site and assemble the same by welding (not only the circumferential welds) followed by local PWHT of site welds. Such situations arise when the diameter, length and weight are too high for safe transportation from fabrication shop or harbour in case of imported vessels to the plant site.

Field Welding

Field welding of equipment has to take into consideration limitations in the availability of facilities at site. The alternatives considered are as follows:

1. Site fabrication of new vessel brought at site in knocked out condition.
2. Site erection of spheres.

3. Site fabrication of new equipment or component to be replaced as a part of maintenance by local heating.
4. Maintenance repair of equipment in situ.
5. Site construction of process and utility piping.

All these activities involve welding and many of these are to be subjected to PWHT as per the code or service requirements for which the most commonly used procedure is the local PWHT which has been discussed in some detail.

12.4.1.5 Local Post-Weld Heat Treatment

In any local PWHT, the major consideration/requirements are as follows:

- If the original vessel is PWHTed then all repair weld is also to be subjected to the same treatment, with some well-defined exceptions.
- PWHT of site welds done partly or fully should cover 360 °C of the circumference, for which circumferential heating band of suitable width is to be provided.
- Industry practice is to generally follow code-recommended procedures. ASME originally termed the weld, HAZ and limited volume of metal around weld subjected to PWHT temperatures as *soak band* (SB), which in turn was defined to consist of the weld + HAZ + a portion of base metal adjacent to both side of the weld. The minimum width of this volume was specified as the widest width of weld + 1t or 2 in., whichever is less, on each side or end of the weld [39]. These local heat treatments have many times failed due to environmental-related damage like stress corrosion or hydrogen-related cracking because of a narrow heating band width which did not reduce the hardness or residual stress to an acceptable value. Number of instances of failure has been cited by Bruce Levan [40] and others [41, 42]. The present author has also investigated number of cases of cracking of both original and repaired local post-weld heat-treated welds in CO_2 absorber and regenerators of the original Giammarco-Vetrocoke (GV) process with arsenic oxide as activator and inhibitor. Considering the in adequacy of the specified PWHT procedure in preventing environment-related failures, in the recent years ASME has qualified the above soak band by adding the sentence "For additional detailed recommendations regarding implementation and performance of these procedures, refer to Welding Research Council (WRC) Bulletin 452, June 2000, "Recommended Practices for Local Heating of Welds in Pressure Vessels [39]."

Improvements in Local PWHT

The ineffectiveness of local heating has been recognized and considerable work has been done to find out the reasons and develop better procedure to minimize chances

of such failures. The historical development in this case has been discussed to explain why desired level of stress is not relieved using ASME recommended soak band, and the various recommendations/ practices normally used. To understand the problem, following points are to be considered:

- PWHT leads to both circumferential and lateral expansion and contraction when heated and cooled, though within the elastic limit. This can be calculated for different cases but broadly expansion of carbon and low-alloy steels at typical PWHT temperature of 650 °C (1200 °F) may be estimated as 8 mm per metre (0.1" per foot) [43].
- There is temperature gradient laterally and across the thickness resulting in thermal stresses.
- The width of the heated band and axial temperature distribution also control the bending moments and shear stresses which can cause distortion and induce residual stresses on completion of PWHT.
- In cases where the heat is applied from OD, which is more common, various studies have shown that unless temperature beyond the *soak band* is also extended, it is not possible to attain the minimum PWHT temperature throughout the weld thickness. Study by Bloch et al. [44] has shown that by proper sizing of the band on an 0.46 m (18″) diameter 25-mm (1″)-thick pipe at temperatures of ~621 °C (1150 °F), a temperature difference of 25 °C (45 °F) could occur between the centre of the weld at 12 and 6 O'clock positions when there is no insulation on inner side. This difference can be reduced to 13 °C (24 °F). This extension of length beyond *soak band* is termed as *heat band* (HB).
- With effect of multiple stresses acting on and around the weld, a considerable part of welding stresses removed during heating cycle, reappears on cooling. To avoid this, it is also necessary to provide proper temperature gradient beyond the heated band. Objective of the gradient control band is to control axial temperature gradient. Though no code-specified recommendation existed, industry practice in USA was to use gradient control band as two to three times the heated band against $5\sqrt{Rt}$ cantered on weld of international codes [45]. As per McEnerney [46] such a band of $2\sqrt{Rt}$ on either side of heated band can also serve the purpose. This portion is known as *gradient control band* (GCB).
- The rate of change in *axial temperature gradient* plays an important role in inducing stress during PWHT. The stipulation of international code that the axial temperature gradient should be controlled such that the temperature at the edge of heated band will not be less than ½ of the peak soak band temperature is now accepted.

Thus to ensure proper PWHT it is necessary to provide three bands taking the weld at centre. These, as stated earlier, are termed as *soak band, heat band and gradient control band*, schematically shown in Fig. 12.13]. Based on work by Rose [47] and Burdekin [48] many of the international pressure vessel and piping codes (not ASME) stipulated a heated band size of $5\sqrt{Rt}$, where R is inside radius and t = thickness, cantered on the weld along with limiting the axial temperature gradient.

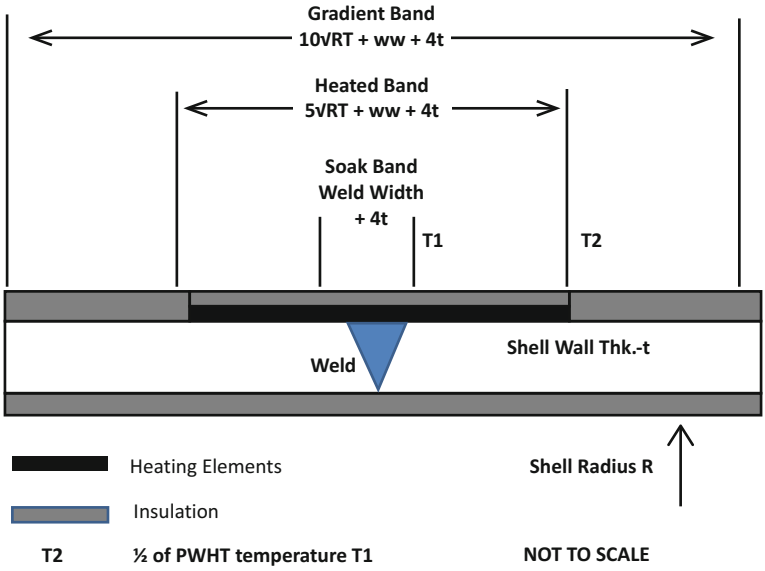


Fig. 12.13 Local PWHT heating band as per WRC Bulletin 452

Table 12.3 Summary of local PWHT methodology as given in different codes

Soak Band	* ASME Section VIII, Div.1—twice the thickness of the weld or 50.8 mm either side of the weld, whichever is the lesser. * BS EN 13445 does not specify a soak band
Heated Band	* ASME ASME Section VIII, Div.1—No specific requirement. Directs to consult Welding Research Council (WRC) Bulletin 452, June 2000 * BS EN 13445—Heated bandwidth of $5\sqrt{Rt}$ centred on the weld and where R = inside radius and t = thickness.
Gradient Control Band	* ASME Code—Does not specify * BS EN 13445—Recommends $10\sqrt{Re}$

The heated band size of $5\sqrt{Rt}$ was considered to be too conservative and changing the band size to $4\sqrt{Rt}$ was suggested [49]. J.W. McEnerney while discussing the various aspects of local PWHT agreed that the heated band size of $4\sqrt{Rt}$ would be adequate [44].

Based on various studies a new guideline was issued by Welding Research Council [50, 51], defining the conditions for local post welding. Figure 12.13 illustrates schematically the heating and insulating requirements included in WRC Bulletin 452. This procedure has been included in the under finalization API 934G for PWHT of Coker drum [52].

Though the basic principle is the same there are some small variations in the length of bands in different codes and practices. The existing code-recommended practices in ASME and EN are summarized in Table 12.3.

Recommended practices other than those given in Table 12.3 are as follows:

1. WRC 452: Refer Fig. 12.13 for details.
2. API 934G, 2013: As per WRC 452.
3. API 945 1997: Reference Table 9.15, Chap. 9.
4. API 582: Recommends procedure using formula with $5\sqrt{Rt}$ (similar to WRC 452).
5. ASME B 31.3-2006: A circumferential band of the run pipe shall be heated until the specified temperature range exists over the entire pipe section(s), including branch or bent, gradually diminishing beyond a band which includes the weldment and at least 25 mm (1 in.) beyond the ends thereof.
6. PCC-2-2011 includes local PWHT as per WRC 452.

Procedure for Local PWHT

Local PWHT in field can be carried out using various sources of heating, some of the common ones being,

- Electric resistance (high or low voltage) as contact pads or radiation elements.
  - Electric resistance flexible ceramic heating pads (low voltage) can be wrapped outside the vessel directly in contact with vessel or piping and then covered with insulation outside and also inside where approachable. Series of circumferential bands placed raise the welded area to the full heat treatment soak temperature and control the heated and gradient bands as per the requirement [53]. Alternately electric resistance heating elements (high voltage) can be placed inside but away from the internal wall. For this purpose a bulkhead (partition) is provided on which electric elements are mounted. In other words a part of the vessel to be PWHTed is converted into a furnace. In this case the insulation is placed on external surface.
- Induction coil (in case of piping)
  - Induction heating can be used for both pre- and PWHT of pipework and pipeline weldments. It is however used more for preheating than PWHT because of high rate of heating that can be achieved by it. The fact that the temperature can be more easily and precisely controlled by induction heating makes it attractive for PWHT also.
- Combustion burner (high velocity gas, luminescent flame, infrared burner)
  - The use of combustion burner is quite often practiced for PWHT of field erected large size vessels like Horton sphere or vessels and columns for in situ local PWHT during repair or modification [54].

It is essential that during PWHT the temperature is maintained within stipulated limits in all three bands as under exposure may result in the stress and HAZ hardness not being reduced below the desired extent. In many cases this can lead to

cracking during service. This would require suitably spaced placement of thermocouples throughout the length and circumference; placing insulation of suitable thickness on OD and also ID, wherever the same can be approached; regular calibration of all thermocouples and recorder. There are number of instances of failure of field-welded joints and repair welds because of deficiencies in the control of PWHT parameters.

12.5 Repair, Alteration and Rerating

12.5.1 General Background

As discussed earlier to ensure the health and continuous running of a plant it is necessary to periodically undertake inspection of any equipment or piping. Based on the data generated, necessary steps are needed to be taken to restore the reliability and integrity of equipment. However, there was no code for undertaking repair activities. The Pressure Vessel Codes deal with design and fabrication of new equipment but is silent about steps to be taken to ensure serviceability during its lifetime. Considering these limitations of codes various guidelines were prepared in USA by the National Board Inspection and API which are universally used.

- The oldest of these is the *National Board Inspection Code* (NBIC) which was first published in 1945 as a guide for chief inspectors for the installation, inspection and repair and/or alteration of boilers, pressure vessels, and pressure relief devices [55]. However, in the process industry API recommended practice is more commonly used.
- API/ASME *Code for Unfired Pressure Vessels* published in 1934 contained a section (Sect. 1) which dealt with recommended practices for vessel inspection and repair. This was later included in modified form as non-mandatory requirement in ASME Section VIII issues of 1950, 1952 and 1956 but later discontinued. In 1958 API published API 510 which today is more comprehensive and applicable for process industry in general [56].

12.5.2 Repair Procedure

Once any damage like general or localized loss in thickness, erosion, cracking, pitting, etc. is identified after inspection and its analysis indicate the necessity for repair, then for each situation different repair procedures are to be adopted. Depending on circumstances and production requirement the repair may be permanent or temporary for a limited period till it is possible to take planned shutdown. Under certain conditions it may also be necessary to (i) rerate (change the operating parameters) the equipment for less severe design conditions, without taking any

major repair, or (ii) rerate for new design conditions because of changes in operating parameters. There can be other situations where alterations like upgradation of the MOC and changes in operating conditions are required because of changes in characteristics of the feed being processed. In some cases these changes may be too large and have to be undertaken as a part of revamp and not repair. Some common examples are

- Use of high-sulphur crude in unit designed for processing low-sulphur crude.
- Processing of high-TAN crude in unit designed for processing crude containing sulphur.
- Sweet gas turning sour after some years of operation of the oil and gas field.
- Replacing process heaters of low thermal efficiency with ones having high efficiency.
- API 510 and API 570 deal with repair which have been identified as temporary or permanent repairs. The standards, however, do not give details but broad outline and limitations of the same.

As regards implementation, the size and location of a pressure vessel in an operating plant make repair or alteration difficult because of obstruction in access by adjacent equipment, unfavourable conditions for maintaining all necessary welding parameters, difficulties in carrying out local post-weld heat treatment, etc. Thus jobs done at site are considerably more difficult compared to fabrication of the vessel in a shop. As such it may not be possible to meet all the requirements of the original pressure vessel code. However, repairs done should as far as possible restore its original/ intended operating conditions, safe operation and prolong trouble free service life. In this process attempts are made to meet original code requirement which is not all the time possible. In lieu of it attempts are made to follow accepted alternative procedures to have equivalent integrity and reliability although they may deviate from a literal interpretation of Code criteria.

- Considering the absence of any code to deal with various damages during service, an Ad Hoc Task Group on Post Construction was formed by ASME in 1993 on whose recommendation Post Construction Committee (PCC) was established in 1995. The objective of the Committee was to develop separate, product specific, codes and standards addressing issues encountered after initial construction for equipment and piping covered by Pressure Technology Codes and Standards [57]. Till date the following codes have been published:

1. PCC–1–2000 (Updated in 2010): Guidelines for Pressure Boundary Bolted Joint Assembly
2. PCC–2–2006 (Updated in 2011): Repair of Pressure Equipment and Piping
3. PCC–3–2007 (Reaffirmed in 2011): Inspection Planning Using Risk-Based Methods

Present editions of API 510 and API 570 while not giving details also suggest to consult PCC–2 before finalization of any repair activities.

12.5.2.1 Salient Features of ASME PCC–2

PCC-2 has the advantage that it takes into account some basic design considerations along with various issues connected with the implementation of repair. PCC-2, however, cannot be considered as administrative code but more as "RAGAGEP (recognized and generally accepted good engineering practice) Standard [58]. Scope of PCC-2 mentions "These repair methods include relevant design, fabrication, examination, and testing practices and may be temporary or permanent, depending on the circumstances" [43]. This standard therefore does not classify repair methods as permanent or temporary as in case of API 510, API 570 and NBIC, though many of those included are considered to be permanent.

Outline of a Few Repair Techniques

A few of the repair techniques dealt in PCC-2 have been illustrated taking the case of a vessel which has suffered heavy internal wall thinning in a localized area because of erosion crossing. Some important aspects of three types of repairs commonly experienced are given.

Butt-Welded Full Penetration Insert Plates in Pressure Components (Article 2.1, PCC-2)
Covered under this has been recommended as best process if criteria below are followed:

- Conformation of replacement material, welding consumables, to original construction code.
- Getting the corners of plate rounded with radius which increases with plate thickness. This is unlike API 510 which mentions a 25 mm (1″) minimum radius [59].
- In case of more than one patch, the code-specified minimum distance between plates shall be maintained.
- Code or service mandated PWHT will be carried out.
- After repair quality of weld shall be established by U/S/radiography. Prior to hydrotest leak test will be performed, if required.

The repair method discussed above may also be used for cladded vessels, pipe and cylindrical, spherical and conical shells. Flush inserts in pipe or tube are however round or oblong

External Weld Overlay to Repair Internal Thinning (Article 2.2, PCC-2)
In case of internal thinning permits repair by weld overlay on the external surface as a permanent repair provided the recommended overlay profile is followed. The requirements to be fulfilled consist of

- Overlayer matching or exceeding properties of original material.
- The size of overlay shall cover some minimum distance beyond the periphery of affected area as given in the code. Formula for determining the minimum distance has been given.
- Overlay is to conform to other requirements like edge profile, minimum distance between more than one overlay, fulfilling engineering design criteria and burst test, etc.

Internal Weld Build-Up to Repair Internal Thinning (Article 2.11, PCC-2)

- Thickness of internally affected portion can also be restored by weld build-up of both vessel and piping which can be entered for executing the job. The procedure to be followed is included under Internal Weld Build-up, Weld Overlay, and Clad Restoration of ASME PCC-2, Article 2-11.

Fillet Welded Patches (Article 2.12, PCC-2)

Fillet welded patches are considered to be temporary repair in API 510, which requires to be replaced as soon as possible. It has been reported that this sort of repair method has not been authorized in Japan because the acceptance criteria for this repair method, such as "dimension of fillet weld throat", "wall thickness of patch plate" and "overlap length between patch and base metal", are not clearly stated [60]. PCC-2 deals with this mode of repair in greater detail taking into account the transverse and longitudinal stresses to which the patch is subjected. Some of the salient features of the procedure are as follows:

- The size of the patch plate should be such as to completely cover the damaged area + minimum 25 mm (1″) of surrounding sound-based metal. In case the extent of further growth of damage area during lifetime is known then the same should also be included within the patch plate.
- The design approach for this repair method is based on design calculations consisting of (i) calculating circumferential and longitudinal force acting on repaired patch for internal pressure and (ii) sizing of fillet weld so that allowable load on the weld exceeds the longitudinal and circumferential loads. Relevant formulas for these are included in the code.
- The maximum design fillet weld size shall not exceed the thickness of the thinner material being joined nor 40 mm (1.5″).
- Parts to be fillet welded patch shall be formed so that it tightly fits to the surface as far as possible. In no case there shall be a gap of more than 5 mm (3/16″) between the patch plate and the equipment concerned.

12.6 Specific Inspection Procedures

A general idea of the inspection techniques has been given in the beginning of this chapter. Inspection procedures especially applicable for some of the critical equipment in the petrochemical industry are described next.

12.6.1 Inspection of Equipment Subjected to Hydrogen Damage

12.6.1.1 Equipment Operating in Sour Service

In number of instances, equipments in oil and gas processing and refineries are exposed to sour condition where hydrogen-related damages like SSCC, HIC (SWC) and SOHIC are likely to take place. Being surface defect, the presence of SSCC is detected using WFMPI technique. But for assessing the spread of surface defect inside and for the identification of midwall defects like HIC and SOHIC, various advanced ultrasonic techniques are available. As stated earlier techniques like manual UT, TOFD, Phased Array Ultrasonics (PAUT) and Automated Combined UT (Triplex) techniques are available [60]. If detailed information on the nature and extent of defect is desired use of more than one technique is advisable.

12.6.1.2 Equipment Operating at High-Temperature High-Pressure Service (HTHA)

For HTHA, the important criteria to be considered before planning inspection are as follows:

(i) Whether original material used is well within the limits specified by Nelson curve?
(ii) Whether specified material is C–0.5 Mo?
(iii) Whether the design is based on hot or coldwall?
(iv) Has there been any excursions in operating temperature and pressure or rise in metal skin temperature beyond specified limit due to failure of refractory coldwall equipment and finally?
(v) If there has been any earlier history of failures due to hydrogen attack?
(vi) Layered or solid-wall vessel?

Based on these considerations, the inspection schedule has to be prioritized and planned. The techniques which can be used are as follows:

Attenuation Measurement

Attenuation technique was developed and described by Standard Oil Company (Indiana) but the experience has, however, been mixed because attenuation is affected by number of factors other than the presence of fissures and unless attenuation characteristic of original material is known, the reliability of the result is in doubt.

Advanced Back-Scattered Ultrasonic Testing (ABUT)

Developed by Shell in the early 1990s presently ABUT is considered to be a better option. Due to attenuation of ultrasound from grain boundary fissures change in the shear wave velocity occured. On the basis of ratio of shear wave to longitudinal wave velocity and back-scattered pattern obtained from attenuation measurement the presence and depth of attack can be determined. Figure 12.14 shows a result of case study carried out on a pipe which suffered HTHA [62]. It may be mentioned that though API RP 579 [33] and NACE RP0296-96 [63] give good direction for the assessment of HTHA but expertise and experience of inspector is critical to assess correctly the damaged condition of materials and determine when replacement becomes necessary.

Time-of-Flight Diffraction (TOFD)

With the use of TOFD it is also possible to inspect damage due to HTHA. It can be used for the detection of both macro- and micro-cracks though macro-cracks can be more easily identified with TOFD. Identification of micro-cracks, however, can be difficult as it cannot discriminate from other types of small-size defects.

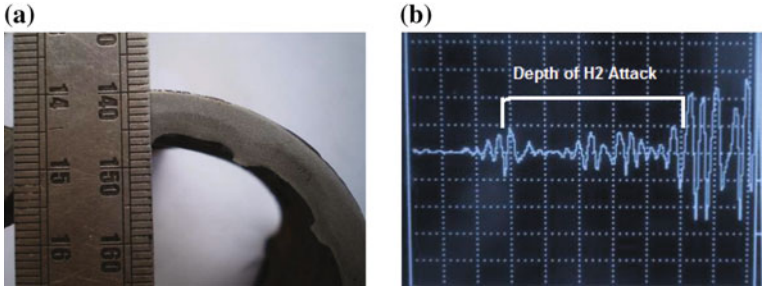


Fig. 12.14 **a** HTHA attack of pipe [61]. **b** Measurement of depth of HTHA (4.5 mm) using back-scattered ultrasonic technique [61]

Velocity Ratio Measurement

The percentage of attack can also be measured from the longitudinal and transverse sound velocity affected by HTHA. By this method it is possible to differentiate between small inclusions and HTHA damage.

All the last three techniques are covered under API RP 941 requirements [64] which also describe various other inspection methods based on ultrasonics.

Surface Replica Test

HTHA attack starts with the formation of methane bubbles at grain boundaries, density of which increases with time. Finally the bubbles link together and form fissures. There is however an incubation time before the noticeable attack starts, the period of which decreases with increase in temperature and partial pressure. From replica therefore initiation of attack can be ascertained. The curves showing the time for incipient attack of carbon and C–0.5Mo alloys at different temperatures and hydrogen partial pressure can be used to find out if hydrogen attack has started [64]. Figure 12.15 shows surface replica of a portion of C–0.5Mo transfer line where insulating refractory brick got dislodged. Because of constraint in taking an immediate shutdown the plant was continued to be run for 6 months with external cooling with the help of deluge of water. The HTHA was initiated during this period.

12.6.2 Inspection of Tubular Items

The reformed gas (RG) boiler of hydrogen plant and some of the high-pressure tubular equipment in urea plant are critical and required to be regularly inspected. In urea plant tubular equipment, depending on their decreasing criticality, can be stated as urea stripper, carbamate condenser and MP decomposer. The tubes are made of non-magnetic titanium, and austenitic stainless steels like 25Cr–22Ni–2Mo

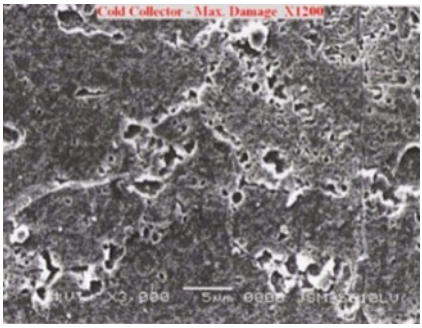


Fig. 12.15 Initiation of H2 attack in RG transfer line of C-0.5Mo

(2RE-69) and 316L UG, respectively. Being non-magnetic eddy current testing (ECT) is done on this equipment for detection and degree of metal discontinuities such as corrosion, erosion, tube-to-tube wear, pitting, fretting, cracks, etc. As regards the RG boiler of hydrogen plant, the tubes of which are of low-alloy steel, RFET based on the principles of Remote Field Electromagnetic Technique is commonly used. The inspections are conducted from the tube ID (inner diameter). However, due to the nature of the remote field signals it is not possible to distinguish between external and internal defects but tube loss can be obtained with accuracy of 0.1 mm. Cracks, pitting and through holes can also be identified. RFET gives fast result as the puling speed of REFT is $\sim$0.2 m/s against 5 cm/s for IRIS which is based on rotating ultrasonic probe.

12.6.2.1 Inspection of Hydrogen Reformer Tubes

Dimensional Changes

This is the most popular method which involved measuring periodically the change in the diameter of the reformer tubes. As a rule of thumb the industrial practice is to consider the increase in diameter prior to cracking varies in the region of 2–3% for HK40 and 5–7% for HP Mod alloys [65] because of latter's higher creep ductility. These measurements are made either with no/no-go gauge (for rough indication) with the calliper set at a predetermined figure or by strapping method. Because of larger dimension of the circumference, the changes by strapping can be measured with greater accuracy.

Surface Replica

Normally along with dimensional measurements, changes in metallurgical characteristics of the tube material are monitored periodically by taking replica at the OD. While dimensional changes do reflect the creep-induced strain, replica primarily gives an idea of temperature to which the tube has been exposed, especially when operational upsets lead to the tube running hot. Figure 12.16 shows how the morphology of uniform carbide network changes with increasing temperature

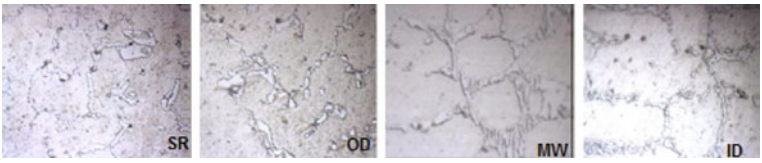


Fig. 12.16 Variations in microstructure from OD to ID along with surface replica of reformer tube SR (Surface Replica) → OD (Outer Diameter) → MW (Mid Wall) → ID (Internal Diameter) [66, 67]

across the tube wall from ID to OD. The replica microstructure (SR) showed complete break up of carbide network. Optical microscopy across the thickness showed decreasing degree of spheroidization from OD towards ID, that is, from higher to lower temperature. The reformer tube had been in service for over 6 years and ran hot (at 980, ~20 °C over the normal operating temperature) for a few months due to catalyst degradation [66, 67]. It is quite often believed by operators that the replica gives an idea about the extent of creep damage which is not correct. The creep damage (formation of voids and fissures) in reformer tubes starts at midwall, proceeds inward up to ID and then back towards OD at which stage failure is expected. Thus any creep-related damage would be visible in replica only during its final stage before rupture.

Ferromagnetism of Tube

Because of reducing nature of reformed gas, carburization of austenitic reformer tubes on ID is sometimes experienced which have been related to premature tube failures. It is not uncommon for some plants to include periodical measurement of magnetic permeability of tubes as a measure of in service damage. However, one has to be cautious as mostly the magnetism is detected when the tube runs hot. Due to higher oxidation, chromium content of alloy immediately underneath the scale decreases making the same magnetic. Thus such instances of magnetisms are not connected with process side carburization or creep but a surface phenomenon due to excessive oxidation. Whenever such observation is made the said surface should be lightly ground and tested. If the magnetism disappears then it indicates it to be a case overheating. This method is however used for determining the extent of carburisation of ethylene cracker tubes which are non-magnetic and develop magnetism because of carburisation.

Eddy Current Examination

This method is repeatable and very accurate but historically its use has been limited. Normally when the tubes are manufactured, each section is eddy current tested before they are assembled. The reason why it has not been used as extensively is that the catalyst is to be removed for inserting the probe prior to inspection. Thus the technique can be used only during the period when the spent catalyst is dumped for replacement. The present-day catalyst has more than 6 years life thus increasing the period of inspection frequency. More recently an eddy current device that can crawl up the outside of the reformer tubes in much the same way as the ultrasonic devices has been developed.

Ultrasonic Attenuation

It measures changes in attenuation due to creep cavities, fissures and crack. The device moves on crawler along the tube length. The changes are calibrated against known degree of damage. Because of its simplicity it is being used in spite of limitation and possible inconsistent results of this technique as discussed earlier. One advantage of this method is to use it as a tool for periodic monitoring during shutdown.

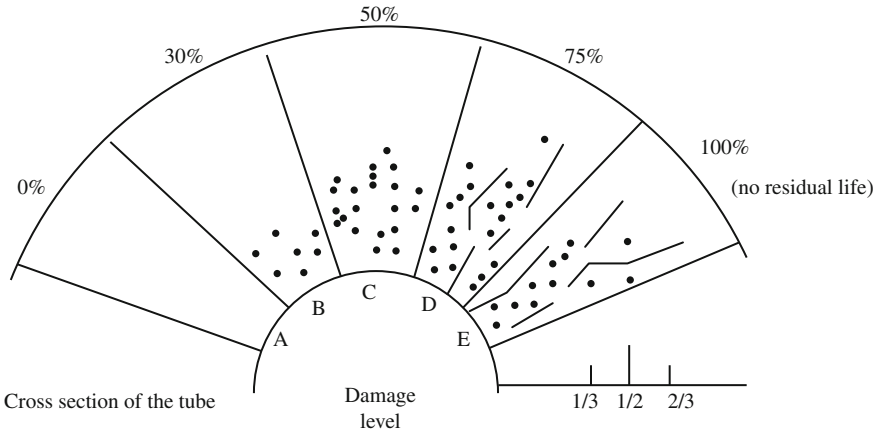
H-Scan

An instrument recently developed uses combination of five non-destructive testing techniques, i.e. ultrasonic attenuation, TOFD, eddy current, change in OD and wall thickness. This technique predicts tube worthiness at five levels of soundness. Levels 1 and 2 are acceptable for use. Levels 3 through 5 are analysed before taking decision about retiring of tube. Being a costly technique its use is considered either after considerable period of run or under emergency conditions, when operational upsets are suspected to cause considerable damage of tubes.

Laser Profilometry

It is claimed to have been accepted as a viable inspection method for early detection and characterization of creep by the process industry in New Zealand, South America, Canada and the USA. The device measures the ID (measure of creep strain) along the length of tube at high speed with great accuracy. The instrument consists of a diode laser light source mapping probe (compatible with Laser-Optic Tube Inspection System-LOTIS) which is pulled up at speeds of up to 76 mm per second. From the data generated it is possible to see the entire inner surface in a straight-forward format to locate and quantify damage. This test can however be performed only after removal of catalyst and therefore its use is planned along with schedule for catalyst change.

All test methods grade the degree of creep damage and do not give absolute values, the reason being considerable scatter observed in the data generated. Generally creep damage is classified based on the one used by Neubauer and Wedel [68] for boilers and high-temperature equipment. Based on the above Le May et al. [69] have introduced five levels of damage A to E with Level A referring to no detectable voids. The five levels along with the depth and nature of creep damage in case of reformer tubes are shown in Fig. 12.17 [70]. Retiring of tube is considered once the stage D is reached.



Level A - No detectable voids; Level B - Isolated cavities; Level C - Oriented cavities; Level D - Micro-cracks; and Level E - Macrocracks.

Fig. 12.17 Classification of creep damage [70]

12.6.2.2 Corrosion Inspection Under Insulation and Fireproofing

API 510, 570 and 653 give considerable emphasis on inspection of insulated vessels, piping and tankage. While it is difficult to remove and re-install insulation system for inspection the best method is to use non-destructive techniques. It is only in the recent years that many conventional techniques have been successfully modified for under insulation or under fireproofing inspection. Some of these are Pulsed Eddy Current (PEC), Guided Wave Testing Examination Method (GWT) and various Radiographic Examination Methods (RT), like Profile and Film Density Radiography, Real-Time Radiography (RTR), Flash Radiography, Computed and Digital Radiography (PET PEC), etc. As regards under insulation chloride stress corrosion cracking (ESCC) of stainless steel is concerned, the same can be detected only by removing the insulation, using Liquid Penetrant Examination Method (PT). For details one must refer to the recently published API 583 [71].

12.7 Repair Welding of Equipment

Major part of repair or alteration in petrochemical industry involves welding for joining or local repair of carbon steel, mostly P1 material; Cr–Mo alloy steels; various grades of stainless steels; dissimilar metals and in some cases special materials like thermo-mechanically treated steels, high-strength Q & T steels, etc. Comparatively repair of non-ferrous materials like cupro nickel, Monel, titanium

and zirconium is much less. Welding is highly specialized subject and the procedure and quality control used are to be well planned and executed with the help of guidelines given in codes, inputs from welding consumable manufacturers, alloy manufacturers/developers and also experts in special cases. A plant personal associated with welding may not have the expertise for welding of all types of material but it helps if he has general idea about the various considerations that go in getting reliable weld joints. Commercial use of many alloys like DSS, high-strength pipeline steel of API X 70 and above for gas transmission has taken number of years before a reliable welding procedure was developed. Some basic aspects of welding have been given in Chap. 7 but as far as repair welding is concerned, the ones connected with commonly used carbon and alloy steels have been discussed. The topics related to repair covered are as follows:

- In the three industries covered in this book, there are processes and environmental conditions where the materials being handled get charged with hydrogen either as a result of corrosion in sour service or high-pressure high-temperature operation. The hydrogen picked up by the metal (specially ferritic materials) interferes in the production of a good weld due to its embrittlement effect. For getting good-quality weld it is necessary to introduce some corrective steps prior to welding.
- In most of the cases the repair may have to be followed by PWHT, as a Code or environmental-related requirements. This activity is to be carried out in situ, using special procedure.
- Special precautions are required while repair welding and PWHT of alloy steels (especially Cr–Mo), tempered steels and welding of dissimilar metals (ferritic with austenitic).
- Repeated PWHT adversely affects material properties. In case of situations where repeated repairs become necessary it is necessary to determine how many PWHT can be repeated in a particular situation.
- After repair or opening of equipment like exchangers in many cases, hydrostatic test is to be carried out. Nature and quality of water used for hydrotest has a bearing on in service damage, especially of stainless steel equipment.

12.7.1 Repair Welding of Ferritic Steel Equipment in Hydrogen Charging Service

In sour service or high-temperature high-pressure services, hydrogen atoms entering steel are free to diffuse inside metal but some of it can get trapped as atoms or hydrogen molecule at lamination, voids, dislocation, etc. as shown in Fig. 12.18 [72]. The former is known as diffusible hydrogen which causes brittle failure or weld cracking. The amount of trapped hydrogen would depend on the quality of material with respect to various types of imperfections present and therefore can

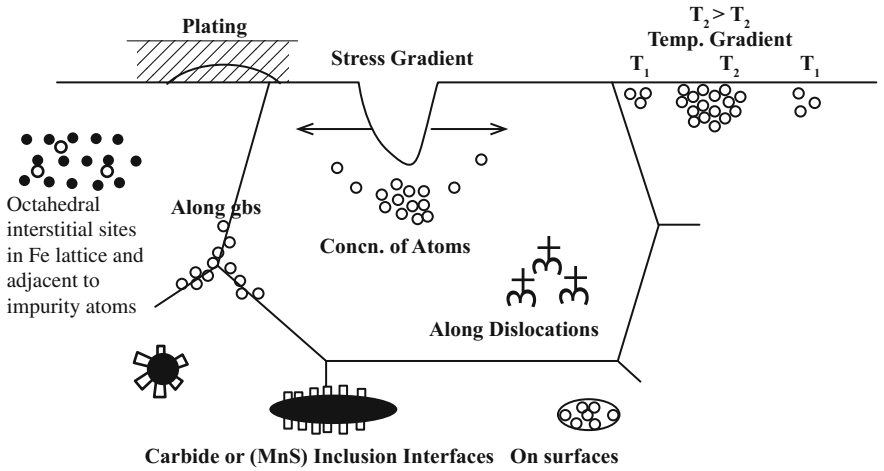


Fig. 12.18 Sites where hydrogen can get trapped in steel [72]

Table 12.4 Variations in hydrogen content of blistered vessel in sour service

Locations of the sample with respect to blisters	Hydrogen content (ppm)
Relatively unaffected area	9.0
Affected area	47
Blister inside surface	70
Blister inside surface at maximum bulge	189

vary within wide limits. For example, samples taken from different locations of a heavily blistered vessel in sour service were analysed for hydrogen content. The results given in Table 12.4 showed large variations understandably due to hydrogen trapped at the defects in the metal [73].

During weld repair carried out on hydrogen-charged equipment hydrogen dissolved in the weld bead has an important role in cracking once the weld cools down as the hydrogen embrittlement effect is observed in the temperature range between −100 and +100 °C and is most severe near room temperature [74]. This hydrogen embrittlement (HE) is required to be controlled by taking various measures. Depending on material, HE occurs only when hydrogen in weld is above a certain threshold limit (limit depends on alloy), temperature falls below 93 °C (200 °F) and the HAZ structure is crack sensitive. The concentration of hydrogen in the completed weld will be sum total of the same from consumable used + hydrogen content of equipment being repaired − hydrogen diffusing out during the process of welding. The rate at which hydrogen diffuses in metal is time/temperature dependent as would be evident from Table 12.5 [75]. Similar phenomenon would occur in case of high-temperature high-pressure service (HTHP) but extent of diffusible and trapped hydrogen would vary.

Table 12.5 Diffusion rate of hydrogen at different temperatures in steel

Temperature	Diffusion rate of Hydrogen
230 °C (450 °F)	25 mm (1″) per hour
105 °C (220 °F)	25 mm (1″) per 48 h
Room temperature	25 mm (1″) per 2 weeks
For Bake-out 200–230 °C (400–450 °F)	25 mm (1″) per hour/hydrogen gets redistributed

12.7.1.1 Designation of Consumables with Respect to Diffusible Hydrogen

With respect to hydrogen content welding consumables are designated as 'very low' (up to 5 mL/100 g); 'low' (5–10 mL/100 g); 'medium;' (10–15 mL/100 g); and 'high' (more than 15 mL/100 g) of weld metal deposited by the International Institute of Welding (IIW). On the other hand the American Welding Society uses logarithmic scale for diffusible hydrogen levels, that is, H16 for 16 mL/100 g of weld metal (17.6 ppm), H8 for less than 8 mL/100 g (8.8 ppm) which is the common upper limit for 'low hydrogen', and H4 for less than 4 mL/100 g (4.4 ppm). This, however, has no relation to the H1 (extra-low hydrogen ≤ 5.5 ppm or 5 mL/100 g), H2 (low hydrogen ≤ 11 ppm or 10 mL/100 g) and H3 (hydrogen not controlled) designations in AWS D1.1 Annex XI. Diffusible hydrogen of deposited weld metal also increases (18 mL/100 g or 20 ppm) in case of contact between basic low hydrogen SMAW electrodes and oil contamination of surface to be welded [76].

12.7.2 Avoidance of Hydrogen Embrittlement of Repair Weld

To avoid the HE of repair weld the following procedures can be considered:

12.7.2.1 Control of Preheat Temperature

- Carbon Steel: One of the methods used for reducing the adverse effect of hydrogen picked by metal during weld repair of equipment in sour and high-temperature high-pressure hydrogen (HTHP) service is to control preheat temperature along with the use of low hydrogen consumable. With higher preheat temperature the cooling rate slows down which helps hydrogen to diffuse from the weld area and minimizes chances of cracking when it cools down. Studies have shown that the carbon equivalent (CE) and sulphur content of carbon steel play an important role in controlling cracking susceptibility [77]. The conclusion arrived at is that cracking can be avoided in hydrogen containing

steel having CE of $\leq 0.45\%$ if the preheat temperature is raised to at least 50 °C above the temperature recommended in BS EN 1011-2. It is, however, essential that welding is carried out with heat input of ~ 0.8 kJ/mm.

- Cr–Mo Alloy Steels: Cr–Mo steels are normally used in HTHP hydrogen processes and the deleterious effect of hydrogen picked up during service on welding cannot be fully ensured only by preheating even if the amount of hydrogen picked up is comparatively small. A pre-weld hydrogen bake-out treatment is required in such cases [77].

12.7.2.2 Hydrogen Bake-Out Prior to Welding

From practical point the industry prefers to carry out bake-out to ensure that there will be no problem during welding which may require more than one attempt or in extreme case damage the equipment requiring replacement. A good practice is to do a 'bead-on-plate' test on the surface to be welded. A 150-mm (6″)-long bead, using the welding procedure intended to be used for the repair or alteration, is deposited on the surface and then inspect for cracks after 24 h by wet fluorescent magnetic particle testing (WFMT). If cracking occurs, then a bake-out procedure is needed to be included in the weld procedure. If cracking does not occur, welding without hydrogen cracking may be possible. Some important points to consider in this regard are as follows:

– Bake-out is preferably performed before weld preparation because in case of heavily charged metal cracking can occur even while grinding.
– In case of clad equipment, especially austenitic stainless steel cladding, the hydrogen content in clad material would be much higher compared to that in base metal. During bake-out hydrogen from cladding can diffuse into base metal which may create problem in getting good weld. For successful performance of bake-out it is necessary to first remove the cladding.

Hydrogen bake-out is a two-step process:

(i) Furnaces or electric resistance equipment heats the section to the desired temperature and holds it at that temperature for predetermined hours to allow the hydrogen to diffuse from the steel.
(ii) The temperature is then lowered or increased, as the case may be, to the preheat temperature in preparation for welding.

Guidelines for Hydrogen Bake-Out

For successful outgassing of hydrogen there are several issues which are to be taken into consideration. Some of the important ones are as follows:

(1) The amount of hydrogen charged in the steel from exposure to process gas or corrosion.
(2) The amount of hydrogen traps (e.g., interfaces at inclusions and precipitates, and voids at hydrogen blisters or SSCC and HIC).
(3) The solubility and diffusivity of hydrogen in the alloy.
(4) The wall thickness of component.
(5) The alloy's susceptibility to hydrogen embrittlement.
(6) Whether or not the equipment is weld overlaid/clad with a corrosion resistant alloy or is uncladded.
(7) Bake-out temperature and time.

To decide time and temperature needed to bake-out the hydrogen is not easy. Traditionally people have used rule of thumb where temperature varies generally from as low as 204 to 315 °C for 2–4 h, to as high as ~600 °C (normally known as intermediate PWHT temperature). However, actual time and temperature varies within considerable limits. A more realistic approach would be to calculate diffusion data, based on Fick's Law of diffusion and such data has been generated (Table 12.6) [78] and used. From the table it appears that the temperature of 204 °C used by some is too low. When bake-out at moderate temperatures does not give satisfactory result, intermediate PWHT at ~600 °C will prove to be successful [79].

Rather than relying on 'rule of thumb' use of a prescribed bake-out time for a particular thickness, monitoring of diffusing out during welding has been developed [80]. Here probes (Fig. 12.19) are fitted around the area being welded. The diffused hydrogen collected by the probes is continuously measured and once its quantity at all probes decreases below 1000 pL/cm^2/s, called '*trigger*', the bake-out is considered to be complete.

Table 12.6 Calculated diffusion rate of hydrogen in steel

Thickness (inch)	0.375	0.5	0.75	1.0	1.5	2.0
Time (HRS) @ 426 °C (800 °F)	0.5	1	2	3	7	13
Time (HRS) @ 315 °C (600 °F)	1	2	3	6	12	25

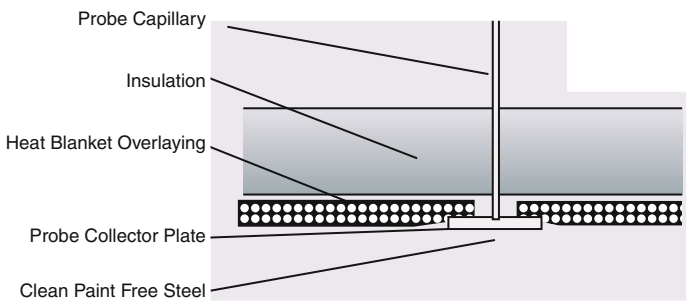


Fig. 12.19 Monitoring of hydrogen diffusing out of area to be welded

12.7.2.3 Post-Heat Treatment

Repair welding is required to be performed during service on alloy and steels are generally susceptible to HE, such as 2.25Cr–1.0Mo, 5Cr–0.5Mo, 9Cr–1.0Mo, etc. In such cases a good weld can be obtained by what is known as low-temperature *post-heat treatment* after welding, which is akin to dehydrogenation treatment (DHT). The *post-heat treatment* is carried out immediately on completion of welding and without allowing the weldment to cool below the minimum preheat temperature to help in the diffusion of any hydrogen in the weld or heat-affected zones out of the joint. In such a case recommended temperature and time have been variously stated as below:

- Post-heating temperature of 230 °C (450 °F) is to be maintained for 1 h per inch (25 mm) of thickness [81] or
- To maintain for 3–4 h a temperature of 100 °C above the preheat temperature [82].
- ASME Section III Code requires mandatory post-heating at 230–290 °C (450–550 °F) for a minimum period of 2 h
- For P-No. 1 material in case of the National Board Inspection Code (NBIC), post-heating at 260–290 °C (500–550 °F) for a minimum period of 2 h is a code requirement.
- In case of alloy steels having higher susceptibility to cracking, intermediate stress relief at ~600 °C are preferred to ensure that maximum amount of hydrogen has diffused out.
- As per API, in case of P22 and P3 conventional (2 1/4-Cr–1Mo/3Cr–1Mo) and enhanced (2 1/4 Cr–1Mo–0.25V/3Cr–1Mo–0.25V) steels, the DHT shall be performed at a minimum metal temperature of 300 °C (570 °F) for conventional steels and 350 °C (660 °F) for enhanced steels when approved by Purchaser [83]. The API however prefers intermediate stress relief (ISR) instead of DHT.

12.7.3 PWHT of Repair Weld

Once weld repair is done, PWHT is considered necessary if the original equipment had been subjected to PWHT but this can be exempted under certain conditions. To decide it is to be first ascertained that the original PWHT was done because of

- Code requirement (thickness) or
- Service requirement (sour service, stress corrosion cracking environment, etc.).

12.7.3.1 Where PWHT Is not Exempted

1. In case of the original PWHT is service related it is mandatory to have PWHT after repair weld.
2. Code exemption of PWHT for P-4 and P-5 materials is not permitted for applications in sour or hydrogen service or where the nominal chromium content of the material exceeds 1.25%.
3. Exemption of code required PWHT for ferritic materials based on the use of austenitic or nickel-base filler materials is not permitted [84]. However, it is common practice in industry to weld repair alloys like 5Cr–0.5Mo, 9Cr–1Mo, etc. with austenitic or nickel-base filler materials to avoid PWHT. It is popular with the maintenance personnel as this procedure minimizes possibilities of cracking due to HE as hydrogen gets dissolved in austenitic stainless steel because of its higher solubility and weld cracking is avoided. However, hardness of HAZ of Cr–Mo steel remains high (Refer Fig. 7.20) which can result in failure.
4. For P-No. 3, Group No. 3 materials, which are more susceptible, the quality of weld shall be examined after the material has been at ambient temperature for a minimum period of 48 h to determine the presence of possible delayed cracking of the weld. AWS D1.1 also specifies a delay of 48 h. for inspection after completion of weld in case of high-strength Q/T steels having crack-sensitive HAZ like A514, A517 and A 709 Gr. 100 [85].

12.7.3.2 Where PWHT Can Be Exempted

However, if it is a code requirement (1st case) PWHT can be avoided if certain conditions during welding are met. Some of the important procedures to be followed as per API 510 [86] are given below:

Impact Testing Is Not a Requirement

- The procedure is limited to P1-Gr. 1 & 2; P3–Gr. 1 & 2 (excluding Mn–Mo steels).
- The weld area along with additional 4″ (100 mm) or 4 times thickness around it would be preheated and maintained at a minimum temperature of 150 °C, during welding.
- The maximum interpass temperature shall not exceed 315 °C.
- The welding shall be limited to the shielded-metal-arc welding (SMAW), gas metal arc welding (GMAW) and gas tungsten arc welding (GTAW) processes.

Where Notch Toughness Is a Requirement

- For P-No. 1, 3 and 4 steels temper bead welding can be used to carry out repair.
- For welds made by SMAW the weldment temperature shall be raised to 260 ± 30 °C directly from preheat temperature and held for minimum period of two hours. This would ensure diffusing out of hydrogen picked up during welding.
- If the filler metal with supplemental diffusible hydrogen designator of H4 (such as E7018-H4) is used then the hydrogen bake-out may be omitted.
- Where hardness limitation is desired (such as in sour service) the same shall form part of weld procedural qualification.
- Temper bead welding does not ensure reduction in welding stresses. In case of service where resistance to stress corrosion (amine, caustic, carbonate service) is required, then alternative to PWHT shall be developed and evaluated before implementation [87].

12.7.3.3 Effect of Multiple PWHT on Mechanical Properties of Carbon and Low-Alloy Steels

Pressure vessels are designed on the basis of minimum specified tensile and yield strength of material used. In some cases the material is required to additionally meet minimum toughness values. These properties are normally achieved during production by combination of chemical composition and heat treatments like annealing, normalizing, normalizing and tempering and quenching followed by tempering. During fabrication and later during repair welding, the equipments are again subjected to multiple heat treatment cycles like preheat, de-hydrogen treatment (DHT), intermediate stress relief (ISR) and PWHT. In case of tall vessels PWHT in shop is sometimes to be done in two halves if a furnace of required size is not available. In such a case an overlap of at least 1500 mm is to be ensured. The base material in the overlap section is thus subjected to two heat treatment cycles. These heat treatment cycles cause modification of microstructure, consisting mainly of spheroidization of iron or alloy carbides, which is time/ temperature-dependent phenomenon. The major effect of this on the base metal properties is the reduction in tensile, yield and hardness levels along with significant reduction in toughness. Higher the thickness greater are these changes due to the increase in duration of exposure at high temperatures and inherent decrease in toughness with thickness. These changes are expected both for different periods at a fixed temperature or for different times at different temperatures. No destructive test can be done on a fabricated vessel to determine the above changes and so we have to follow other non-destructive means.

Use of Equivalent Parameter

As we have to deal with three variables, that is, time, temperature and mechanical properties, a quantitative evaluation can be carried out using time–temperature dimensionless Larsen Miller Parameter (LMP) (also called Hollomon-Jaffe parameter), according to the following equation:

$$\mathrm{LMP} = \mathrm{T}(20 + \log t) \times 10^{-3}, \tag{12.7.1}$$

where

T is the thermal treatment temperature (in degrees Kelvin)
t is the time of exposure to thermal cycles in hours.

In cases where thicknesses are high, the time related to heating and cooling should also be taken into account. For this the following formula is used [88, 89]:

$$\Delta t = \frac{T}{2.3S(C - \log S)}, \tag{12.7.2}$$

where

S (K/hour) is the heating or the cooling rate (ignoring the change of sign of the slope)
C is a constant with a value of 20 for C–Mn and low-alloy steels

Change in Mechanical Properties Versus LMP of Alloy Steels

Figure 12.20 shows the changes in tensile and yield strengths of 2.25Cr–1Mo steel with time, which follows logarithmic law [90].

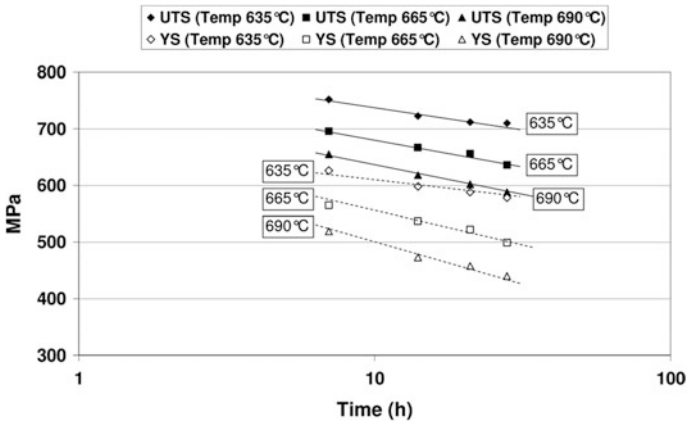


Fig. 12.20 Influence of temperature and time on tensile properties (grade A387Gr 22 Cl2) [90]

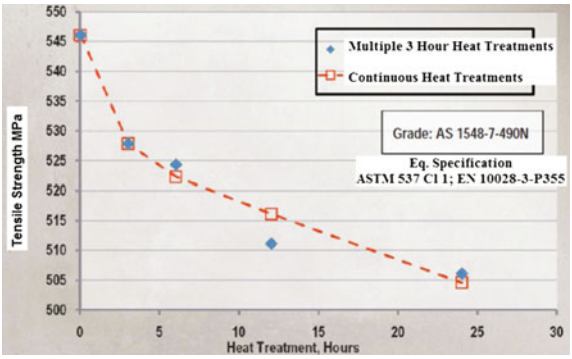


Fig. 12.21 Comparison of multiple 3-h heat treatment cycles with continuous treatment [91]

It has been shown in case of Australian AS 1548 steel (Equivalent ASTM A537 Cl1) where each thermal cycle is carried out for different times at the same temperature, the effect with respect to time of both multiple cycles or continuous treatment is same (Fig. 12.21) [91]. However, if the time and temperatures vary, the effective time at a common temperature (say PWHT temperature) is to be determined for each case. It has also been established in case of AS 1548 that the strength and impact properties linearly decrease and increase, respectively, beyond LMP of 17.88 (tempered for 3 h at 600 °C). Thus once the time/temperature parameter is known, the changes in properties can be estimated to get answers to query "How many PWHT can be done on carbon and low-alloy steels?"

Change in Mechanical Properties Versus LMP of Carbon Steel

The effect of temperature and time of PWHT of A516 Gr. 70 on lowering of tensile strength of normalized carbon steel (A 516 Gr 70) was studied [92]. Changes in tensile stress due to PWHT were determined from the plot of percentage change with respect to as-normalized steel of 500 MPa (73,000 psi) against LMP. As an example change in tensile strength determined under two conditions is stated below:

- 97.8% if PWHT was performed at 610 °C (1125 °F) for 2 h—488 MPa (70,416 psi)
- 93.0% if PWHT was performed at 635 °C (1175 °F) for 8 h—464 MPa (66,960 psi)

It will be apparent that while the first case is acceptable the second case is not as in this case strength will fall below the code required minimum specified strength of 485 MPa (70,000 psi). Tests have shown that in case of A516 each increase of LMP by 1.0 magnitude above 17.5 (LMP) in general lowers tensile strength by approximately 2%.

Similar data was obtained on the change in toughness by determining 35 ft-lb transition temperatures. In this case also similar effect of deterioration in impact

properties is observed. In case of the above-mentioned steel the transition temperature was found to be −61 and −40 °C when heat treated at 610 °C (1125 °F) for 2 h against 8 h at 635 °C.

Achieving Acceptable Property Both in Original and Simulated PWHT Conditions

Normally for fabrication of vessel the order for the material is placed by the fabricators. The fabricator prepares material data sheet (MDS) giving the requirements to which the product should conform. In case where PWHT is a requirement, the fabricator as a part of weld procedure also estimates the time and temperature of PWHT. The number of PWHT which the equipment may have to undergo during its lifetime is then assumed and total time of exposure to PWHT temperature is estimated. For thicker vessels normally four such cycles are considered which consist of 2 PWHT during fabrication + 2 PWHT during lifetime of the equipment for repair welding. If time for each PWHT cycle is estimated to be say 5 h then the material should meet the minimum specified property after being subjected to the PWHT temperature for a total period of 20 h. In such cases the steel manufacturer has to submit requisite test data to confirm that the properties of base metal both in original and simulated PWHT condition (heated at the PWHT temperature for 20 h) are within the minimum specified limits.

12.7.3.4 Implementation of PWHT

Not much problem is experienced in carrying out code-related in situ PWHT using normal ASME defined *soak band* (SB) consisting of the weld + HAZ + a portion of base metal adjacent to both side of the weld (1*t* or 2″ whichever is less) where no service-related cracking occurs. However, this procedure does not ensure reduction of stress below the threshold limit of service-related cracking. In such cases the local PWHT is to be carried not locally but as a band around the circumference, discussed earlier (Sect. 12.4.1.5). In implementing this number of constraints related to the size, orientation (vertical or horizontal), location with respect to other equipment, etc. are to be taken into consideration. Salient features of some of the important considerations in carrying out the above-mentioned PWHT are suggested taking an example of a tall column in amine service (subjected to stress corrosion cracking) requiring local repair at three locations at different elevations A, B and C.

1. Repair of Tall Column (Fig. 12.22).

- Repair of weld at location A

The length being small in top section it may not be possible to attain total band width to meet the requirements of WRC Bulletin 452. Further, because of proximity of the top head to the band, the growth of expanding shell may be restrained by

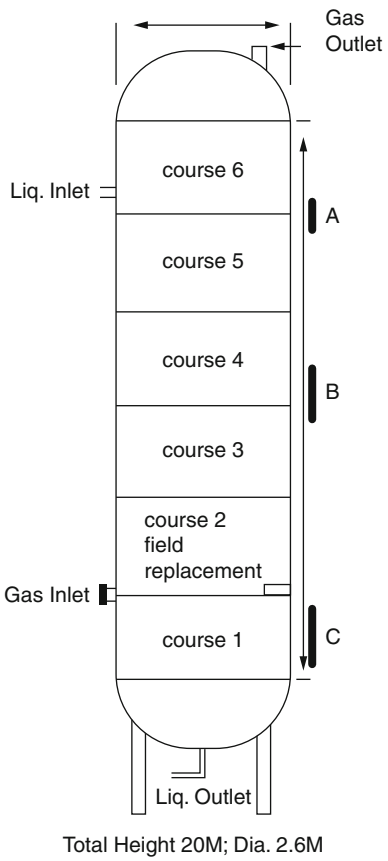


Fig. 12.22 PWHT considerations for repair of column damaged at three locations

relatively cold head. In such cases it is necessary to carry out finite element analysis (FEA) before taking up the job.

- Repair at location B

Compared to situation A local weld repair or replacement of shell course (s) followed by PWHT can be easily carried out at location B as per the WRC Bulletin 452. However, because of the reduction of mechanical strength of the shell at the PWHT temperature, it is essential that the structural stability of the column is fully assessed taking into consideration the column dimensions, dead weight of column and internals above the heated area, possible wind and earthquake loading and the risk of general and local buckling [54]. External support may also be required to reduce compressive load and buckling in the heat-treated region.

- Repair at location C

In case of repair in the bottom section, in addition to the considerations for locations A and B, the effect of PWHT temperature on skirt needs to be given due

attention. In most cases, skirts are long enough such that the baseplate is not impacted by the temperature gradient from heat treatment. In cases where skirt is small a 'hot box' provided below the bottom head helps in keeping the top portion of the skirt hot. In such cases, however, the buckling resistance of the skirt should first be evaluated. Typical hot box design is included in PCC-2 [93].

2. Repair of Heads and Spherical Shell

As per ASME "*In case of double curvature heads or spherical shells PWHT can be performed by local area heating around nozzles or welded attachments in the larger radius sections. The soak band shall include the nozzle or welded attachment. The minimum soak band size shall be a circle whose radius is the widest width of the weld attaching the nozzle, reinforcing plate, or structural attachment to the shell, plus the nominal thickness or 50 mm (2") whichever is less. The portion of the vessel outside of the soak band shall be protected so that the temperature gradient is not harmful*" [94]. Similar method can be adopted for domes.

3. PWHT of Other Configurations

ASME permits PWHT performed by local area heating of other configurations such as 'spot' or 'bulls eye' as per the details given under 6.4.3.8 provided the soak band includes a circle that extends beyond the edges of the attachment weld in all directions by a minimum of the nominal thickness or 50 mm (2 in.), whichever is less [97]. This would, however, require conducting FEA by competent person [85].

12.7.3.5 PWHT Temperature

As discussed earlier, a number of heating methods are available for PWHT, of which electric heating and gas firing are more common. For jobs involving large vessels or major modifications, it is prudent to take the help or advice of organizations specializing in such activities. API 582 gives recommended PWHT and holding temperatures for different materials in different service environments [84].

12.7.3.6 Precaution Against Physical Restraints

During PWHT there is both longitudinal and circumferential expansion which at typical PWHT temperature of 650 °C (1200 °F) for carbon and low-alloy steel can be taken as 8 mm per metre (0.1″ per foot). Any restrain in the expansion can lead to distortion and therefore some of the important steps but not limited to the following are:

- Internal structural components

1. Non-welded vessel internals, such as catalyst bed support systems, trays, distributors, outlet collectors, impingement plates, etc., should be removed or

individually heated and monitored when welded to ensure compatible thermal expansion with shell.

- External Structural Components

1. Restraint due to external components like stair case, piping, instrument and conduit, etc. if attached to the column should be free to move. Depending on the nature of attachment, these should be supported at one elevation and guided at others; pipes should be disconnected from column, etc.
2. Possibilities of platforms interfering with radial expansion of the vessel and connections to adjoining vessels and structures should be suitably evaluated.
3. External support with the help of a crane can also be provided by using enough tension to reduce compressive load in the heat-treated region. Care should be taken not to overstrain to avoid permanent deformation.
4. In case of horizontal vessels rested on saddles free movement should be ensured. It is advisable to slip in a thin sheet of stainless steel between the baseplate and bearing plate in between the anchor bolts to reduce friction and allow easy movement.

12.7.3.7 Inspection After PWHT

After heat treatment, the vessel shall be visually and with NDT examined for any damage; hardness taken to verify the requirements of the code of construction and/or post-construction codes; integrity of cladding shall be checked; and vertical vessels checked for plumbness. The maximum deviation from the vertical applied to a shell shall not exceed 1/10-in. (2.5 mm) in 10-feet (3 m) or ½-in. (13 mm) in 50-feet (15 m) [95].

12.7.3.8 Post-Weld Cleaning of Stainless Steel

It is not uncommon to get heat tint on both sides of weld on stainless steel which is an indication of oxidation due to inadequate gas shielding. The colour observed is due to thickening of the naturally occurring oxide layer which causes 'light interference' effects resulting in the development of various colour similar to temper colours. The thickening in oxide layer leads to chromium depletion of steel immediately underneath and also development of defect in the film due to stresses generated. The end result is that the heat-tint area becomes vulnerable to localized corrosion where aqueous corrosion is likely to occur though it has no adverse effect if intended application is for high-temperature service. Figure 12.23 [96] shows the change in oxide thickness and chromium depletion zones adjacent to weld.

The removal of heat tint can be done by mechanical, chemical or combination of both. Mechanical method involves blasting, grinding, brushing and polishing. Brushes made of stainless steel or nylon should be used. It is essential that the

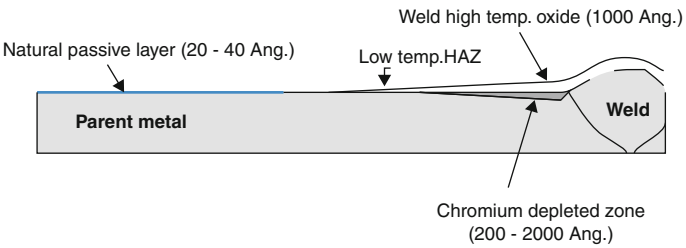


Fig. 12.23 Nature of oxide film formed during process of welding of stainless steel [96]

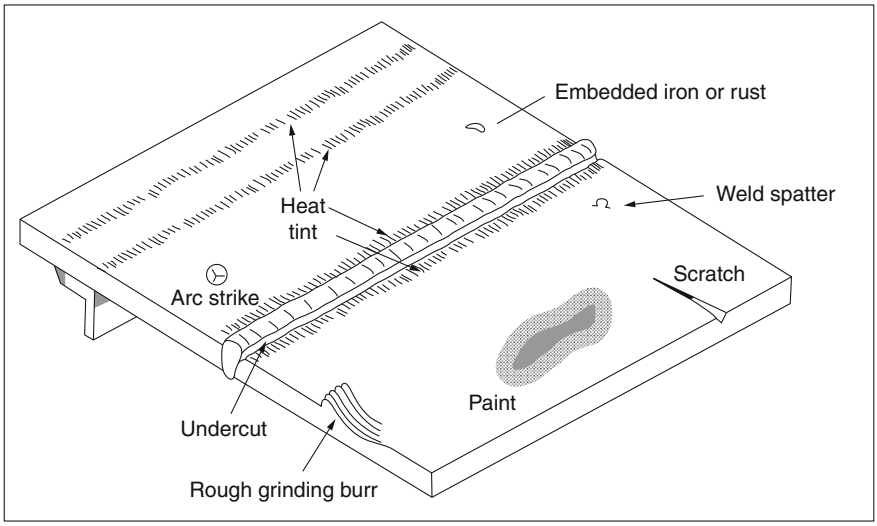


Fig. 12.24 Typical surface defects observed on stainless steel after fabrication

brushes made of iron or those which have been used to clean iron surface are not used for cleaning, as any contamination of surface by iron would cause breakdown of protective film and rust spots will develop on stainless steel surface. For chemical cleaning of clad equipment normally brush-on-paste or gels is used to remove heat tint from welded areas. For piping, vessels and tanks made of stainless steel, spray, immersion or circulating acid pickling is used. Pickling solution consists of a mixture of 8–20 vol.% nitric acid (HNO_3) and 0.5–5 vol.% hydrofluoric acid (HF). The nitric acid used in these treatments will also leave the steel surface in 'passive' condition. The advantage of acid cleaning is that it not only removes the heat tint but other fabrication defects/ surface contaminants (Fig. 12.24) to improve the overall performance [97– [99]. Excessive contact times with hydrofluoric acid containing solution should be avoided and in case better surface finish is desired for

aesthetic appearance or improvement in corrosion resistance, electro-polishing is normally carried out.

12.8 Post-Repair Hydrotesting

Hydrotest is quite often required to be performed after repair for which attention is to be given to quality and quantity of water used depending on MOC of equipment, nature of water available at site and the source of water. Though water is drained out there is every likelihood of its being retained in small quantities at dead ends, corners or crevices which can result in damage like under deposit corrosion, MIC, pitting, etc. In addition, small amounts of water remaining in pockets can cause crevice and chloride stress corrosion cracking in case of stainless steels. The nature of water used and the related treatment required form important part of hydrotesting. Figure 12.25 gives the general ranking of quality of water used [100].

The following points are required to be considered during hydrotest:

- For carbon steel equipment raw or potable water supplied in the plant is also used for hydrotest. It is, however, to be ensured that large quantities of bacteria and suspended solids are not present. If necessary, chlorine and/or organic biocide where SRB is suspected can be added to water against MIC. Free chlorine level should be maintained between 0.1 and 0.2 ppm. If necessary, potable water with low suspended solids can also be used. For carbon steel equipment where water contact exceeds 14 days, including filling and draining as in case of large size tank, addition of oxygen scavenger, inhibitor and a biocide along with addition of caustic to raise the pH to > 10 may be considered [8, 101].

12.8.1 Hydrotesting of Carbon Steel with Sea water

In installations in coastal areas, seawater becomes an attractive alternative for hydrotest of large size crude and product tanks and pipelines when there is shortage of freshwater. Filling and emptying may take sometimes as long as 30 days or more during which corrosion is likely to occur. In case of pipeline sometimes the water is not drained but left for some time till it is taken on line. Thus both short-term and relatively long-term protection is required for which the following preventive measures have been used:

- Addition of biodegradable oxygen scavenger and corrosion inhibitor. These additives provide required period of protection and are disposable in sea without creating any pollution-related problems.

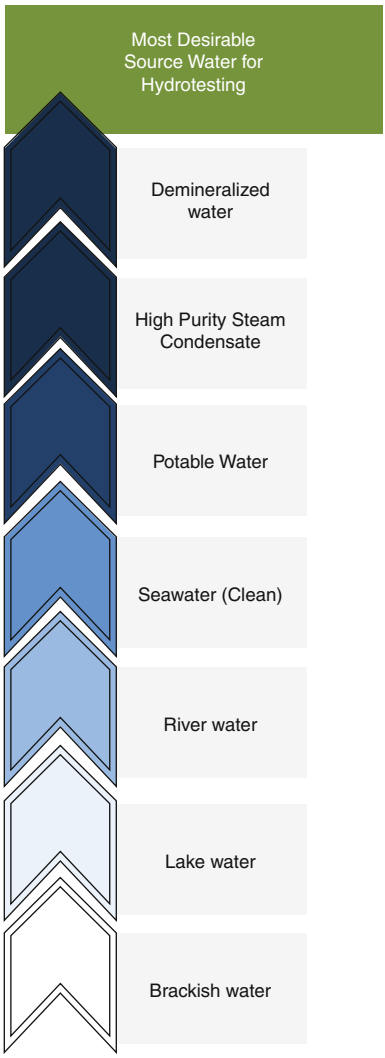


Fig. 12.25 Ranking of water used for hydrotest. Selection is on the basis of cost and availability [100]

- Use of amino-carboxylate-based vapour-phase corrosion inhibitors is claimed to prevent corrosion of metals in three phases: within the solution, at the water line and above the water line [102].
- Hydrotesting with seawater along with catholic protection has also been used for LNG storage tanks. Its advantages are claimed to be, efficient corrosion prevention, short payback period, and no problem with disposal of seawater because of the absence of any polluting chemical [103].
- For deepwater hydrotesting, seawater should preferably be sourced from a location free from external contamination that is more than 50 ft above the seabed and 50 ft below the sea surface.

- Before using seawater for hydrotest of tank it should be ascertained if the shell thickness can withstand hydrostatic pressure of seawater, which has higher density compared to water, 1.023 kg/m^3 against 1.0 kg/m^3 of water.

12.8.2 Hydrotesting of Stainless Steel

For stainless steel, the quality control of hydrotest water is of greater concern due to its susceptibility to localized attack related to chloride and also bacterial activities [104]. Cleanliness of water and its chloride content along with temperature play a major role in controlling corrosion of stainless steel. Hydrotest water left over after drainage has reported to result in penetration rates of 304L to the extent of 3.2 mm in a month and 4 months for 316L [105]. Potable water supplies should be free of particulates. Water from other sources should be used after settling of suspended solids or screened before use. Composition of various alloys has also an important role. As regards chloride content, different limits have been suggested but the best approach is to maintain the amount as low as possible, with preference for distilled or condensed water. Some of the recommended/suggested conditions of water for hydrotest of stainless steel equipment are given as below [104–106]:

– Piping fabricated of or having components of 300 series stainless steel should be hydrotested with a solution made up of potable water with low chloride. After testing is completed, the piping should be thoroughly drained (all high-point vents should be opened during draining), air blown, or otherwise dried. If potable water is not available or if immediate draining and drying is not possible, water having a very low chloride level, higher pH (>10), and addition of an inhibitor (trisodium phosphate) may be considered to reduce the risk of pitting and microbiologically induced corrosion.
– For sensitized austenitic stainless steel piping subject to polyphonic stress corrosion cracking, consideration should be given in using an alkaline water solution for pressure testing (NACE RP0170) [107].
– After the test, the vessel should be completely drained and dried. The inspector should verify the specified water quality has been used and that the vessel has been drained and dried.
– Various API codes related to maintenance inspection, rating, repair, and alteration of vessels, piping, tanks, exchangers, valves, etc. include chloride limit of water used for hydrotest, which range from maximum 20 to 50 ppm.
– Limits of temperature and chloride content for different grades of stainless steels are shown in Fig. 12.26 [108].

Thus users have to give consideration to various factors stated above before selecting the water to be used for hydrotest. However, unlike during construction of grass root plant, in an operating unit water of various qualities, such as raw, potable, demineralized, process and condensed water, are available .

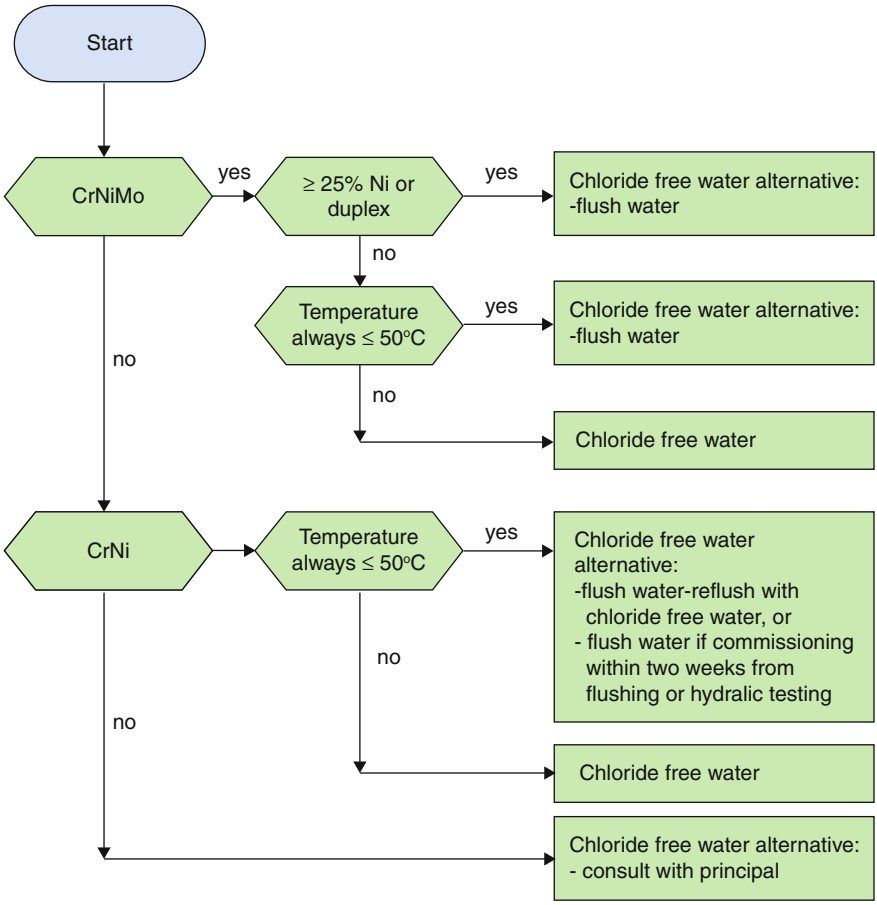


Fig. 12.26 Hydrotest water quality for stainless steels and nickel-containing alloys [108]

12.9 Integrity Operating Window

It is universally accepted today that process plants require well-developed mechanical integrity (MI) program to ensure reliability of stationary equipment (pressure vessels, process piping and storage tanks). The first step in this direction is to conduct review of damage mechanism and inspection data in a particular unit (using the information given in API and other sources along with the data collected in-house) and assess their continuous service with respect to code requirement and fitness-for service assessment using API 579-1/ASME FFS-1 2007. These studies are then followed by establishment of a cost-effective modern risk-based inspection (RBI) program, API 580 and API 581. A designer ensures mechanical integrity by sound mechanical design, proper material selection and setting the operation within the design limits, during the lifecycle of a plant. If the plant is operated without

deviating much from the parameters set, originally planned inspection schedule can be adhered to. In case of deviations from original design conditions due to changes in feed quality, final product specification, capacity enhancement, increase in severity of operation to meet new market driven product mix, change of catalyst, etc. new severe damage mechanisms may be introduced, affecting the remaining life of an asset. These additional factors and their damaging effect if not envisaged beforehand and the unit operation not modified accordingly damage suffered would go unnoticed. Any subsequent inspection planned on the basis of historical data can then lead to serious consequences. A plant operates within specified zone of *safe operating limits*. However, in case of deviations discussed above, the plant personnel should be kept informed about the possible damaging effects of long-term operation above or below the safe zone. It has been assessed that under these changed conditions while 80–95% of equipment can be properly handled by RBI analysis using earlier inspection data, the remaining 5–20% of equipments require input of additional real-time or other process data under changed conditions. In simple term it can be stated that "*a set of operating ranges needs to be established for key process variables to keep the material degradation process in control. These limits are generally called operating limits or operating envelopes or Integrity Operating Window (IOW) that focus only on maintaining the integrity or reliability of process equipment. Typically IOW addresses issues that involve process variables which when not adequately monitored or controlled, can impact the likelihood and rates of damage resulting in a loss of containment. Once a detailed set of IOWs is identified, the operator has to be informed for corrective action needed so that he is not caught unaware and continue operation in normal way. Similarly the inspection personnel is also to be brought in the loop so that required inspection planning is done before hand*". An integrated guideline on this aspect has been dealt in API 584 [109].

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Chapter 13
Failure Analysis

Abstract In spite of best of efforts failures do happen in industries resulting in complete breakage or localized damage that may lead to failure. Economy demands that recurrences of such incidence are minimized by failure investigation. The study involves identification and quantification of damage in the equipment using (i) visual, (ii) NDT, and (iii) replica examination. In case of failed components additional data on mechanical properties, metallurgical details, fracture mode, etc. can be generated to give better understanding of causes of failure. The analysis of data generated along with operating conditions help in finding the root cause of failure. Once the conclusion is reached the recommendation should take into account the feasibility of its implementation. The chapter describes various field and laboratory tests for conducting destructive and non destructive tests. It has been suggested that depending on nature and increasing complexity of damage, the failure analysis can be carried out in-plant with available expertise, or in centralized testing or R&D facility of a large corporation or with the help of an outside organization having necessary expertise.

Keywords Visual inspection · Non-destructive testing · Metallurgical analysis · Root cause analysis

13.1 Introduction

Failure can be defined as the condition under which equipment or its component fails to perform the desired duty expected from it. A leaky tube exchanger, a cracked pump shaft, a corroded pump impeller, leaking welds is some of the common examples of failure of equipment in industry. However, in long-term perspective it becomes necessary to know the root cause of failure so that proper action can be taken to minimize repetition of the same. This involves material failure analysis (MFA), which should form an important part of a company's activities.

All engineering materials have certain degree of ductility. On the other hand, these also contain visible or invisible defects which can be described as discontinuities in

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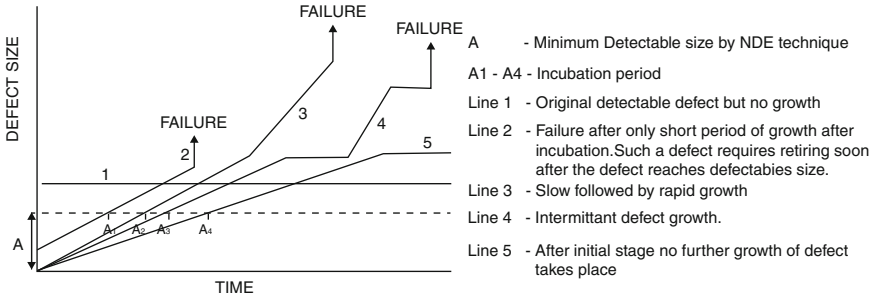


Fig. 13.1 Various stages in failure of a component

metallurgical structure, e.g., inclusions, flaws, non-homogeneity, etc. or design and fabrication deficiencies, e.g., stress raisers, weld crack or undercut, physical restraints, etc. Presence of defects will not necessarily lead to failure in service. A particular defect that is unlikely to cause failure under one set of service conditions may be hazardous under another condition. Except in instances like over pressurization, super cooling, overheating, etc., where the failure may be sudden or within a span of short period, most of the failure modes are time dependent. Therefore, incidences of failure can be divided into three stages; (i) incubation/initiation (ii) growth and (iii) final failure (Fig. 13.1). MFA should therefore start after the stage (i) itself i.e. when the damage or defect reaches a size which can be identified by NDT or other methods. If this approach is taken, many of the ultimate failures can be predicted and then prevented or corrective action taken before complete breakdown occurs. Similar approach is also used for fitness-for-purpose and residual life assessment, which is not the subject of this chapter.

Failure analysis approach can be compared to the stages leading to death of a human being. While generally accepted meaning of MFA can be compared to "post mortem" after the death; any pathological and other tests carried out on a living person to establish the causes of any illness or damage to any body parts (which may finally lead to death) and continuous monitoring of the same are equivalent to initiation and growth of defect. These steps of diagnosis followed by treatment to cure the illness form the basis of prolonging human life. In the final analysis failure analysis comes under the overall category of deterioration, diagnosis and treatment of human health, to avoid premature death. The time span of the three stages of failure, stated earlier, may vary from case to case, depending on the original structural, metallurgical and fabrication defects, environment induced defects and stresses and temperatures to which the components are subjected.

13.2 Causes of Material Failure

Material failure in process industry commonly falls under two broad categories:

Table 13.1 Study of industrial failures during 1971

Types of failure	% of failure
Corrosion (all types)	33.0
Fatigue	18.0
Brittle fracture	9.0
Mechanical damage	14.0
Fabrication and welding defects	16.0
Other	10.0

(i) Environment related
(ii) Stress or mechanical related
(iii) Metallurgical degradation

The environment related failures are associated with corrosion, oxidation, sulphidation, carburization, etc. Mechanical failures, on the other hand, are basically stress related. Examples are fatigue, creep, overheating, overloading etc. Embrittlement of material due to, graphitization, sigma formation, temper embrittlement, phase precipitation etc. fall under the category of metallurgical degradation. Table 13.1 gives results of a survey carried out on the nature of failures experienced during 1971 [1].

13.3 Steps in Material Failure Analysis

The various steps involved in failure investigation are shown in Fig. 13.2.

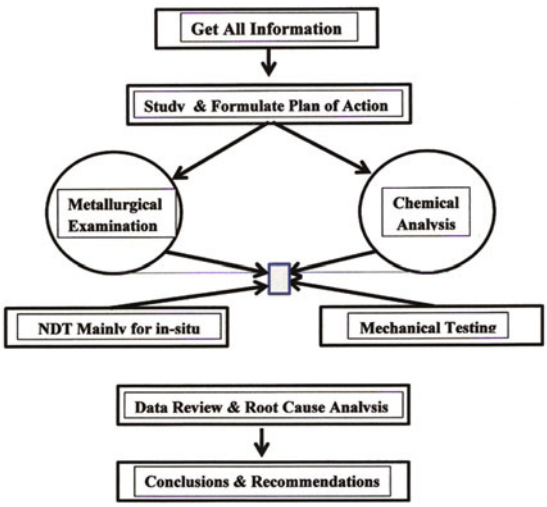


Fig. 13.2 Steps in failure investigation

13.3.1 Visual Examination

The first and the most important step in MFA is the visual examination. This gives an overall picture of the conditions that have led to the failure. If not properly conducted, many of the evidences for analysis of the problem can be lost. The salient features of visual examination are:

- Examine visually and with the aid of a magnifying glass, the nature of damaged/failed surface. Look for any specific features of damage, e.g., on or near weld, bottom or top of pipe, near keyhole in shaft, opposite of inlet nozzles, presence or absence of deposits, etc.
- Type of damage, e.g. uniform, pitting, localized, directional feature, grooving, roughness, cracking, etc.
- Take dimensional measurements of defects, e.g., depth of pits, length of crack, loss in thickness, etc. Examine nature and colour of deposits around corroded and failed portion, e.g. rusty, blackish or whitish deposits, greenish/bluish deposits in case of copper alloys, etc.
- Appearance of failed cross section, e.g., grainy, columnar, smooth, striation or beach marks, etc. Examine under microscope at low magnifications ($\times$ 5–$\times$ 10), where possible.
- Take photographs of the failed/damaged part.
- Make a sketch and record all observations made and data collected for future reference. Where pieces of failed samples are collected, these should be carefully stored without cleaning, grinding, etc. Any fracture surface should be suitably protected against mechanical damage during handling. If these precautions are not taken some of the important evidences may be lost and investigation may be faulty or difficult.

13.3.2 Operating Conditions

For failure analysis it is essential to have an overall idea of the process and detail information on design and operating conditions. Thus before taking up the investigation one has to analyse various design, recommended and actual operating-conditions. For this purpose, the procedures to be adopted are:

- Check process flow diagrams for design conditions, e.g., temperature, pressure, fluid composition and any additional corrosion control measures provided, e.g. inhibitor, neutralizing chemicals, etc. Check for presence of water and corrosive constituents (even if in ppm level) in a non-corrosive hydrocarbon stream, both from the process data sheet and from the individual operators.
- Study design details, e.g., code requirements, corrosion allowance, type and thickness of lining or coatings, application techniques, water quality in case of boilers or cooling water, etc.

- Discuss with operating personnel and study operating logs for any variations from the design conditions, e.g., changes in temperature, pressure, fluid composition, control of pH and injection of inhibitor or neutralizing chemical. Find out if any unusual vibration of piping, pumps and compressors was experienced prior to failure. In case of fired equipment like boilers and heaters collect information on flame pattern, flame impingement, temperatures in various zones, skin temperatures, etc.
- Study material and fabrication certificates for conformation to standard specifications, codes and specified special requirements. Check if the material supposed to have been used, is as per the original specification of the process licensor/engineering consultant.
- Collect failure history of the equipment and any modifications in material, operation or design since plant start-up.
- Check, where applicable, for source of chemical fumes, and spillage, presence of pollutants in water, either from the plant or from other sources in the vicinity.

13.3.3 Investigation

Once on-site visual examination and collection of data have been completed, the next step is to conduct detail investigation. By correlating the observations with operating conditions and from the past experience, in the majority of cases it is possible to have an overall-idea about reasons for the failure at this stage itself. In most of the instances, plant inspection engineers themselves can handle the failure related problems, if an experienced group along with minimum facilities is available at site. However, in number of instances the findings need to be investigated in greater detail by competent specialists. There are also some instances where the reasons are not easily identified and in such cases a detailed investigation involving multi-disciplinary approach becomes absolutely necessary. The extent and type of investigation, therefore, depend on the type of failure, amount of information that need to be generated and the availability of test facilities.

The various steps that have to be followed for MFA are:

- Chemical analysis of failed material to establish its actual composition and see for any deviation from specified standard. In special cases look for any specific requirements, other than that included in specification but asked for, low sulphur for HIC resistance, Mo and carbon contents in 316L, limit of carbon equivalent (CE), etc.
- Chemical analysis of corrosion products or deposits for various elements, e.g. chloride, iron, sulphide, nitrite, nitrate, phosphate, copper, nickel, calcium, sulphate, pH of water extract, loss on ignition, etc. Depending on amount of corrosion and scaling products available, both qualitative or quantitative analysis can be carried out. In some situations, only chemical analysis is not

sufficient and the identity of the chemical compound is to be established. For this purpose x-ray diffraction can be used.

- Metallurgical examination is an important tool in establishing causes of corrosion damage and failure. It reveals the structural variations and damage type, e.g., spheroidization, banding, dealloying, inter or trans granular nature of cracking, presence of sigma or delta ferrite in high alloy steels, carburization/decarburization, intergranular carbide precipitation and attack, depth of crack, formation of creep voids, etc.
- Changes in mechanical properties, with respect to the specified values, e.g., reduction in ductility, increase or decrease in hardness, strength, elongation, etc. can be done only on cut samples and, therefore, fall under destructive tests. However, some of these tests can also be done on miniature samples made from boat or core-plug samples. In situ measurement of surface hardness also gives useful information regarding the mode of failure, where the damage initiates from the surface.

13.3.4 Samples for Testing

Methods used for failure investigation largely depend on the nature of failed component and whether it can be destroyed for conducting the tests. There are various situations depending on whether sample pieces are available or not.

13.3.4.1 Where Samples are Available for Destructive Examination

Such cases include where the failed component is unusable or where the affected portion from a pipe or vessel can be cut (the cut portion is replaced with a new piece of same specification without affecting production) or retrieved (as in case of a leaky tube in a heat exchanger). This falls under destructive study. Samples can be sectioned, polished and examined under optical microscope, not only to study the structural characteristics but also the mode and depth of attack. These can also be examined by SEM and subjected to mechanical and impact tests, if required. The advantage is that maximum information can be got from such investigation, using advanced laboratory instruments.

13.3.4.2 Where Samples are Not Available and Non-destructive Tests are to be Conducted

Under such conditions, in situ (at location) metallography using either an optical microscope or replica technique, chemical analysis, hardness measurements are carried out. The disadvantage is that it gives only the surface condition of the

material. Inspite of this, it is a very strong tool, especially where the changes are uniform in the bulk material. The method, however, does not give any indication of the depth of attack and characterization of damage is to be supplemented with NDT and other methods.

13.3.4.3 Where Samples can be Obtained by Semi-destructive Methods

In some instances a semi-destructive method of removing failed sample can be used. Tools and methods have been developed for removal of both core-plug and smaller surface samples. The former is used for characterizing through-wall damage but the latter is useful for only surface and sub-surface damages. The various types of samples removed are cones, boat and core-plug. The area from where surface sample is taken out is later repaired by weld build-up or left as it is, after grinding to a hemispherical shape to minimize any stress concentration. In case of core-plug sample, the hole is either repaired by welding onto it a dummy over size stub or a nozzle with a cover plate. The nozzle size and rating are to be as per the pressure vessel code requirements. As would be evident, it is possible to carry out various tests on these sample pieces including mechanical tests. As it is not possible to get a sufficiently large sample in many cases, there is great demand for mechanical tests that are capable of assessing small samples. The small punch test (SPT) has been considered as a suitable small specimen mechanical test technique [2]. In the recent years, this technique is being increasingly used, where mechanical properties can be characterized on the basis of tests carried out on small thin sample (usually with a section of 10×10 mm and a thickness of 0.5 mm). These tests can be of great help in MFA, especially of thick vessels.

13.4 Tools for Failure Analysis

The various steps involved in the MFA have been discussed earlier. Over the years considerable advances have been made in developing new techniques and improving the existing ones. Both laboratory and field tests (NDT) are required to assess the nature and extent of damage. Introduction of electronics and microprocessors have improved the accuracy of the measurements, increased the range of information that can be collected, processed and output displayed. Over and above this, it has been possible to decrease the size of instruments making it possible to use these in the field. It is of interest to note that in spite of these developments, some of the older and simpler methodologies and the tools still play an important role. Some aspects of the conventional and recent techniques, available to the industries today or in advance stage of development are described.

13.4.1 Tools for Visual Examination

For visual examination, use of simple tools like magnifying glass, flashlight, pocket microscope, magnet, abrasive paper, knife, tweezers etc. help in collecting required information. In case the failed samples are available for being brought to the testing laboratory, use of stereoscopic microscope can give a three-dimensional feature of the surface characteristics of the failed piece. It is essential to use a camera to record the details for future reference. Visual observations are supplemented with dimensional measurements using callipers, micrometres, measuring gauges, pit-depth gauges, etc. for quantification of damage. One of the recent developments for visual inspection is the Video Image Scope, which can be used for internal inspection requiring remote visual access to assess conditions of flaws, defects and other anomalies in tanks, piping vessels, turbines, etc. in a non-destructive manner. Owing to its very high resolution and brightness Video Image Scope is capable of providing a detailed view for inspection and specially facilitates observation of dull, corroded surfaces. Internal surface of heat exchanger tubes, which suffers from pitting and corrosion cracking, the boiler drum weld ligament areas, super heater header ligaments, which are ordinarily not easily accessible, can be inspected with comparative case by the use of this instrument. The usefulness is limited in case of surfaces having considerable surface deposits. Quantification of damage is, however, difficult and requires good expertise. These are normally available in 3–10 m lengths.

13.4.2 Chemical Analysis

For chemical analysis of metals and alloys and also the corrosion products, standard analytical procedures are more common. The methodology to be used depends on the quantity of material available. For small amounts of sample, various instrumental techniques, e.g., spectroscopy, x-ray fluorescence, colorimetry, etc. are used. In situations where bulk samples cannot be obtained for chemical analysis, either chipping or drillings (up to a depth of 1–2 mm but preferably not more than the corrosion allowance) can be sufficient for the purpose of investigation. Where these procedures are not permissible, light surface grinding to collect powder sample can be practiced. When samples from surface are collected, the surface should be properly cleaned to avoid contamination from corrosion product and other deposits.

Table 13.2 gives an overview of most common laboratory and field equipment that are used for chemical analysis along with their limitations [3]. Presently, for rapid analysis of metals and alloys Portable Alloy Analyser is used for Positive Materials Identification (PMI) tests. These can be used both in situ and in the laboratory. Radioisotope sources placed in the instrument, generally Fe-55 and Cd-109, emit low energy gamma radiation that interact with the material to be analysed, emitting characteristic x-rays of the elements present. The characteristic x-rays are passed through special filters that subtract the background radiation. The

intensity of the emitted characteristic x-rays is compared with standards, in-built in the microprocessors, to give the weight percent of alloying elements. The equipment is capable of detecting the entire general alloying elements in steel copper and nickel alloys. It is highly versatile and portable and also used to identify and confirm use of specified alloys during construction and maintenance activities and avoids any future failures during service.

13.4.3 Metallurgical Examination

Metallurgical examination is an important tool for MFA as it throws light on (a) the metallurgical structure of the material which can lead to a particular mode of failure, (b) the nature of failure and (c) any in-service changes taking place by the process of metallurgical degradation. The following important information can be derived by the three most commonly used techniques:

- Optical Microscopy (OM)—Normal 1000 magnification (Maximum magnification attainable is 2000 × by observing the structure through cedar oil)
- Grain size, types of phases, overall phase distribution and cleanliness, grain boundary phases, cold deformation, recrystallization, depth of carburization, heat affected zone (HAZ), nature of cracking, dealloying.
- Scanning Electron Microscopy (SEM)—Normally maximum magnification used is × 50,000
- Mode of fracture (ductile, brittle, fatigue, and inter or transgranular), corrosion details, phase distribution and morphology, etc.

13.4.3.1 Macroscopic Examination

A broad indication of the characteristics of defect or failure over quite large areas of metals can be obtained by macro-examination at low magnifications. The actual metallurgical structure is developed by using a technique, known as *etching*. Etching is a process by which selective corrosion is effected by using a suitable corroding or etching solution. The major advantage is that a large part can be examined at a time, including both damaged and good portion of the piece. This method provides easy indications of:

- Non-uniform composition due to the segregation of alloying elements
- Non-metallic inclusions like slag, sulphides and oxides
- Methods of manufacture, e.g., casting, forging, welding
- Physical defects formed during manufacture, e.g., blowholes, seams, laps, etc.
- Uniformity of heat treatment
- Surface carburization or decarburization

Table 13.2 Various instrumental analytical techniques for laboratory and field testing

Equipment	Principle	Accuracy	Carbon included	Effect on surface	Remarks
Stationary Laboratory Spectrometer	OES[a]	+++	+	Arc strike	Samples min. ~5 × 5 × 3 mm
Laboratory X-ray analysis	X-ray Fluorescence Spectrometry	+++[b]	÷	None	Only very small samples needed
Scanning electron Microscope Analysis	Electron reflected radiation spectrometry	+++[b]	(+)[c]	None	Only very small samples needed. Microscopic details can be analysed
Transportable/on-site Metorex, Arc Met Analoy, Metalscan Spectro, Baird	OES[a]	+	÷	Arc strike[e]	Usually without shielding gas to improve flexibility[d]
Metorex, X-met Texas nuclear Alloy analyser	Isotope Fluorescence Spectrometry	+[f]	÷	None	Isotopes are to be renewed periodically
Diamond Paper Rubbing	X-ray fluorescence spectrometry on metal dust collected in special abrasive tape	+[b]	÷	Finely ground or polished surfaces will become slightly dull	The surface has to be very clean

[a]Optical emission spectrometry, spectrum from electric arc between tungsten electrode and sample
[b]Highest accuracy is obtained when using known reference standards for correction
[c]Can be estimated but accuracy lower than for other heavier elements
[d]With inert gas shielding carbon may be detectable but accuracy usually poor on alloyed steel
[e]To be removed on hardenable steels and on stainless steels
[f]Some elements as molybdenum and chromium can be analysed with high accuracy, most other element will generally be less accurately estimated depending on the actual set of isotopes in the probe

Macro-examination is done at low magnification after etching. The etchant used depends on the nature of metal and type of information desired. Macro etching requires deeper etching to reveal the details. Some of the common macro-etchants are given for information but other etchants can also be used:

For Carbon or Alloy Steels

(a) To reveal segregation: Iodine-10 g; Potassium iodide-20 g; Water-100 ml
(b) To reveal variations in crystal structure: Ammonium persulphite-10 g; Water-90 ml or Nitric Acid-10 ml; Water-90 ml.
(c) For deep etch: Hydrochloric Acid-140 cc; Sulphuric Acid-3 ml; Water-50 ml (Temperature 90 °C). Wash in dilute ammonia solution after etching.
(d) To reveal deformation line: Cupric Chloride-40 g; Hydrochloric Acid-100 ml. (Specimen should be heated to 200–250 °C prior to etching)
(e) To reveal dendrite structure: Copper Ammonium Chloride-9 g; Water-91 ml.

For Stainless Steels

Hydrochloric Acid: 15 ml; Nitric Acid-5 ml; Water-100 cc

For Aluminium and its Alloys

Hydrofluoric Acid: 10 ml; Nitric Acid: 1 ml; Water-200 ml

For Copper and its Alloys

Nitric Acid: 45 ml; Potassium Dichromate: 0.2 g; Water: 50 ml

Figure 13.3 shows macrograph of the cross section of cracked fillet weld which commonly occur in carbon and alloy steels [4].

13.4.3.2 Microscopic Examination

This is the most commonly used method where reflected light is used for examination. The sample to be examined is cut, mounted in a resin (where required) and then ground and polished mechanically or electrolytically to a mirror finish. Under polished condition, the light reflected from the surface shows a featureless and very

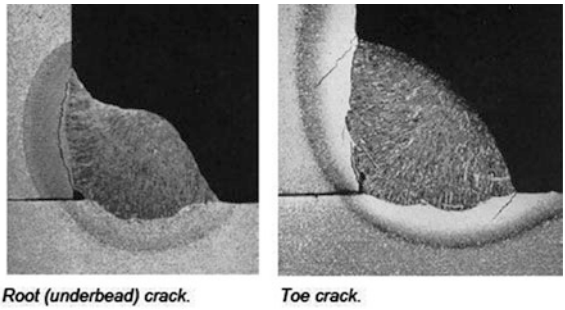


Fig. 13.3 Macrograph of cross section of fillet weld failed due to hydrogen embrittlement [4]

Table 13.3 List of common etching reagents for microscopic examination

Sl. No.	Materials	Etching reagents	Composition	Remarks if any
1.	Carbon steel 2.5Cr–1.0Mo 5.0Cr–0.5Mo any other alloy steel	(a) Nital (2%) (b) Picral	Nitric acid-2% Ethyl/Methyl Alcohol-98% Picric acid-4 g Ethyl/Methyl Alcohol-100 ml	
2.	Stainless steel (304,316,321)	Oxalic acid Glyceregia	Oxalic acid-10 g Water-100 ml HCl-15 ml Glycerol-10 ml Nitric acid-5 ml	Electrolytic Etching
3.	Copper base alloys	NH_4OH and H_2O_2 solution $FeCl_3$ and HCl solution	NH_4OH-25 ml H_2O_2-50 ml (3%) Water-25 ml $FeCl_3$-5 g HCl-50 ml Water-100 ml	

bright surface, except for inclusions, graphite, blow holes, cracks and constituents harder or softer than matrix, which stands out in relief. Here also, the actual metallurgical structure is developed by *etching*. This is a very important part of the process and specific etchants are to be used for different metals and alloys and also for the identification of different phases. Etching is done either by swabbing with the solution or electrolytically, depending on the type of alloy. Sometimes to get clear structural details repeated polishing and etching is to be performed. Etchants are also available to impart distinctive colours to different phases for more reliable identification of phases. Table 13.3 gives the list of some important etchants used for commonly used metals and alloys in the process industry.

Optical Microscopy

For optical microscopic examination, metallurgical microscope (reflecting type) is used. This consists of two lenses, one objective and the other eyepiece. Basic principles of the microscope are shown in Fig. 13.4. The magnification is controlled by power of eyepiece, focal length of objective (F) and distance between the back of objective and the eye piece (D). These can be roughly related as follows:

$$(D/F) \times \text{Power of eye piece}$$

The usefulness of magnification is also dependent on to what extent distinctly separated two adjacent phases can be seen. This is known as resolving power and depends on numerical aperture (NA) and wavelength of light employed. In optical microscopy a resolution of approximately half of the wavelength of visible light can

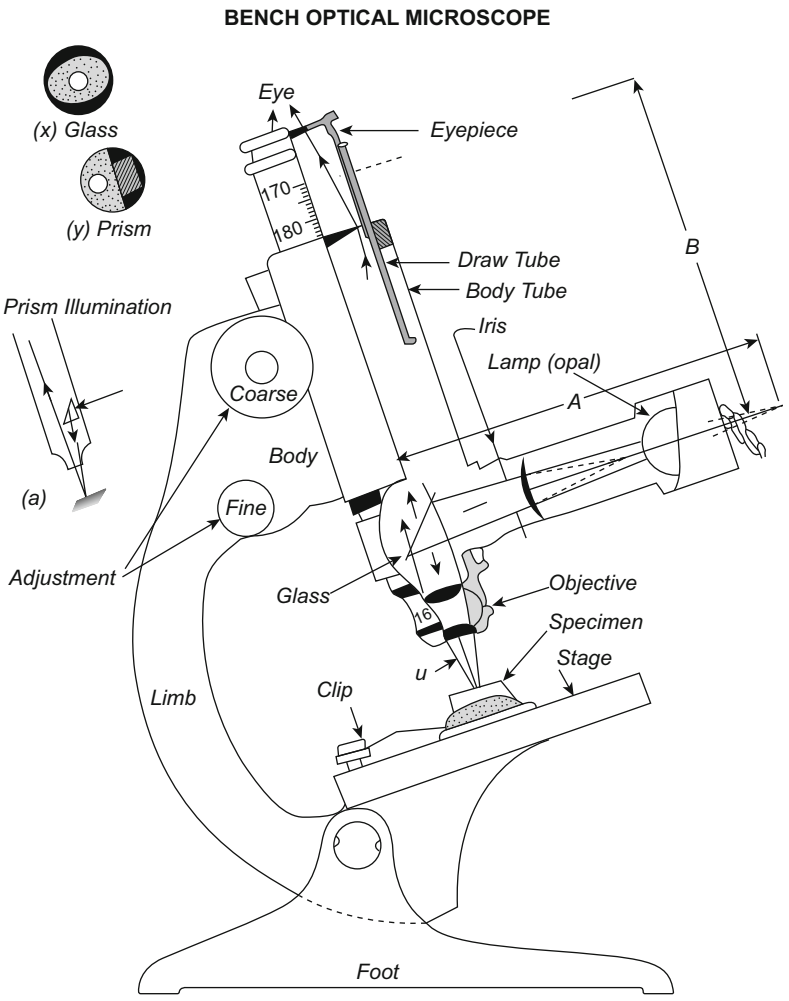


Fig. 13.4 Optical microscope showing different components

be obtained which comes to around 2 μm. In addition its magnification is limited to 1000 ×. This limits the use of optical microscope to study finer features of microstructure. As NA is related to refractive index of the medium between the specimen and the objective (1.0 for air) by use of cedar oil (refractive index 1.5) the maximum practical magnification in optical microscope can be raised up to 2000 ×. After etching, grain boundaries and different phases get differentially attacked producing ups and downs (Fig. 13.5) on the polished surface. On being examined under the microscope, all the light rays do not get reflected back towards the objective but are scattered in different directions, some of which also return back to the objective. The latter condition produces a combination of light and dark

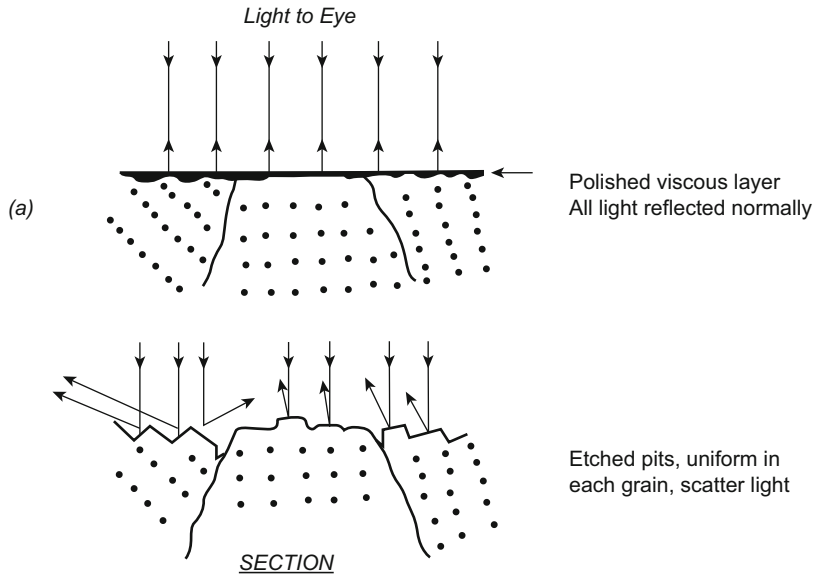


Fig. 13.5 Etching results in differential attack finely roughening the surface

visible image, thus giving a picture of the metallurgical structure. Since the birth of light microscope around 1600 AD, considerable advances have taken place, especially during the last 50 years. The modern optical microscopes use fibre optic accessories along with micro-hardness tester, image analyser, digital camera, etc.

Colour Metallography

Normal optical microscope reveals the structure in black and white. In many cases it becomes difficult to distinguish the phases. In colour etching different phases are etched in different colours. Also, the colour etchants reveal information about the specimen that is not visible in black and white general-purpose etchants. Anodic tint etchants that colour the matrix grains usually reveal grain orientation information, that is, they colour the grains as a function of crystal orientation. Thus random texture can be distinguished from preferred orientation. Segregation is vividly revealed by colour etchants as variations in colour within the grains. Residual deformation is also clearly revealed by colour, but is often difficult to detect in bright field. Most colour etchants are selective in nature, that is, they will colour only certain phases or constituents. The common chemicals used for colour etching are given below single are combination of these are used for colour etching:

- Ammonium acid fluoride
- Ammonium chlorocuprate
- Ethyl alcohol
- Ferric chloride
- Hydrosulphuric acid

- Potassium ferricyanide
- Potassium permanganate
- Molybdenum trioxide
- Oxalic acid

Scanning Electron Microscopy (SEM)

Because of limits in optical microscope it became necessary to develop a method where electron wave instead of light can be used for surface structural details by reflection method. This led to the development of scanning electron microscope (SEM), where a finely pointed electron beam of diameter less than 10 mm scans the sample point-by-point and line-by-line. Simultaneously, the electron beam of a cathode ray tube scans the display surface synchronously. The brightness of the corresponding point on the display tube increases with increase in the amount of electrons. Thus bright, dark and shades of gray in combination give the picture on the display tube. Because of the finally pointed and cylindrical cross-section of the electron beam, the same small area of specimen surface is excited into emitting electrons, regardless of whether these are elevated or low-lying. This gives the excellent depth of focus shown by SEM images. Image contrast is obtained by the angle of inclination of the specimen to the electron beam while the resolution is determined by the diameter of the area of emission of secondary electrons on the object being examined. A resolution of less than 10 μm (100 A°) can be achieved. The resolution is less with back-scattered electrons or emitted x-rays (approximately 100 nm). Useful magnification of SEM for metallurgical studies extends from 25 × to as high as 50,000 ×.

In case of failure analysis, examination of fracture surfaces of the as received surface should be first examined, followed by examination of cleaned surface. Cleaning is done in an ultrasonic bath using either aqueous solution used by watchmakers or alcohol, acetone or ether. Firmly adherent rust layers on the surface can be removed in a saturated solution of ammonium hydrogen citrate in the ultrasonic bath. Figure 13.6 shows a trans-crystalline fractured surface of a stainless



Fig. 13.6 Typical trans crystalline fracture of stainless steel which failed due to CSCC in hydrodesulphuriser [5]

steel drain valve which failed due to CSCC from which rust layer has been removed by ultrasonic cleaning [5].

Microanalysis by Means of SEM

X-rays emitted by incident of electrons on the specimen can be used to analyse the elements contained in the sample. For this purpose, both the detector systems i.e. energy dispersive or wavelength dispersive systems are used.

Energy-Dispersive System
In the SEM, energy dispersive x-ray (EDAX) detector is located in the plane of the specimen at right angles to the primary electron beam. Electrical pulses proportional to the energy of each incident x-ray quantum, are amplified and sorted according to their energy in a multi-channel analyser. The usual specimen angle of 45° permits an excellent secondary image to be formed, gives a favourable collection angle for the x-ray quanta and allows analysis at various points on irregular surfaces to be carried out.

The advantages of the energy dispersive system are:

- High speeds as no mechanical adjustments are required.
- All elements between sodium and uranium can be simultaneously detected.
- Small particles can be selected using the secondary electron mode even on rough samples.
- Qualitative analyses and distribution images of elements can be obtained out on large surface up to 7×5 mm^2 and on an even or rough surface.

Wave Length Dispersion System
Wavelength dispersive systems make use of the refraction of x-rays at crystal lattice planes. The characteristic diffracted x-rays are then counted in a gas-filled or gas-containing proportional counting tube.

13.4.3.3 Some Case Studies

Given below are summary of some case studies where the causes of failure could be identified using advanced techniques.

(1) ***Leakage of A 5Cr–0.5Mo (P5) Heater Tube***

A P5 heater tube in a refinery was replaced after ~22 year service because of thinning. After only one year leak occurred at tube to bend weld, which resulted in a small fire. The fire was not serious because the joint was outside the furnace box. Visual examination indicated the attack to be confined to the weld only, forming a deep groove (Fig. 13.7). A detailed investigation was conducted, including EDAX analysis of weld and base metal which showed chromium content of ~1.0 and 5.5%, respectively. The analytical spectrum of the weld is shown in Fig, 13.8. As

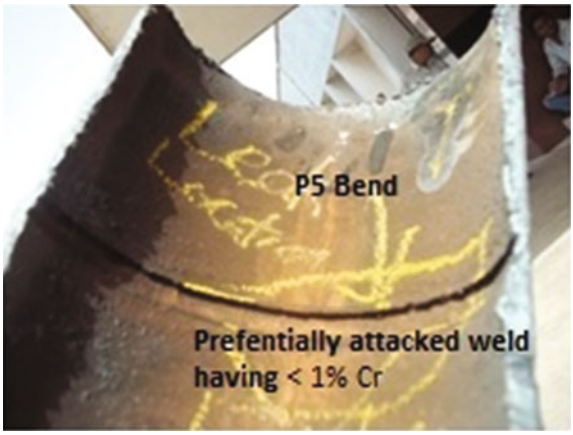


Fig. 13.7 Preferential attack of P5 heater tube weld

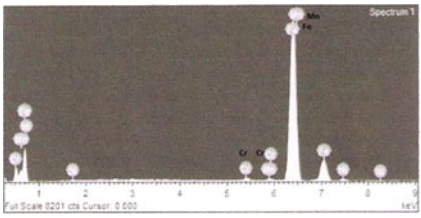


Fig. 13.8 EDAX spectra of weld showing low chromium [6]

regards Mo, the base metal had 0.50%Mo but the same was not detected in the weld [6]. Higher level of hardness of HAZ compared to weld and base metal, was an indirect evidence of the weld being of low alloy steel with very low chromium content. The study clearly indicated the failure to be due to use of wrong electrode. In this case PMI of the heater tube and bend was done but not of the electrode used for welding.

(2) ***Corrosion of Carbon Steel Condenser Tubes***

To investigate frequent leakage of carbon steel condenser tube detail analysis was carried out for different constituents present in the rust layer, using EDAX technique. The major observations are summarized in Table 13.4 [6] with elements comprising the inhibitor shown in bold letters. The main conclusions drawn were:

Table 13.4 Possible sources of various compounds identified in rust

Location	Constituents	Possible sources
Bottom of rust	C; O; Cl; S; Fe;	C–HC + Bio; O–Iron and Other Oxides: S–Sulphate; Fe–Iron Oxide; Cl–NaCl
Middle of rust	C; O; Mg; Al; Si; **P**; Cl; S; Fe;	C–HC + Bio; O–Oxides of Fe, Si, and Al,: S–Sulphate; Fe–Iron Oxide; P–Phosphate (inhibitor) Cl–NaCl/Mg Cl_2
Top of rust	C; O; Mg; Si; **P**; Cl; Ca; S; Fe; **Zn**	C–HC + Bio; O–Oxides of Fe and Si; S–Sulphate; Fe–Iron Oxide**; P–**Phosphate (inhibitor) Cl–NaCl/Mg Cl_2; Ca–Scale; **Zn**–(Inhibitor)

- Rust nearest to the metal surface consists of mainly corrosion product of iron and there is no indication of the presence of corrosion inhibitor added to cooling water (zinc/poly phosphate treatment).
- The top of the rust layer appears to be mixture of rust, suspended solids and surprisingly a large amount of zinc and phosphorous, which were added as corrosion inhibitor. Actually zinc and phosphorous, being inhibitors, should be in the bottom most layers but their complete absence indicates that inhibitors are being prevented from reaching the metal surface, reducing their efficiency against corrosion and causing under deposit corrosion.

13.4.3.4 Field Microscopy

Metallographic examination by normal techniques, e.g. optical, SEM, etc. requires that samples should be removed from the concerned component, which is not always possible in case of operating equipment unless it is to be replaced because of total failure. While this approach is a must in case of sub surface defect or where through thickness damage assessments are required, in many instances study of exposed surface is sufficient to give the desired information. In such cases, examination has to be made directly on the component in situ (on-site). To meet this need, field metallography consisting of tools for grinding, polishing, etching and lightweight optical microscopes, which can be carried to the site, was developed. In spite of special attachments to hold the microscope on the component, this technique proved to be too cumbersome with difficulties in getting good image for study or taking photographs. Further, examination could not be carried out at higher magnifications to reveal structural details.

Development of replication technique has dramatically changed the situation and provided a tool that can be used to examine structural details both optically and by SEM. This method can also be utilized to examine and chemically and structurally identify precipitated particles by extraction techniques. The principle of surface replication technique is to reproduce the surface metallurgical structure on a film, which can subsequently be examined under the microscope. The basic steps involved are: (i) grinding selected surface with different grit emery papers, (ii) polishing with diamond paste, (iii) repeated polishing and etching with a suspension of alumina or diamond paste and etching solution to get a high degree of finish and clarity of structure, (iv) replication of prepared surface by firmly pressing onto it a 1–2 mils thick cellulose acetate replicating film softened by immersion in acetone, and finally, (v) peeling of the replica when it becomes dry and harden (Fig. 13.9) [6]. This film then can be examined under optical or scanning electron microscope. For further clarity, the primary replica can be vapour coated using Cr, Al or Au/Pd on the impression side. Figure 13.10 shows replica microstructure of reformer tube OD. Replica capability has considerably improved specially with development of two component rubber gel which is applied with the help of a gun. The three dimensional replica obtained gives better details of structure.

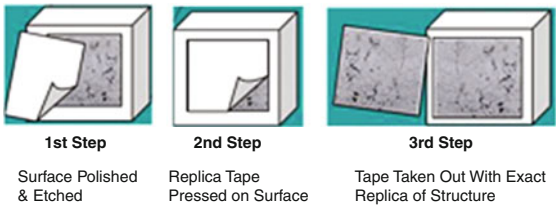


Fig. 13.9 Conventional technique for taking replica [6]

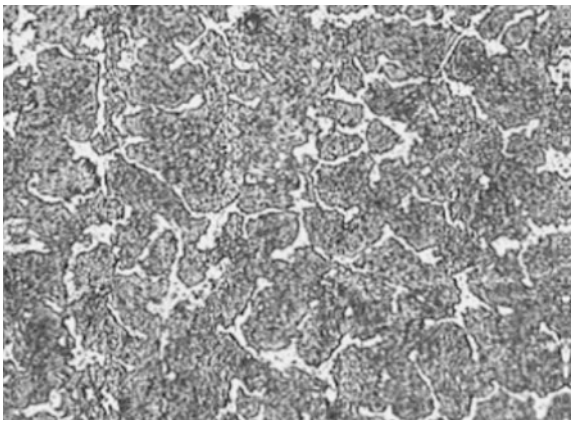


Fig. 13.10 Reformer tube replica taken using conventional technique showing primary and fine secondary carbide

For extraction replica, at the end of step (iii), the area is heavily etched, washed with alcohol and dried in air. A dilute solution of 1% Formvar resin in chloroform is applied on the surface. When dry, the film is stripped off, coated with carbon on the impression side. Small pieces of the stripped film mounted on grids are washed in acetone and acetate foil dissolved. Particles are left behind embedded in the carbon film along with micro structural impression. Investigation is carried out using scanning transmission electron microscopy (STEM) combined with energy dispersive x-ray analysis (EDAX).

13.4.4 X-ray Diffraction

When any matter solidifies the atoms are arranged in a geometrical order, which is specific for the concerned matter. These are known as crystals and the whole matter is built up of three-dimensional stacking of these crystals as discussed in Chapter 4. When observed in totality, the atoms can be represented by spheres just touching one another and stacked one over the other in a format typical of the crystals. These atoms, when connected form specific planes, represented by Miller indices, e.g.

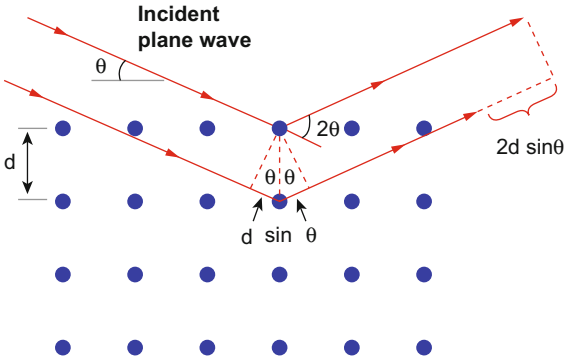


Fig. 13.11 Scattering of x-rays from crystal planes

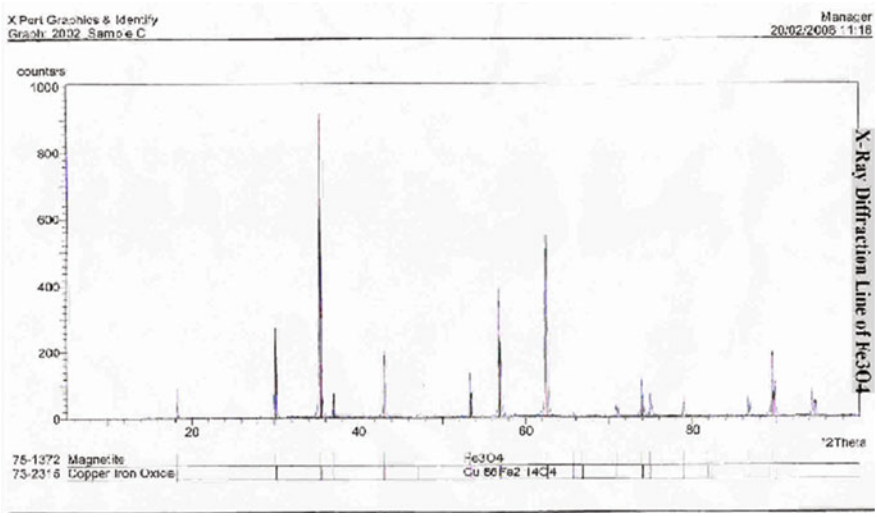
(111), (100), etc. Using x-ray technique the type of crystals can be identified on the basis of reflection of x-rays from different planes. Different planes give separate peaks as the angle of reflection θ is related to the spacing of atomic planes (d), the wavelength of the x-rays (depends on x-ray source) by Bragg equation:

$$n\lambda = 2d \sin\theta \quad \text{where, } n \text{ is an integer.} \tag{13.4.1}$$

The narrow pencil of monochromatic x-rays directed at a solid, are reflected from the various planes of atoms (Fig. 13.11) at an angle to the axis, specific for a particular plane. The sample is rotated about the diffractometer axis and a counter, rotated at twice the angular velocity picks up the diffracted x-rays and the intensity of the beam is directly recorded on a chart against the angle. Thus spacing (d) of the various atomic planes and also the unit size of the plane, related to the crystal structure are obtained. Similar to x-ray diffraction, electron diffraction can also be used to determine crystal structure. X-ray diffraction forms an important tool in MFA as it reveals (i) crystal structure and thus identification of elements and compounds, (ii) grain size, (iii) increase in lattice parameter, (iv) internal stresses, etc. It also helps in identifying the chemical compounds formed as a result of attack on metals. Figure 13.12 shows x-ray scan of reaction product in methanation reactor of hydrogen plant [6]. While x-ray is basically a laboratory tool, a smaller and lighter version, suitable for field use, is also now available. This forms a handy tool for in situ measurement of weld residual stresses in case of mechanical failures and stress corrosion cracking.

13.4.5 Non Destructive Examination (NDE) Techniques

Some of the NDE techniques are also useful in failure examination to determine types of defects and their sizes, especially when tests are to be done on failed equipment itself or on large size samples. Some of the commonly used techniques are given below.



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Fig. 13.12 X-ray scan of reaction product from methanation reactor

13.4.5.1 Dye Penetrant (DP)

It is a sensitive non-destructive method of detecting minute defects, e.g., cracks, shrinkage and porosity which open-up on the surface. Parts or areas to be tested are smoothened, cleaned and then treated with a penetrant. After some time the surface is wiped clean and then followed by spraying with a suspension of powder known as developer, which acts as sponge in drawing the penetrant inside the defect. In case of normal DP, contrasting colours of penetrant (normally red) and developer (normally white) are used. In case of fluorescent penetrant (no developer is required) the penetrant contains a material that emits visible light under ultraviolet radiation, for which the black lamp is used. Of the two, the latter shows up fine defects more clearly. For penetrant examination, careful surface preparation is essential. Use of heavy grinder should be avoided so that the surface of the defect is not closed due to deformation of metal and indication is masked. Figure 13.13 shows identification of under insulation crack on SS alcohol distillation tower [6].

13.4.5.2 Magnetic Particle Inspection (MPI)

A technique that is very much similar and more sensitive than DP, except that the penetrant used contains suspension of fine black iron power. After application of developer (normally white) a magnetic field is applied using permanent magnet or electromagnet (AC or DC). The iron powder under the influence of magnetic field aligns itself, perpendicular to the field, along the defect. The basic principle is



Fig. 13.13 DP of crack (*inset*) on SS alcohol distillation tower [6]

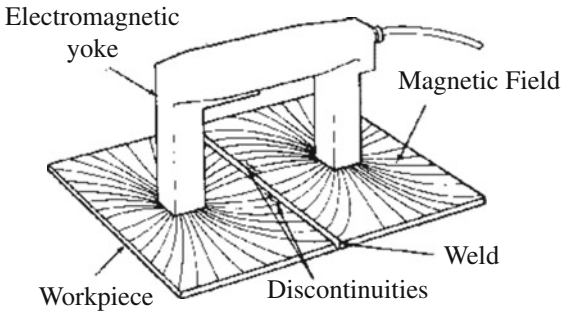


Fig. 13.14 Principle of magnetic particle inspection

shown in Fig. 13.14. If fluorescent material is used with the penetrant, no developer is required and the aligned iron powder particles become visible under black light (ultra violet). Yoke type hand held magnets are normally used. Same care as for DP is to be taken in case of dry and wet MPI. Sand blasted surface is preferred to ground surface. The advantage of MPI is that it can detect not only surface opening but also sub-surface defect up to 1–2 mm below the surface. However, this method is applicable only in case of ferromagnetic materials.

13.4.5.3 Ultrasonic Testing Technique

Ultrasonic testing is a versatile tool used for measuring thickness, location of internal defects and also measuring and sizing of cracks when doing failure analysis. Other important uses are in detecting internal lamination or de-bonding of clad plates, weld defects, etc. Ultrasonic uses sound waves above the audible range, normally with a frequency of 1–5 MHz (cycles per second), which in special cases may also be 10 or 15 MHz. Two common methods are based on transmission and pulse-echo. Considerable advances have been made in use of ultrasonic technique. It is possible to get direct digital readings for thickness, more correct mapping of

internal defects and also a three dimensional picture of defects. Thus automated ultrasonic has become one of the most important tools to detect sub-surface defects. The various techniques available are A, B and C-scan, Time of Flight Diffraction (TOFD), etc.

13.4.5.4 Radiography

The basic principle of radiographic examination of metallic objects is the same as in any other form of radiography. Any discontinuities decrease the attenuation of the x-ray and produce greater exposure on the film (darker areas on the negative film). On the other hand, any increase in density and thickness would increase attenuation and produce lighter area. Using radiographic technique (RT) it is possible to detect cracks and wall thickness. RT depends on density differences, so cracks with tightly closed surfaces are much more difficult to detect than open ones.

13.4.6 Mechanical Testing

Testing to determine various mechanical properties has an important role in MFA. This is done to establish if the original material used for fabrication conformed to the specification. The other purpose is to find out if any in-service material degradation has led to the failure. The basic laboratory facilities, required for testing are well known to all engineers and these are: (a) tensile testing, (b) hardness testing (Brinell, Vickers, and Rockwell) and (c) Charpy impact testing, etc.

13.5 Stages in Failure Analysis

Industrial failure analysis based on various tests can be carried out in different stages depending on the nature and complexity of the analyses involved. Broadly these can be categorized as:

13.5.1 In-plant Failure Analysis

All large chemical process plants have well-organized inspection group. With proper manning and providing some minimum instrumental facilities, majority of failure cases can be analysed in the plant itself. The advantages of such an approach are that inspection engineers are familiar with the concerned equipment and its past history. Further, all relevant information regarding the operation and process details and concerned persons are available for constant interaction for the review of data

and discussion. In cases where the equipment is to be repaired and put on-stream in shortest possible time, causes of failure are to be established based only on in situ tests and inferences from operating data and past experiences as there is no time available for calling an outside agency. For example, in case of economizer tube failure the time available for conducting any test is short and the inspection group has to make all relevant observations and collect necessary data, e.g., nature and location of attack, wall thinning, etc., collect deposits on the tube, cut and replace the affected tube and then box up the boiler for start-up. The tube samples can then be metallurgically examined, deposits analysed, based on which the causes of failure can be established. Any corrective measures required in many cases then can be introduced in shortest possible time. Similarly, in case of a leak due to cracking in a vessel, the first priority is to repair the damage and put the plant on stream. However, for long term benefit it is necessary that the importance of establishing the causes of cracking is not overlooked and the inspection and related groups have to take necessary steps to collect maximum possible data, including taking boat samples, in the short time available before the repair is done. The failure investigation should then be taken up to establish why the crack had occurred?

13.5.2 Centralized In-house Failure Analysis

For large chemical complex or companies owning number of plants, a centralized facility for undertaking the failure analysis goes a long way in the study of problems which require use of sophisticated instruments and in-depth experimental and theoretical analysis. As the centralized group gives services to number of units/plants, it is cost effective to invest in setting up a well equipped laboratory and staffed with competent personnel. The advantage of such an arrangement is that in-house specialists are familiar with the operation of various units and, therefore, they require less of interaction with plant personnel than an outside investigating agency. Further, it becomes possible to centralize all failure histories for future reference. The failure experiences can also be passed on to the other sister plants to take preventive actions for equipment used in similar service.

13.5.3 Failure Analysis by Outside Specialist

The importance of failure analysis is realized, but many organizations either do not have the necessary in-house facilities or are too small to have one. In such cases, the failure analysis can be done by an outside specialist having access to well established laboratory and knowledgeable engineer/scientists from different disciplines as many problems require multi-disciplinary inputs. Outside specialists being unfamiliar with the process details and the design of equipment, in most of the cases require greater input and interaction with plant engineers. Unless such a feedback is

provided, the conclusions and especially the solutions will either not be a correct one or impractical to implement. Unfortunately, the information passed on for the investigation is generally sketchy. It is, therefore, essential that relevant field observations should also sent along with the failed sample. A visit to the plant and vice versa by concerned investigators, where possible, is of great help. Further, during investigation constant dialogue between the specialists and the counterpart in the plant is required to be maintained.

13.6 Analysis of Data and Recommendations

Data and information collected for MFA are to be analysed carefully to establish the root cause of failure. Data collection and simultaneous analysis are on-going process throughout the period of study. It is not necessary in all cases to undertake each and every step discussed above. To reach the conclusion in shortest possible time, the objective should be to collect minimum amount of information required for the purpose. After final analysis of data and establishing causes of failure, suitable corrective measures are to be recommended. The corrective action normally would consist of one or more of the followings:

- *Material Change:* Upgradation of metallurgy.
- *Design Modifications:* Avoiding sharp corners or notches, providing longer radius bends, change of water from shell to tube side, providing suitable expansion joints, rerouting of piping, introduction of sleeves, providing impingement plates, stress analysis, etc.
- *Corrosion Control Measures:* Introducing or changing type of inhibitors, neutralizing or water treatment chemicals, providing coating or lining, installing cathodic or anodic protection systems, etc.
- *Heat Treatment:* Post-weld heat treatment, solution annealing, etc.
- *Operational Changes:* Decreasing temperature, de-rating of vessel, introducing stricter controls on operating parameters, on-stream monitoring, vibration monitoring, etc.

In any recommendations made, the following points need to be kept in view:

- It should be as far as possible easy to implement.
- Any shutdown required for implementation is to be of as short duration as possible.
- Ensuring easy availability and maintainability of modifications.
- The recommendation should suit the budget of the company. The best solution may not always be possible to implement. In such a case alternate solutions, which may not be as effective as desired, should be suggested. It should be left to the users to select to what extent he would accept future failures or short life compared to the cost of various alternatives.

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