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CORROSION AND DEGRADATION OF METALLIC MATERIALS

Understanding of the phenomena
and applications in petroleum
and process industries

Preface by

Yves CHAUVIN

Nobel Prize in Chemistry 2005

Translated from the French

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Preface

I was honoured by François Ropital's request to introduce his book which provides an update of the knowledge on the understanding and prevention of the main phenomena causing corrosion and degradation of metallic materials in the petroleum and process industries.

As we will see throughout this review of the mechanisms involved, corrosion is a serious problem encountered at every stage in the production, transport, refining and chemistry of oil, especially due to the consequences of the resulting unplanned stoppages.

Due to the nature of the role it plays in this domain, IFP is well aware of the problems related to corrosion in the petroleum industry; this of course explains why companies frequently rely on its expertise.

Nearly twenty years ago now, I liked to visit the "museum" created by the sadly missed Yves Lefebvre, who at the time was responsible for corrosion problems at IFP. Amongst all the "horrors" exhibited, the one that impressed me the most was bacterial corrosion which had made a perfectly cylindrical hole in the bends of steel tubes over 10 mm thick!

I also remember more serious problems, such as mercury corrosion of aluminium exchangers in a natural gas liquefaction plant in Algeria; it took quite some time to discover that the corrosion was in fact due to mercury contained in the gas itself.

Personally during my career at IFP, I have never been faced with problems related to corrosion, since the various processes I studied only involved relatively pure olefins under moderate temperature conditions. For instance, after a few preliminary investigations on specimens, the lifetime of the carbon steel used to manufacture the reactor was found to be very long, not suffering any corrosion: although the reaction medium contained Lewis acids such as aluminium chloride, the corrosion mechanism was blocked by absence of protons.

This book benefits from several decades of experience acquired by IFP in the field of corrosion. It undoubtedly represents an effective vector in the transfer of knowledge of the processes involved in the corrosion of metallic materials and its prevention.

Yves Chauvin
Nobel Prize in Chemistry 2005

Contents

Preface	XI
Acknowledgements	XIII
Introduction	XV

Chapitre 1

MAIN CORROSION PHENOMENA ENCOUNTERED IN OIL AND GAS PRODUCTION, REFINING AND PETROCHEMISTRY INDUSTRIES: CORROSION MECHANISMS AND PREVENTIVE SOLUTIONS

1.1	Presentation	1
1.2	Carbon dioxide corrosion	3
1.2.1	Equipment concerned by CO ₂ corrosion	3
1.2.2	Mechanisms and parameters influencing CO ₂ corrosion	4
1.2.3	Example of CO ₂ corrosion	7
1.2.4	Acidity and CO ₂ corrosion prediction models	8
1.2.5	Prevention of CO ₂ corrosion	8
1.3	Corrosion by water containing H₂S	8
1.3.1	Equipment concerned by H ₂ S corrosion	8
1.3.2	Mechanisms and parameters influencing H ₂ S corrosion	9
1.3.3	Selection of materials for use in H ₂ S environment	13
1.4	Corrosion by mercury and liquid metals	13
1.4.1	Equipment concerned by mercury corrosion	13
1.4.2	Mechanisms involved in mercury embrittlement of aluminium	14
1.4.3	Example of mercury corrosion	14
1.4.4	Other metallic materials sensitive to liquid metal embrittlement	15
1.4.5	Prevention of liquid metal embrittlement	15
1.5	Corrosion by the bacteria present in water, soil and crudes	16
1.5.1	Stakes of biocorrosion in the petroleum industry	16
1.5.2	Means used to detect and combat biocorrosion	17
1.5.2.1	Use of non-corrodable materials	17

1.5.2.2	Construction of a non aggressive bacterial environment	17
1.5.2.3	Use of bactericides.	17
1.5.2.4	Use of cathodic protection	19
1.5.2.5	Protective coatings.	19
1.5.2.6	Detection of corrosive micro organisms.	19
1.6	Corrosion caused by the chlorides present in water	20
1.6.1	Equipment concerned by corrosion due to chlorides present in water.	20
1.6.2	Mechanisms and parameters influencing corrosion by water containing chlorides.	20
1.6.3	Example of corrosion by water containing chlorides	22
1.6.4	Prevention of localised corrosion of stainless steels by water containing chlorides.	22
1.7	Hydrolysis of chlorides into HCl	23
1.7.1	Equipment concerned by hydrolysis of chlorides into HCl	23
1.7.2	Mechanisms and parameters governing corrosion	23
1.7.3	Example of corrosion by HCl formed by hydrolysis of chlorides.	25
1.7.4	Prevention of corrosion by HCl formed by hydrolysis of chlorides	25
1.8	Corrosion by concentrated acids: HCl, H₂SO₄ or HF	26
1.8.1	Corrosion by concentrated hydrochloric acid.	26
1.8.1.1	Equipment concerned by HCl corrosion.	26
1.8.1.2	Mechanisms and parameters governing HCl corrosion	26
1.8.1.3	Example of HCl corrosion	27
1.8.1.4	Prevention of HCl corrosion	27
1.8.2	Corrosion by concentrated sulfuric acid	27
1.8.2.1	Equipment concerned by H ₂ SO ₄ corrosion.	28
1.8.2.2	Mechanisms and parameters governing H ₂ SO ₄ corrosion	28
1.8.2.3	Example of H ₂ SO ₄ corrosion	29
1.8.2.4	Prevention of H ₂ SO ₄ corrosion	29
1.8.3	Hydrofluoric acid corrosion.	30
1.8.3.1	Equipment concerned by HF corrosion	30
1.8.3.2	Mechanisms and parameters governing HF corrosion	32
1.8.3.3	Example of HF corrosion	33
1.8.3.4	Prevention of HF corrosion.	33
1.9	Stress corrosion in alkaline and quasi-neutral media	34
1.9.1	Caustic stress corrosion.	34
1.9.1.1	Equipment concerned by caustic corrosion.	34
1.9.1.2	Mechanisms and parameters governing caustic corrosion	34
1.9.1.3	Example of caustic corrosion	34
1.9.1.4	Prevention of caustic soda corrosion	34
1.9.2	Carbonate stress corrosion.	36
1.9.2.1	Equipment concerned by carbonate corrosion.	36
1.9.2.2	Mechanisms and parameters governing carbonate corrosion	36
1.9.2.3	Example of carbonate corrosion	37
1.9.2.4	Prevention of carbonate corrosion	37
1.9.3	Stress corrosion in near neutral medium	38
1.9.3.1	Equipment concerned by corrosion in near neutral medium	38
1.9.3.2	Mechanisms and parameters governing corrosion in near neutral medium	38
1.9.3.3	Example of corrosion in near-neutral medium	38
1.9.3.4	Prevention of corrosion in near-neutral medium	38

1.10 Alcohol (methanol and ethanol) corrosion	39
1.10.1 Equipment concerned by alcohol corrosion	39
1.10.2 Mechanisms and parameters governing methanol corrosion	39
1.10.3 Mechanisms and parameters governing ethanol fuel corrosion	40
1.10.4 Example of ethanol corrosion	40
1.10.5 Prevention of alcohol corrosion	40
1.11 Corrosion by acid gas chemical solvents	41
1.11.1 Introduction: principles of acid gas removal by chemical solvents	41
1.11.2 Mechanisms and parameters governing corrosion in acid gas treatment plants	43
1.11.2.1 Acid gas corrosion	43
1.11.2.2 Corrosion by amine solution	44
1.11.3 Equipment concerned by corrosion	45
1.11.3.1 Absorber	45
1.11.3.2 Rich amine lines	45
1.11.3.3 Rich/lean amine exchanger	46
1.11.3.4 Regenerator and acid gas outlet (condenser, reflux drum)	46
1.11.3.5 Reboiler	46
1.11.3.6 Lean amine lines	46
1.11.4 Examples of corrosion by acid gas solvents	47
1.11.5 Prevention of corrosion in acid gas treatment units	47
1.11.5.1 Operating conditions of the units	49
1.11.5.2 Use of corrosion inhibitors	49
1.11.5.3 Corrosion monitoring	50
1.11.5.4 Choice of appropriate metallurgies	50
1.12 Corrosion by crude oil containing naphthenic acids	52
1.12.1 Equipment concerned by naphthenic acid corrosion	52
1.12.2 Mechanisms and parameters governing naphthenic acid corrosion	52
1.12.3 Example of naphthenic acid corrosion	53
1.12.4 Naphthenic acid corrosion prediction models	54
1.12.5 Prevention of naphthenic acid corrosion	54
1.13 Corrosion during the formation of polythionic acids	55
1.13.1 Equipment concerned by polythionic acid corrosion	55
1.13.2 Mechanisms and parameters governing polythionic acid corrosion	56
1.13.3 Example of polythionic acid corrosion	56
1.13.4 Prevention of polythionic acid corrosion	58
1.14 Decarburisation by high temperature hydrogen attack	58
1.14.1 Equipment concerned by high temperature hydrogen attack	58
1.14.2 Mechanisms and parameters governing high temperature hydrogen attack	58
1.14.3 Example of high temperature hydrogen attack	59
1.14.4 Prevention of high temperature hydrogen attack	60
1.14.5 Hydrogen-induced disbonding of stainless steel overlays	61
1.14.6 Hydridation of titanium equipment	61
1.15 High temperature oxidation	62
1.15.1 Equipment concerned by high temperature oxidation	62
1.15.2 Mechanisms and parameters governing high temperature oxidation	62
1.15.3 High temperature oxidation prediction models	62

1.15.4	Example of high temperature oxidation	63
1.15.5	Prevention of high temperature oxidation	64
1.16	High temperature sulfidation	65
1.16.1	Equipment concerned by high temperature sulfidation	65
1.16.2	Mechanisms and parameters governing high temperature sulfidation	65
1.16.3	High temperature sulfidation prediction models	65
1.16.4	Example of high temperature sulfidation	66
1.16.5	Prevention of high temperature sulfidation	66
1.17	Carburisation, coking, metal dusting	68
1.17.1	Coking	68
1.17.1.1	Catalytic and pyrolytic mechanisms	68
1.17.1.2	Example of pyrolytic coking	69
1.17.1.3	Prevention of coking	69
1.17.2	Metal dusting	69
1.17.2.1	Metal dusting mechanisms	69
1.17.2.2	Example of metal dusting	71
1.17.2.3	Prevention of metal dusting	71
1.17.3	Carburisation	71
1.17.3.1	Carburisation mechanisms	71
1.17.3.2	Example of carburisation	72
1.17.3.3	Prevention of carburisation	72
1.18	Molten salt corrosion	73
1.18.1	Equipment concerned by molten salt corrosion	73
1.18.2	Mechanisms and parameters governing molten salt corrosion	73
1.18.3	Example of molten salt corrosion	74
1.18.4	Prevention of molten salt corrosion	74

Chapitre 2

PREVENTION OF CORROSION AND DEGRADATION OF METALLIC MATERIALS USED IN THE PETROLEUM INDUSTRY

2.1	Corrosion prevention by appropriate selection and design of materials and equipment.	83
2.1.1	Data concerning the corrosion type and propagation rate	83
2.1.2	Control of operating parameters	84
2.1.3	Equipment design	85
2.2	Use of coatings, corrosion inhibitors or cathodic protection	87
2.2.1	Protection by coatings	87
2.2.1.1	Principle	87
2.2.1.2	Organic coatings and paints	88
2.2.1.3	Composite liner	92
2.2.1.4	Inorganic coating	93
2.2.1.5	Cladding	94
2.2.1.6	Anticorrosion cements	95
2.2.1.7	Surface treatments	95
2.2.2	Cathodic protection of structures	96

2.2.2.1	Principle	96
2.2.2.2	History of offshore and onshore applications	96
2.2.2.3	Problems encountered (design, checks of cathodic protection and cathodic overprotection, shielding, monitoring)	97
2.2.3	Corrosion inhibitors	98
2.2.3.1	Principle	98
2.2.3.2	Liquid phase inhibitors	99
2.2.3.3	Gas phase inhibitors	103
2.3	Corrosion detection, control and monitoring	104
2.3.1	Introduction	104
2.3.2	Corrosion control methods	105
2.3.2.1	Indirect methods	106
2.3.2.2	Direct methods	116
2.3.3	Detection and inspection methods	125
2.3.3.1	Non-destructive testing methods	125
2.3.3.2	Intelligent pigging	131
2.3.3.3	Inspection plans and RBI	137

Chapitre 3

FUNDAMENTALS ON METALLIC ALLOYS AND CORROSION

3.1	Basic information concerning the metallic materials used in the petroleum sector, their structure and properties	147
3.1.1	Structure of metallic alloys	147
3.1.1.1	Crystallographic structures of alloys	148
3.1.1.2	Alloy equilibrium diagrams	152
3.1.1.3	Application to the Fe-C diagram	154
3.1.1.4	Steel heat treatments: time-temperature transformation diagram	155
3.1.1.5	Metallurgical transformations during steel welding operations	158
3.1.1.6	Influence of the various addition elements on steel properties	158
3.1.2	Mechanical behaviour of metallic materials	160
3.1.2.1	Introduction	160
3.1.2.2	Tensile test	161
3.1.2.3	Elastic and plastic strain mechanisms in metals	166
3.1.2.4	Damage and failure mechanisms	167
3.1.2.5	Ductile failure and brittle failure	168
3.1.2.6	Description of mechanical stresses and behaviours	170
3.1.2.7	Types of mechanical test	174
3.1.3	Alloys used in the petroleum industry	187
3.1.3.1	Ferrous metals (iron content > 50%)	188
3.1.3.2	Non-ferrous metals	195
3.2	Basic information concerning the mechanisms involved in the corrosion of metallic materials	199
3.2.1	Information concerning the thermodynamic stability of corrosion reactions	199
3.2.1.1	Free enthalpy of a corrosion reaction	199
3.2.1.2	Ellingham diagrams	201

3.2.2	Chemical corrosion in liquid phase	202
3.2.3	Electrochemical corrosion in liquid phase	202
3.2.3.1	Electrochemical reactions	202
3.2.3.2	Faraday's law	203
3.2.3.3	Metal – electrolyte interface	203
3.2.3.4	Electrochemical thermodynamic equilibrium	203
3.2.3.5	Pourbaix diagrams: potential-pH equilibria	206
3.2.3.6	Electrochemical kinetics	209
3.2.4	High temperature gas phase corrosion	217
3.2.4.1	Main high temperature corrosive gases	217
3.2.4.2	High temperature corrosion mechanisms: oxidation and sulfidation	218
3.3	The various forms of corrosion	224
3.3.1	Uniform corrosion	224
3.3.2	Galvanic corrosion	225
3.3.2.1	Galvanic series of alloys	226
3.3.2.2	Concentration cell	226
3.3.3	Pitting corrosion	228
3.3.4	Crevice corrosion	229
3.3.5	Intergranular corrosion	230
3.3.6	Stress corrosion	231
3.3.6.1	Stress corrosion mechanisms	232
3.3.6.2	Corrosion fatigue	232
3.3.7	Erosion-corrosion	233
3.4	Bacterial corrosion	233
3.4.1	Biofilms and biofouling	234
3.4.2	Anaerobic corrosion by sulfidogenic bacteria	235
3.4.2.1	Microorganisms	235
3.4.2.2	Biocorrosion process	235
3.4.3	Corrosion by iron oxidising bacteria	236
3.4.4	Corrosion by acidogenic bacteria	237
3.5	Other damage modes – Ageing of metallic materials	238
3.5.1	Embrittlement of low alloy steels	238
3.5.1.1	Temper embrittlement	238
3.5.1.2	Creep embrittlement	239
3.5.2	475 °C embrittlement of stainless steels	239
3.5.3	Intergranular sensitisation of stainless steels	239
3.5.4	Precipitation of intermetallic phases	241
	Annexes	245
	Glossary	251
	Index	255

Main corrosion phenomena encountered in oil and gas production, refining and petrochemistry industries: corrosion mechanisms and preventive solutions

1.1 PRESENTATION

This section describes, depending on the chemical environment (and therefore the equipment and/or process), the main corrosion phenomena encountered in the petroleum industry. It also discusses the main solutions frequently used to prevent this corrosion. The mechanisms governing corrosion in these specific petroleum environments are described. If necessary, the reader may refer to the specific chapters in Section 3 provided for reference, to obtain further details concerning the corresponding basic mechanisms of the types of corrosion mentioned. Similarly, for the prevention methods, cross-references are given to chapters in Section 2 describing the techniques.

Seventeen corrosive environments found throughout the petroleum chain (from the oil well to refining or to the basic petrochemical compounds) are detailed. Some of these environments are specific to one petroleum domain (upstream, acid gas treatment, downstream) while others may be encountered in several domains. Table 1.1 lists these corrosive environments and the petroleum domains where they are encountered.

To give the reader an overview of the equipments and units concerned throughout the petroleum chain “from well to fuel” by the various environments listed in Table 1.1, a block diagram is given on Figure 1.1.



Block diagram showing the locations of corrosive agents in the petroleum industry.

Table 1.1 Lists of corrosive chemical environments detailed in Section 1 and the petroleum domains where they are encountered.

Corrosive environment	Paragraph	Oil and gas production	Acid gas treatment	Refining petrochemistry
liquid water + CO ₂	1.2	X	X	X
liquid water + H ₂ S	1.3	X	X	X
mercury and liquid metals	1.4	X		
water + bacteria	1.5	X		X
water + chlorides	1.6	X	X	X
hydrolysis of chlorides into HCl	1.7			X
concentrated acids: HCl, H ₂ SO ₄ , HF	1.8	X		X
bases: soda and carbonates	1.9			X
alcohols	1.10	X		X
acid gas chemical solvents	1.11		X	X
crude with naphthenic acids	1.12			X
polythionic acids	1.13			X
high temperature hydrogen decarburisation	1.14			X
high temperature oxidation	1.15			X
high temperature sulfidation	1.16			X
carburisation, coking, metal dusting	1.17			X
molten salts	1.18			X

1.2 CARBON DIOXIDE CORROSION

1.2.1 Equipment concerned by CO₂ corrosion

Water containing dissolved carbonic acid is corrosive to carbon and low alloy steels.

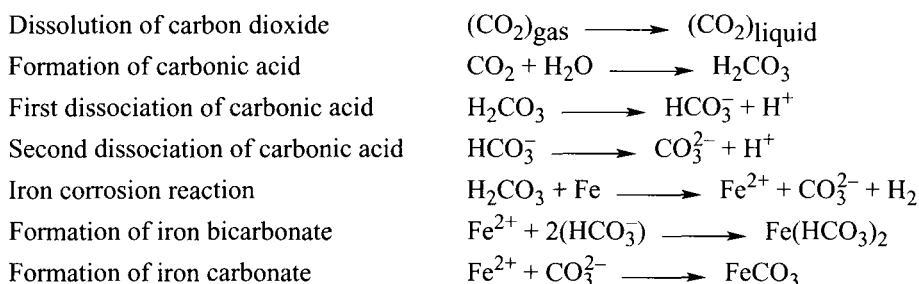
Since CO₂ is an acid gas present in all oil fields in greater or smaller quantities, this type of corrosion concerns all petroleum production equipment where free water containing carbonic acid could come into contact with carbon and low alloy steels: well tubing, wellheads, separators, pipelines, pumps, etc.

Chemical solvent decarbonation units are also concerned, in particular the overhead systems of regenerators.

For the refining units, the boiler feedwater and condensate systems are sensitive to this type of corrosion.

1.2.2 Mechanisms and parameters influencing CO₂ corrosion

Carbon dioxide dissolved in water causes several types of corrosion in carbon and low alloy steels: uniform corrosion as well as three variants of localised corrosion, viz. pitting, mesa attack and flow induced localised corrosion [98]. Carbonic acid is formed when carbon dioxide dissolves in water, producing iron carbonates and bicarbonates on reaction with carbon and low alloy steels:



The corrosion process is an electrochemical one: oxidation of iron and, due to the acidity of the aqueous electrolyte, reduction of hydrogen (for further information on electrochemical corrosion, refer to paragraph 3.2.1).

Types of corrosion caused by carbon dioxide:

- Uniform corrosion by attack of the surface, creating a layer of iron carbonate which helps to protect the metal;
- Pitting: this phenomenon appears under conditions of low flow rate at temperatures close to the dew point of water;
- Mesa attack: this localised corrosion develops in case of instability of the iron carbonate layer, at low and medium fluid flow rates. For surfaces partially covered with iron carbonate, it could also be due to galvanic coupling between the ferrite in the steel and the cementite trapped in the deposit of FeCO₃ [61];
- Flow induced localised corrosion: this form of corrosion is generally initiated by pitting or mesa attack. Due to the local flow conditions and the stresses resulting from the growth of the corrosion deposit, the deposit is torn off and an adherent protective layer of iron carbonate is unable to reform.

Main parameters influencing carbon dioxide corrosion:

Corrosion of carbon and low alloy steels by carbonic acid dissolved in water is influenced by numerous interdependent chemical, physical and metallurgical factors:

- Water composition (presence of basic or acidic elements, possibly organic acids). The acidity of the water in which the CO₂ is dissolved depends on its composition. In addition, the water composition may govern the oversaturation conditions (especially in Fe²⁺ and/or HCO₃⁻ and/or CaCO₃) which play a central role in the formation and stability of the iron carbonate layer;
- The presence, type and concentration of the hydrocarbons associated with water and the hydrodynamic conditions are also determining factors. When there is no free

water on the steel surface but adsorption of a continuous hydrocarbon film, corrosion does not occur. High flow rates and local flow conditions may tear off the corrosion deposits and accelerate corrosion;

- The partial pressure of CO_2 (or more precisely its fugacity) is a predominant parameter: CO_2 solubility is in fact directly proportional to the partial pressure. The water acidity depends on this parameter and numerous models have been developed to calculate the water pH in order to estimate a corrosion rate. When H_2S is also present, its partial pressure must also be taken into account when calculating the water acidity, as indicated on Figure 1.2;
- Temperature has a considerable effect on the nature and morphology of the corrosion deposits which form on the surface of low alloy steels. As shown on Figure 1.3, at temperatures exceeding 70°C , the low solubility of FeCO_3 and the high oversaturation of this compound favour the formation of a protective layer of iron carbonate. Below 70°C the temperature activates the process of the electrochemical dissolution of steel;
- The metallurgy of carbon, low alloy or stainless steels: the chemical composition, heat treatments and the microstructural state all affect CO_2 corrosion. The chromium content plays a dominant role, as shown on Figure 1.4: we see that addition of 3% Cr to the steel reduces its rate of corrosion by a factor of 10, due to the formation of a more protective metal carbonate. Small quantities of V, Ti, Mo, Si and Cu also help reduce the rate of corrosion of micro-alloy steels [96; 97]. When the steel contains more than 11% chromium, its surface is protected by a thin layer of oxide which is highly resistant to carbon dioxide corrosion.

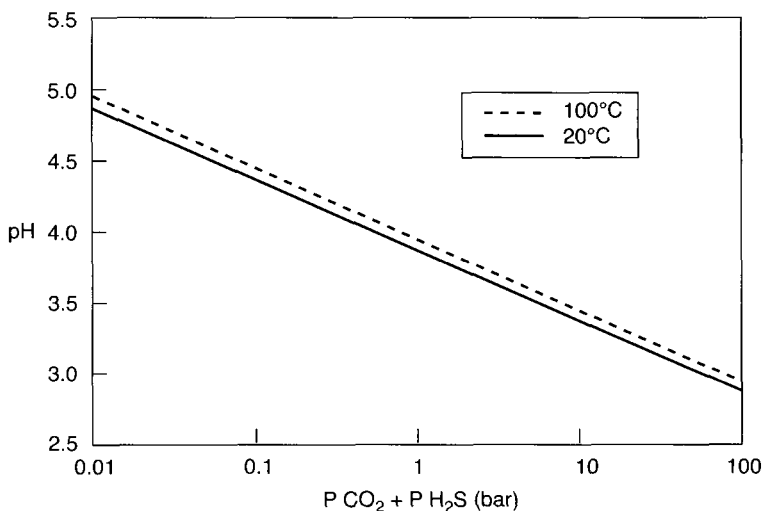


Figure 1.2

pH of condensation water under CO_2 and H_2S pressure [13].

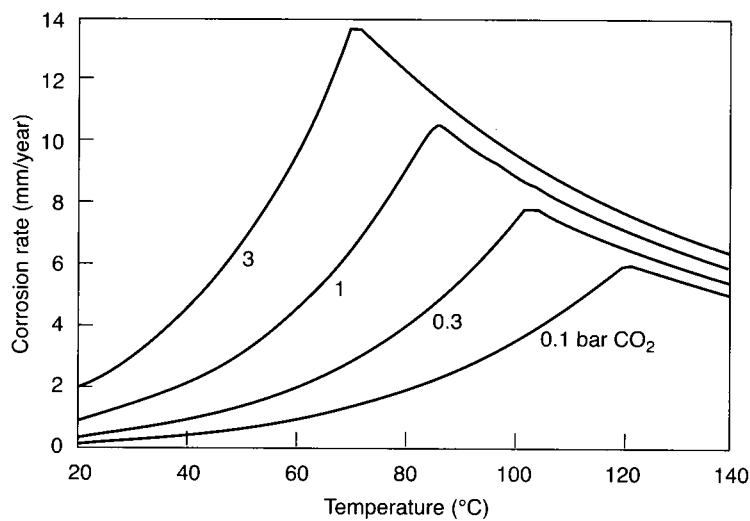


Figure 1.3
Influence of temperature and CO₂ partial pressure on the rate of corrosion of carbon steel [99].

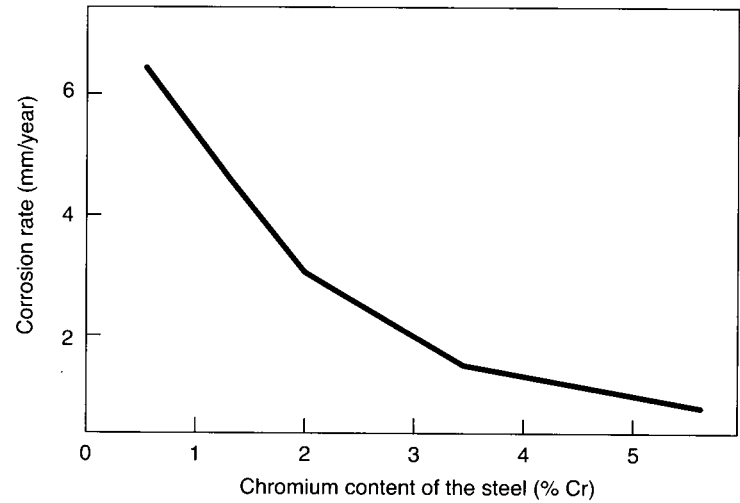


Figure 1.4
Influence of chromium content of steels on the CO₂ corrosion rate [96; 97].

1.2.3 Example of CO₂ corrosion

Heat exchanger on a refining unit:

The carbon steel exchanger is at the reactor head. It was initially designed to last one year. It allowed first cooling of the gas leaving the reactor, down to a temperature of 90 °C-100 °C.

The exchanger is double-pipe counter current type, the average temperatures of the fluids were as follows:

Process side: $T_{\text{inlet}} = 230\text{ °C}$; $T_{\text{outlet}} = 110\text{ °C}$

Cooling water side: $T_{\text{inlet}} = 100\text{ °C}$; $T_{\text{outlet}} = 90\text{ °C}$

The initial thickness of the pipe was 2.1 mm. The pressure on the pipe side was 25 bars including 2 bars CO₂ partial pressure. The speed in the pipes was about 2 m/s to 3 m/s at inlet and the quantity of liquid condensed in the pipes varied from about 200 L/h to 300 L/h.

The exchanger developed a leak after 9 months operation. The photographs on Figure 1.5 show that there is an uniform corrosion of the inside of the pipe. Temperature gradients are probably responsible for the non-uniform loss of thickness around the circumference of the pipe. The rate of corrosion observed on this exchanger is about 2.8 mm/year, a value in agreement with the predictions of the various models detailed in the next paragraph 1.2.4. For this equipment to meet the 1 year lifetime criterion, 3 mm corrosion allowance should have been specified during its design.

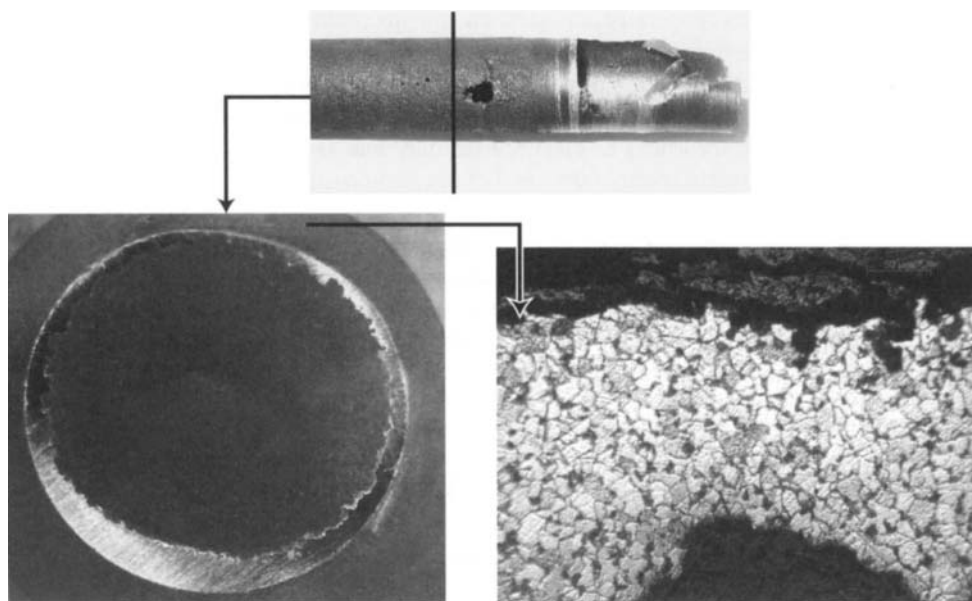


Figure 1.5

Example of CO₂ corrosion of a carbon steel exchanger pipe.

1.2.4 Acidity and CO₂ corrosion prediction models

Numerous models have been developed by the companies and research centres of the upstream petroleum domain to assess the acidity of the aqueous electrolyte and predict the range of the corrosion expected for carbon steel [30; 63; 99]. The input parameters are the water composition, temperature, partial pressures of CO₂ (and of H₂S if this gas is present), iron and calcium carbonate saturation conditions (if applicable) and for some models the hydrodynamic conditions. The corrosion rate predictions are based on laboratory estimations and feedback from oil fields. Models taking into account the physico-chemical and thermodynamic equilibria can be used to obtain the water acidity [59]. These are vital tools for the specialists, but they must not be considered as sufficient engineering means on which to base the choice of materials and their protections.

1.2.5 Prevention of CO₂ corrosion

The main methods used to prevent CO₂ corrosion are:

- Injection of amine-, amide- and imidazoline-based corrosion inhibitors and, more recently, biodegradable additives such as polyamino acids, polysuccinates and polyaspartates. For further information on the use of these inhibitors, the reader can refer to paragraph 2.2. A corrosion *allowance* is often recommended to make up for any malfunction of the inhibition system: it can be estimated using the models mentioned in the previous paragraph while remaining compatible with the design rules (6 mm corrosion allowance is generally considered as the maximum value not to be exceeded);
- For steam condensers and hot wet acid gas pipelines using glycol to control the formation of hydrates, injection of neutralising agents to raise the pH above 6;
- Use a stainless steel whose composition will be selected not according to the CO₂ partial pressure but according to the water salinity and temperature: martensitic (AISI 400 series), austenitic (AISI 300 series) or austeno-ferritic (duplex) stainless steels for well tubing, pipes and pipelines;
- Use of corrosion resistant coatings or cladding:
 - organic coatings (especially for areas where water accumulates) in pressure vessels only,
 - cladding made from stainless steel or even nickel alloys for pressure vessels and pipelines (especially if the water contains large quantities of mineral or organic acids in addition to dissolved carbonic acid).

1.3 CORROSION BY WATER CONTAINING H₂S

1.3.1 Equipment concerned by H₂S corrosion

Like CO₂, hydrogen sulfide is an acid gas easily soluble in water. In aqueous solution, the corrosivity of H₂S with respect to carbon and low alloy steels is very similar to that of CO₂. H₂S has an addition characteristic however: it strongly promotes the absorption of hydrogen in steels and leads to problems of hydrogen embrittlement and cracking.

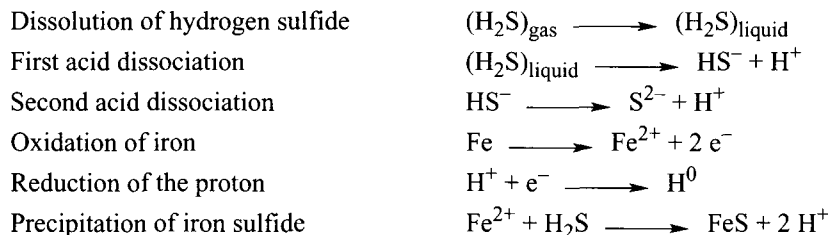
Since H_2S is an acid gas present in numerous oil fields, these types of corrosion concern all production equipment where free water containing hydrogen sulfide could come into contact with carbon and low alloy steels: well tubing, wellheads, pipes, pressure vessels, pipelines, pumps, etc.

Acid gas removal units are also concerned, in particular the overhead system of regenerators.

For the refining units, the boiler feedwater and condensate systems are sensitive to these types of corrosion.

1.3.2 Mechanisms and parameters influencing H_2S corrosion

Concerning uniform corrosion of steels, the action of hydrogen sulfide dissolved in water is very similar to that of CO_2 . H_2S is in fact more soluble but less acidic than CO_2 , the result being that the final pH of the solution is almost the same for a given partial pressure of H_2S or CO_2 . The corrosion reactions are mostly oxidation of the iron and reduction of the proton (for further information on electrochemical corrosion, refer to paragraph 3.2.1). In the presence of H_2S , the main corrosion product formed is iron sulfide (Mackinawite) which may, under some conditions, form an adherent protective deposit on the surface of steels. In this case, the corrosion rates are significantly lower than those encountered in pure carbonic medium. It is generally considered that the presence of H_2S reduces the severity of uniform corrosion as compared to pure CO_2 media. The mechanism of aqueous H_2S corrosion can be described as follows:



Nevertheless, the major risk in the presence of H_2S is not uniform corrosion but the various forms of cracking due to hydrogen embrittlement. Further to the proton reduction reaction, the atomic hydrogen has two distinct options:

- it can either react with another hydrogen atom to form a molecule of di-hydrogen (H_2) in solution (recombination),
- or penetrate the metal as absorbed hydrogen (absorption).

Both reactions occur on the surface of the metal and involve adsorbed intermediates. In the presence of H_2S , the equilibrium between these two reactions (recombination vs. absorption) is shifted strongly towards absorption. The precise mechanism has not been clearly established: some authors [41] consider that the H_2S adsorbed on the surface of the steel acts as poison to hydrogen recombination, favouring the migration reaction; others [57; 58] suggest a mechanism of direct migration of the hydrogen from solution into the metal, via adsorbed H_2S . Whatever the exact mechanism, we must remember that the presence of H_2S favours the migration of atomic hydrogen into the metal, causing specific problems of embrittlement which may lead to cracking. These failure modes represent the main risk in H_2S medium.

The main forms of steel cracking in H_2S media, as defined by NACE MR0175/ISO15156-1 [12] and NACE MR 0103 [24] are:

- *SSC (Sulfide Stress Cracking)*: “cracking of metal involving corrosion and tensile stress (residual and/or applied) in the presence of water and H_2S ”.

This type of failure is mainly encountered in high strength metallic materials, like tubing, casing, wire line, etc. or in hard weld zones;

- *HIC (Hydrogen Induced Cracking)*: “planar cracking that occurs in carbon and low alloy steels when atomic hydrogen diffuses into the steel and then combines to form molecular hydrogen at trap sites”. HIC takes two different forms:

- *blistering* when the mechanical characteristics of the steel are low enough to accept deformation,
- *stepwise cracking*, “cracking that connects hydrogen induced cracks on adjacent planes in a steel”.

This failure mode mainly affects rolled steels with low or medium mechanical characteristics (rolled welded pipes, steel plate for pressure vessels, etc.) that have a high density of planar inclusions and/or regions of anomalous microstructure produced by segregation of impurities (especially MnS inclusions) and alloying elements;

- *SOHIC (Stress Oriented Hydrogen Induced Cracking)*: “staggered small cracks formed approximately perpendicular to the principal stress (residual or applied) resulting in a ladder-like crack array linking (sometimes small) pre-existing HIC cracks”;
- *SCC (Stress Corrosion Cracking)*: “cracking of a metal involving anodic processes of localised corrosion and tensile stress (residual and/or applied) in the presence of water and H_2S ”. This type of cracking is found mainly in Corrosion Resistant Alloys (CRAs) in the presence of chlorides.

Figures 1.6 to 1.9 illustrate some of these cracking modes.

The main parameters affecting the severity of the medium with respect to risks of H_2S cracking are the pH, H_2S partial pressure, chloride content and temperature.

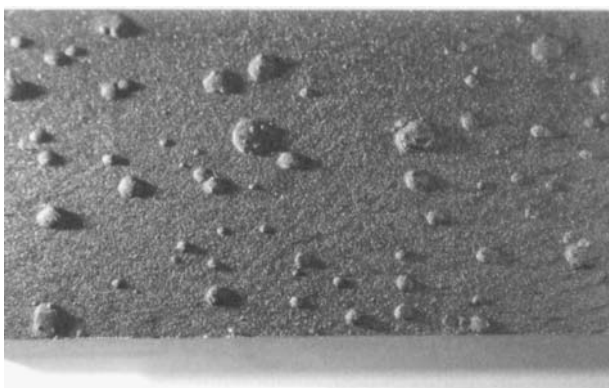


Figure 1.6

HIC blisters at the surface of a low alloy steel.

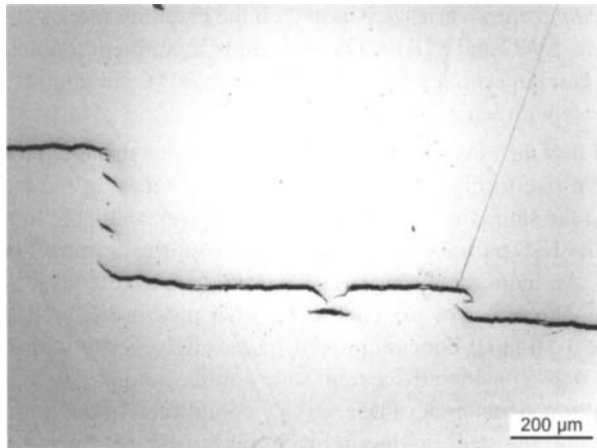


Figure 1.7

Cross section showing SWC.

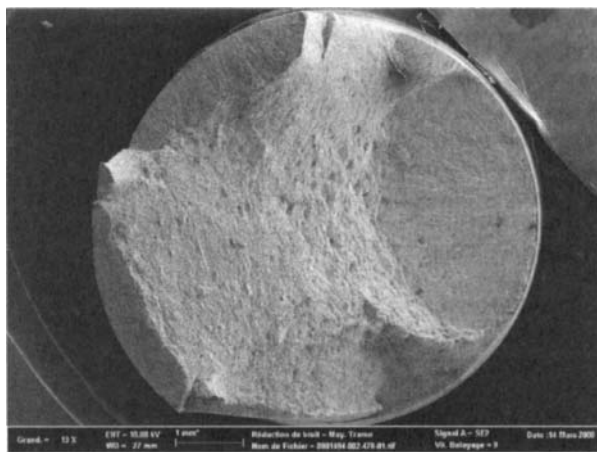


Figure 1.8

SEM image of a fracture surface typical of SSC after uniaxial tensile test in H_2S medium.

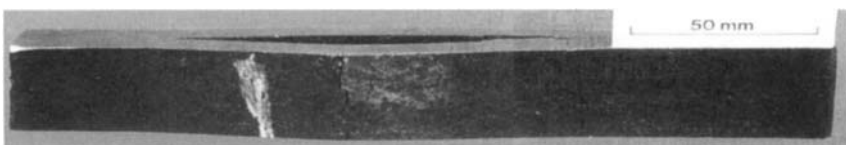


Figure 1.9

Elongated blister associated with mid-wall HIC in a portion of pipeline [55].

The impact of *temperature* varies depending on the cracking modes considered. SSC and HIC (and the variants SWC and SOHIC) occur mainly at ambient temperature. The risks of encountering these cracking modes drop sharply above 60 °C. In contrast, the risks of SCC type cracking increase with temperature.

The effect of pH and the effect of H₂S partial pressure are strongly related. Lower values of pH generally give rise to higher corrosion rates, by increasing the cathodic reaction of proton reduction. At the same time, the quantity of hydrogen available to penetrate the metal is also increased. The H₂S partial pressure also has a significant impact on the migration of hydrogen into steel. An increase in the H₂S partial pressure accelerates the rate of hydrogen migration. *For SSC*, the effect of pH and H₂S partial pressure is well known and can be described by Figure 1.10 [13]. Four regions of increasing severity with respect to SSC are identified. Region 0 is considered as non sour service and no special precautions are required when selecting steels under these service conditions. In contrast, region 3 is qualified as sour service and the steel grades and welding procedures for use under these conditions must have been approved by strict SSC resistance tests.

For HIC, no severity diagram of this type is currently available. As with SSC however, the risks of HIC type cracking increase with H₂S partial pressure and acidity of the medium.

Lastly, *the chloride concentration* mainly affects Corrosion Resistant Alloys (CRAs). Damage to the passive oxide film by halide ions may form SSC or SCC crack initiation areas.

Metallurgical parameters are also important factors controlling resistance to the various forms of cracking.

HIC and its derived forms (SWC, SOHIC) mainly affect carbon or low alloy steels with low or medium mechanical characteristics. Highly oriented microstructures (rolled products)

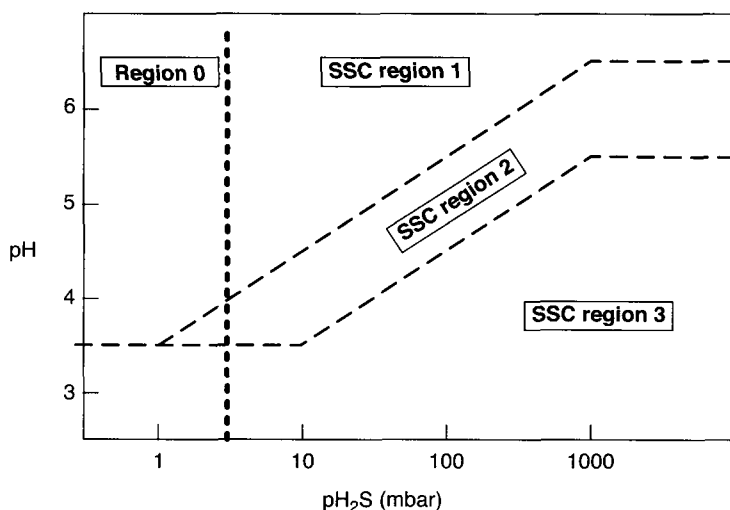


Figure 1.10

SSC severity diagram according to standard ISO15156-2.

are unfavourable, as well as the presence of inclusions, which form areas where hydrogen can be easily trapped. The most unfavourable chemical elements are sulfur and manganese, which may contribute to the formation of elongated manganese sulfide inclusions. With this respect a typical limit of 0.003% by weight of sulfur is generally required for flat-rolled products for use in H₂S service.

SSC primarily affects high yield strength steels and requires the presence of applied or residual stress. Welds are weak points and Post Weld Heat Treatment (PWHT) is generally required. The microstructure also plays a important role. For CRAs, the most sensitive microstructures are ferritic and martensitic. For austenitic and duplex grades, the main cracking mode to be considered is SCC.

1.3.3 Selection of materials for use in H₂S environment

To limit the risks of cracking, the materials and welding procedures for use in H₂S environment must be chosen according to strict selection procedures. The recent NACE MR0175/ISO 15156 series of standard documents summarises the recommendations for selection or qualification of materials for use in H₂S-containing environments in oil and gas production. The first part [12] presents the general principles for selection of cracking-resistant materials; the second part [13] concerns cracking resistant carbon and low alloy steel; the third part [14] is dedicated to cracking resistant CRAs and other alloys. Standard testing procedures are described for the qualification materials to the various forms of cracking. The main qualification tests are based on NACE TM0177-96 [27], NACE TM0284 [11] documents and on EFC 16 [25] and EFC 17 [26] publications. In the field of oil refining, NACE 8X194 [7] document provides recommendations on the choice of materials for pressure vessels used in wet H₂S refinery service, while NACE MR 0103-05 [24] document focuses more especially on materials resistant to Sulfide Stress Cracking (SSC).

1.4 CORROSION BY MERCURY AND LIQUID METALS

1.4.1 Equipment concerned by mercury corrosion

Mercury, in elementary state or as organometallic or inorganic compounds, may be present in small quantities (traces of less than 50 ppb) in some natural gases. Since this metal is a liquid over a wide temperature range, it may weaken *aluminium and its alloys* by a mechanism known as *liquid metal embrittlement*.

In the field of natural gas production, this affects mainly aluminium components used in cryogenic processes for the liquefaction of natural gas, especially heat exchangers. This type of corrosion has appeared on several occasions (Algeria, Indonesia, Thailand, USA) due to incomplete natural gas demercurisation [37].

In refining, although traces of *mercury* may be present in the crude oil to be processed, they may condense at the head of the atmospheric distillation column and weaken the

protective cladding of the Alloy 400 head (65 Ni-32 Cu UNS N04400). In addition, if mercury is introduced by contamination due to breakage of a measuring instrument containing this element, *aluminium*, *copper-zinc* (bronze) and *nickel-copper* alloys (alloys of series UNS N04XXX) may be damaged [10].

1.4.2 Mechanisms involved in mercury embrittlement of aluminium

Corrosion results from liquid metal embrittlement, making the aluminium less ductile due to its contact with liquid mercury.

The first step in the process would be the formation of an AlHg amalgam on the aluminium surface. In the presence of water, the amalgam undergoes the following reaction:



causing localised corrosion by pitting which initiates cracking.

Penetration of liquid mercury in this incipient crack would locally weaken the atomic bonds and hence nucleation of numerous dislocations which would be responsible for propagation of the crack, as shown on Figure 1.11. Cracking propagates according to a mainly intergranular mode.

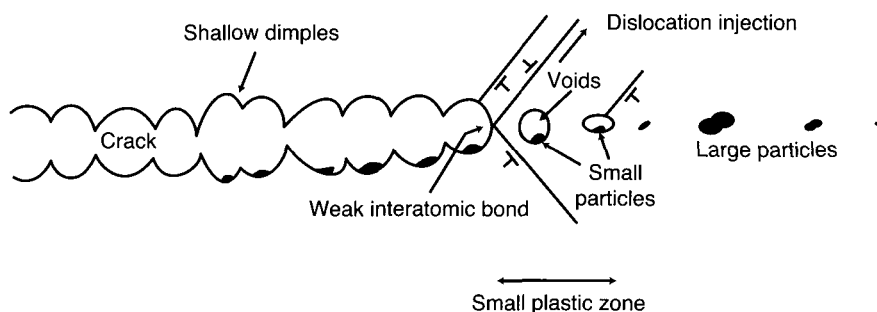


Figure 1.11

Crack propagation during liquid metal embrittlement [54].

1.4.3 Example of mercury corrosion

The example given [37] concerns a turbo expander system used on an offshore platform for natural gas liquefaction. The parts corroded are wheels made from aluminium alloy 6061 T6 (UNS A96061). The main operating conditions were:

- temperature: $-90\text{ }^{\circ}\text{C}$ to $-55\text{ }^{\circ}\text{C}$,
- pressure: between 27 bars and 82 bars.

Figure 1.12 is a macrographic image of the Al 6061 alloy wheel and a detail of the cracked zone.

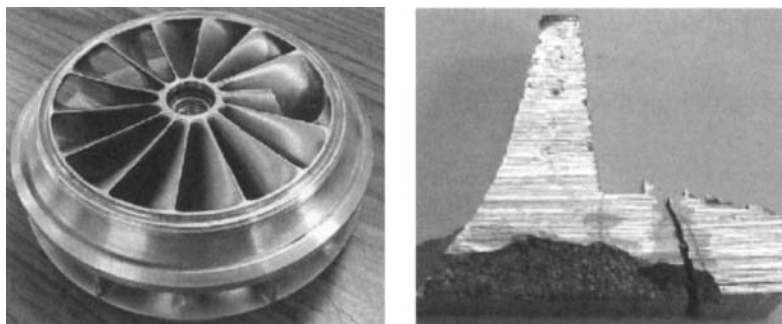


Figure 1.12

Liquid mercury embrittlement of a turbine blade on a liquefied natural gas (LNG) cryogenic exchanger [37].

1.4.4 Other metallic materials sensitive to liquid metal embrittlement

Other liquid metal environments not specific to the petroleum industry may lead to embrittlement of various metallic materials causing, as with the mercury-aluminium pair, a substantial decrease in alloy ductility and cracks under low mechanical stress.

Steels are sensitive to embrittlement by liquid cadmium (melting point = 320 °C), liquid zinc (melting point = 420 °C), liquid lead (melting point = 327 °C). The first two elements are found as additives in some paints that are used to protect steels against atmospheric corrosion. Cracking will quickly appear if these steels, painted or protected by cadmium plating or galvanising, are used at temperatures where the coatings are in liquid state [54].

1.4.5 Prevention of liquid metal embrittlement

To avoid this type of corrosion, the liquid metal (even traces) must not be allowed to come into contact with sensitive alloys:

- Avoid the use of aluminium alloys for treatment of natural gases containing mercury;
- Avoid entry of mercury in the refining circuits;
- Remove mercury from the gas by adsorption on beds of activated carbon or on microporous adsorbents impregnated with elementary sulfur;
- Protect the aluminium alloys with an adherent coating insensitive to cyclic stress cracking. For example, the polymeric coating reinforced with metal particles Magna-plate HCR seems to have proved satisfactory for offshore liquefaction plants [37];
- Do not protect steels which will be used at high temperature or which could occasionally be raised to high temperature (fire) with coatings containing zinc, cadmium or lead (to avoid attack by these metals at high temperature).

1.5 CORROSION BY THE BACTERIA PRESENT IN WATER, SOIL AND CRUDES

1.5.1 Stakes of biocorrosion in the petroleum industry

Biocorrosion, or Microbiologically Influenced Corrosion (MIC), concerns both the upstream and the downstream sectors of the petroleum industry. Upstream, the corrosion problems are similar to those which affect mining infrastructures [56]. Some parts of the installations (especially those made from carbon steel) are more sensitive than others to biocorrosion [78]. In particular:

- the dead zones and zones that are stagnant or crossed by a continuous flow of less than 1.5 m/s,
- zones of pH below 10.5,
- portions whose temperature is less than 100 °C,
- zones containing organic matter, which provide the microorganisms with shelter and nutrients,
- systems and components operating intermittently (decommissioning, maintenance, shutdowns).

For example, large quantities of seawater are used for installation of offshore platforms, as well as recovery and storage of oil and gas. Microorganisms responsible for corrosion may be found in all production systems where seawater is present [36]. The following equipment is concerned:

- the platform legs, filled with water when the platform is lowered into position. Up to 200 000 m³ of seawater may be flooded into the legs as ballast or displaced when the leg is used to store crude oil. The tanks in the platform jacket may also contain ballast water or be used to store drinking water and fuel oil,
- the pipelines, where seawater is used for the hydrostatic tests and may remain for several months,
- the tanks, where the pressure is maintained by injection of seawater.

The external parts of the buried or submerged installations can be protected by paint or coating and cathodic protection. The inside surfaces such as the production columns, well casings, pressurised equipment, pipes and surface pipelines have to cope with a type of corrosion that electrochemists are not used to dealing with: microbial attack [56]. These installations are routinely protected by biocide treatments considered as good value with respect to the risks run. Biocorrosion is an abnormal but permanent threat. Hydrogen sulfide, for example, produced by Sulfate-Reducing Bacteria (SRB) can react with iron to form FeS. The resulting colloidal precipitate combined with the cellular biomass may plug the filters, valves and other control equipment. The danger of biocorrosion has been clearly illustrated in a series of publications by Elf (now Total) after a subsea pipeline in the Congo split twice in 1989. The cost of replacing each pipeline had been evaluated at 10 to 20 million dollars [56]. The corrosion damage emerged very quickly on both occasions, with an unusually high pitting rate of about 1 cm per year [60] the second time the pipe leaked. The results of the laboratory study conducted to determine the causes of the corrosion clearly showed that

SRBs and Thiosulfate Reducing Bacteria (TRBs) played a key role in the damage. Scientific literature describes (in less detail) similar cases of biocorrosion, such as that which occurred on a flowline of an Indian offshore unit after 6 years continuous use. These articles confirm the key role played by SRBs in the localised corrosion of carbon steel [133].

In the downstream sector, biocorrosion problems are not specific to the hydrocarbon industry, but are quite similar to those observed in the other industrial sectors. Biocorrosion problems in the downstream sector can be avoided or solved by implementing standardised procedures [56].

1.5.2 Means used to detect and combat biocorrosion

As indicated by Videla [152], the literature on prevention and control of biocorrosion suggests employing two old sayings:

- better be safe than sorry,
- cleanliness is essential.

The methods applied to stop or delay biocorrosion [114] can be classified as follows.

1.5.2.1 Use of non-corrodable materials

Biocorrosion prevention measures start with the design of the system or installation. The component materials must be selected carefully. Corrosion can be avoided when chemically inert materials, of suitable strength, are available at a price that is competitive compared with that of carbon steel. For example, small diameter polymer pipes can be used for water distribution. Large diameter cement pipes protect unpressurised systems against attack by SRBs.

1.5.2.2 Construction of a non aggressive bacterial environment

The ideal non aggressive bacterial environment for a pipe consists of chalk and chalk-sand mixtures.

1.5.2.3 Use of bactericides

Biocorrosion is most frequently observed during start-up and shutdown activities. Hydrostatic tests conducted on equipment, tanks and pipes generally include emptying and drying procedures. When the water of the hydrostatic tests is reused, biocide treatment is implemented at the same time to prevent microbial contamination. The biocides have varied molecular structures (Figure 1.13). Chlorine, chlorine dioxide, bromine and ozone are typical oxidising agents used industrially (table 1.2). If chlorine is used, its residual content must be controlled to avoid pitting and crevice corrosion or stress corrosion cracking (see paragraph 1.6) which may result from excessive treatment. It has been proposed that non oxidising biocides were more efficient than oxidising bactericides for global control of algae, fungi and bacteria. Their persistence is higher and their efficiency independent of the pH [153]. One example is Kathon® (Rohm and Hass trademark), composed of isothiazolones, which has a broad spectrum of activity.

Table 1.2 Biocides used in industrial water supply networks (source: [153]).

Name	Biocide activity	Properties	Concentration (mg/L)
Chlorine	Bacteria; algae	Oxidising	0.1-0.2
Chlorine dioxide	Bacteria; algae	Oxidising	0.1-1.0
Bromine	Bacteria; algae	Oxidising	0.05-1.0
Ozone	Bacteria; biofilms	Oxidising	0.2-0.5
Methylene-bis-isocyanate	Bacteria	Non oxidising	1.5-8.0
Isothiazolones	Bacteria; algae; biofilms	Non oxidising	0.9-10
Quaternary ammonium	Bacteria; algae	Surface activity	8-35
Glutaraldehyde	Bacteria; fungi; algae; biofilms	Enzymatic inhibition	10-70
Tetrakis Hydroxymethyl Phosphonium Sulfate	Bacteria; algae; fungi	Surface activity	

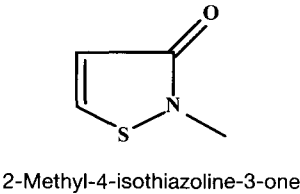
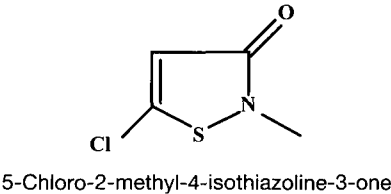
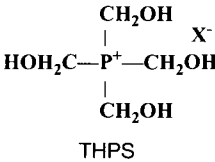
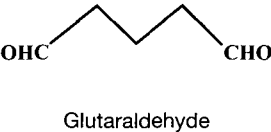
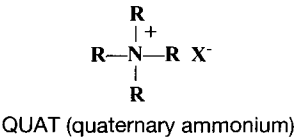
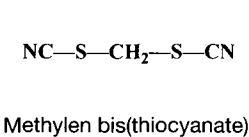
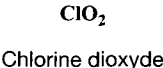


Figure 1.13

Molecular structures of biocides.

In recent years, the environmental acceptability of biocides has largely been taken into account by regulations on the use of commercial products. The use of ozone to protect industrial water supply networks offers various advantages. In particular, ozone does not produce any residual clogging [46]. Tetrakis Hydroxymethyl Phosphonium Sulfate (THPS) is another interesting compound. It has a broad spectrum of action, being efficient against bacteria, fungi and algae [69]. THPS is used in the petroleum industry because of its ability to dissolve iron sulfide [153]. Its main advantage lies in its low environmental toxicity.

1.5.2.4 Use of cathodic protection

Cathodic protection, frequently used on pipes to protect them against corrosion, could have an impact on the development of biofilms. Two cathodic protection techniques are often used. In the first, the metallic structure is electrically protected by galvanic anodes consisting of a metal alloy less noble than the metal to be protected. In the second technique, an external current is applied to cancel out the corrosion current. These protection methods are also discussed in paragraph 2.2.2.

To obtain efficient protection against bacterial corrosion, the current practice consists in reducing the electrochemical potential of the steel to below -950 mV (measured using a saturated Cu/CuSO₄ reference electrode). Locally, cathodic protection increases the pH, generates OH⁻ ions and precipitates Ca⁺⁺ and Mg⁺⁺ as CaCO₃ and Mg(OH)₂. It is thought that cathodic protection reduces the adhesion of aerobic biofilms during the first stages of colonisation.

1.5.2.5 Protective coatings

Protective coatings are an extremely useful tool in preventing the problems caused by biocorrosion. The coating must be coherent, adherent, non porous, mechanically resistant to the dangers encountered during delivery, installation and backfill, and chemically resistant to prolonged contact with all the environments likely to be encountered [113]. Antifouling paints containing toxic metals are frequently used, especially for metallic parts in contact with seawater. Like biocides, they must comply with applicable environmental regulations.

1.5.2.6 Detection of corrosive micro organisms

Some traditional microbial methods can be used for detection and enumeration of SRBs, such as microscopic observation after specific colouring. When the microorganisms cannot be cultivated, immunological or molecular biology techniques can be used [38]. The Rapid-check II SRB detection system, for example, is an immunological test developed by Conoco. This test is based on an *enzyme*-linked immunoassay (ELISA) that detects adenosine-5'-phosphosulfate (APS) reductase, an enzyme of SRBs. Another powerful approach consists in using nucleic probes. A probe is a DNA segment which is marked so that after a DNA hybridisation reaction, any base pairing between the probe and the complementary sequence of a DNA sample can be detected. It has been demonstrated that this technique can efficiently detect SRBs in aerobic biofilms [134].

1.6 CORROSION CAUSED BY THE CHLORIDES PRESENT IN WATER

1.6.1 Equipment concerned by corrosion due to chlorides present in water

The presence in water of dissolved salts, chlorides such as NaCl, MgCl₂ and CaCl₂, may cause localised corrosion of stainless steels (in particular the AISI 300 series): pitting, crevice corrosion, stress cracking by attack of their passive film.

In the field of drilling and petroleum production, all stainless steel equipment may be concerned by this type of corrosion when in contact with water loaded with chlorides and containing dissolved oxygen: formation water, drilling mud brines, seawater, marine atmosphere, water used for hydrostatic testing.

For acid gas treatment units, the reaction zones and the transfer lines for which steel has been chosen to withstand corrosion by amine-based solvents (see paragraph 1.7) may be attacked by the chlorides associated with water and acid pH values.

In the field of refining, all stainless steel pipes and reactors likely to convey water loaded or contaminated with chlorides may be affected: desalting units, water-cool condensers, condensers (process side) at the of the crude distillation column head. Also during the hydrostatic tests on stainless steel reactors and pipelines, special attention must be paid to the composition of the testing water to prevent any attack by chlorides during the test or when the equipment is being heated during startup of the process.

Corrosion may also develop under the insulation of stainless steel pipelines or equipment: penetration of water containing chlorides at the stainless steel-lagging interface may cause corrosion and leaks.

1.6.2 Mechanisms and parameters influencing corrosion by water containing chlorides

The chlorides present in water may be responsible for three types of localised corrosion on stainless steels (the mechanisms are discussed in greater detail in paragraph 3.2.3):

- Pitting corrosion: very locally, the chloride ions attack the stainless steel passivation layer. Although the quantity of corroded metal is very small, this type of attack sometimes results in perforation of the parts affected within a very short period of time;
- Crevice corrosion: this type of corrosion is encountered in small confined spaces containing stagnant electrolyte, such as the gaps between riveted plates or seals. The attack mechanism is related to local modification of the medium composition, the presence of chloride ions causing acidification by local formation of hydrochloric acid;
- Chloride stress corrosion: this type of corrosion is due to the combined action of mechanical stress (applied or residual) and the aqueous environment containing chloride ions and an oxidising agent (O₂ or H⁺). The resulting cracks formed in stainless steels generally follow a transgranular path.

The main parameters affecting these types of localised corrosion of stainless steels are as follows:

- The water chloride ion concentration, acidity and temperature. As shown on Figure 1.8, which illustrates the resistance to pitting corrosion of various stainless steel grades, an increase in each of these parameters increases the sensitivity to the three types of localised corrosion. For highly acid pH values (below 1 or 2), corrosion of stainless steels is no longer localised and becomes uniform (full depassivation);
- The hydrodynamic conditions of low flow rates are an aggravating factor since they favour fixation of chloride ions on the passive layer. In contrast, high speeds are beneficial;
- The presence of oxygen dissolved in the water favours this type of localised corrosion;
- The mechanical stresses responsible for stress corrosion are both applied and residual (including those produced when shaping the component or during welding operations);
- The metallurgical composition can be used to improve the resistance of stainless steels, as shown on Figure 1.14. High chromium, molybdenum and nitrogen contents improve the resistance to pitting and crevice corrosion by strengthening the passivation layer. For nickel, concentrations between 8% and 12% seem to offer the least corrosion resistance. Although the resistance of austeno-ferritic stainless steels containing little nickel is greater than that of austenitic grades (AISI 300 series), they are not totally protected. For high nickel concentrations, alloys containing over 35% are highly resistant and those containing at least 45% are virtually insensitive [10].

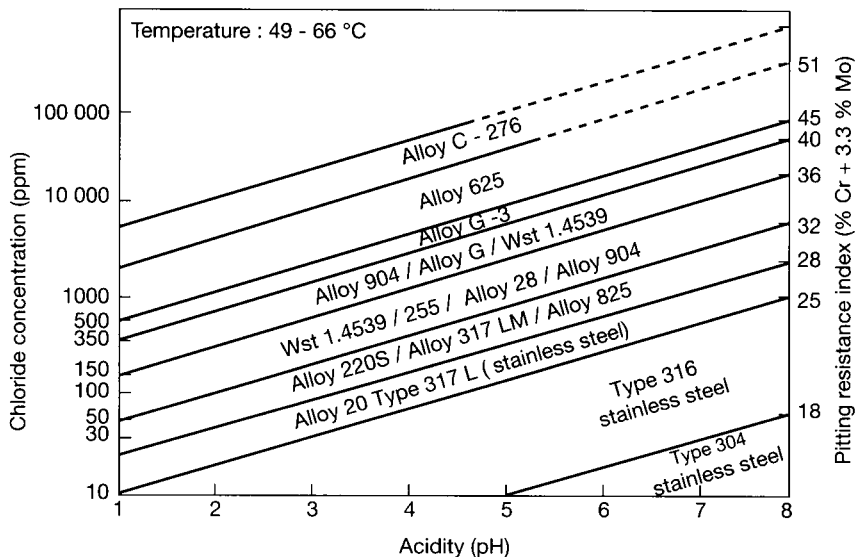


Figure 1.14

Influence of water chloride concentration and acidity on sensitivity of various stainless steel grades to pitting corrosion (50-65 °C temperature range).

1.6.3 Example of corrosion by water containing chlorides

The images shown on Figure 1.15 illustrate the pitting and stress corrosions of an austenitic steel AISI 304 (UNS S30400) pipeline during a hydrostatic test with a chloride containing water. The stress corrosion cracking follows a transgranular path.

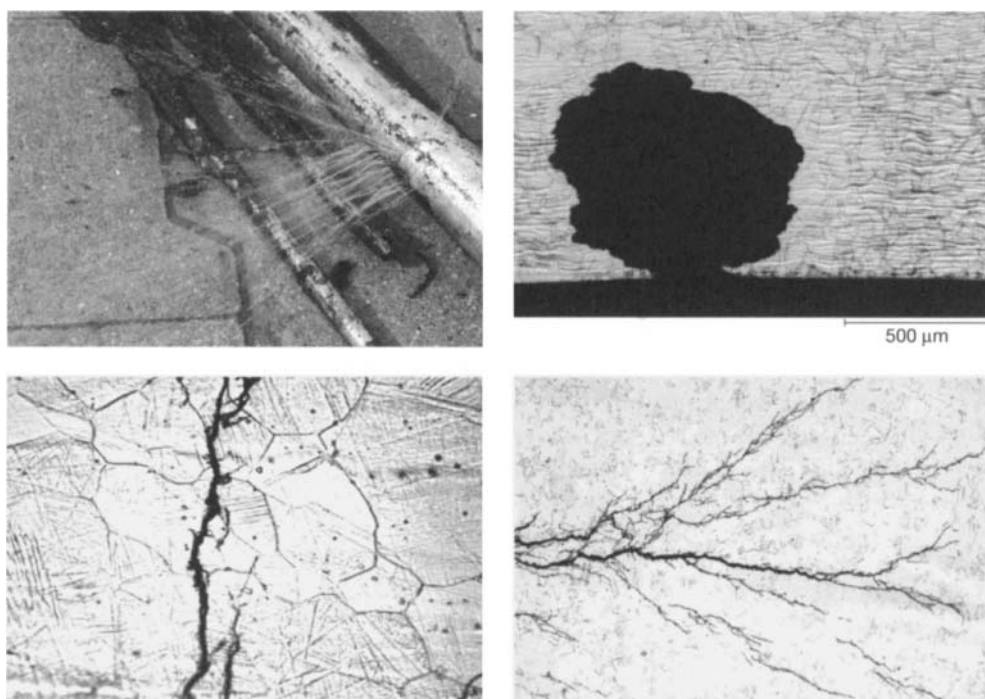


Figure 1.15

Pitting and stress corrosion of a stainless steel AISI 304 after pressure testing with water at ambient temperature.

1.6.4 Prevention of localised corrosion of stainless steels by water containing chlorides

The main recommendations to protect stainless steels against localised damage are as follows:

- Choose the metallic material which offers the best resistance for the water salinity, acidity, oxygen content and temperature conditions according to data and feedback: depending on the severity of the medium, possible choices include an austenitic stainless steel grade containing molybdenum (type AISI 316 – UNS S31600), alloys with high nickel content (35%-45%), austeno-ferritic or superaustenitic grades (see paragraph 3.1.2 for additional information on these stainless steels). For equipment conveying seawater, use of titanium alloys may prove beneficial [106];

- Design the equipment so that there are no confined spaces or areas where chloride containing water could stagnate;
- Conduct the hydrostatic tests on stainless steel equipment with water of low chloride content (a value of less than 20 ppm is generally recommended);
- For lagged stainless steel equipment, application of a coating (such as the aluminium-based thermal spray coatings) on the steel offers a good protection [154].

1.7 HYDROLYSIS OF CHLORIDES INTO HCl

1.7.1 Equipment concerned by hydrolysis of chlorides into HCl

Hydrolysis of chlorides of mineral or organic origin into hydrochloric acid may occur during several oil refining steps:

- Mainly at the head of *atmospheric distillation* units and in the downstream exchangers;
- Sometimes the condensation equipment downstream from the heads of *vacuum distillation columns* may be concerned;
- Organic chlorides may be found with the feedstocks of *hydrotreatment units* or in recycle hydrogen, leading to the formation of HCl in these units;
- For *catalytic reforming units*, chlorides from the catalyst may also generate HCl.

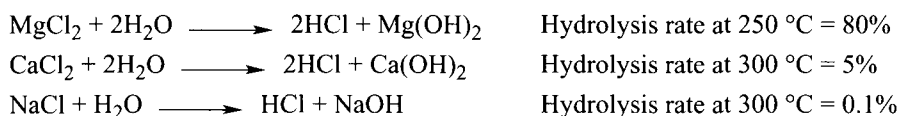
The hydrogen chloride so formed is highly corrosive to numerous metallic materials.

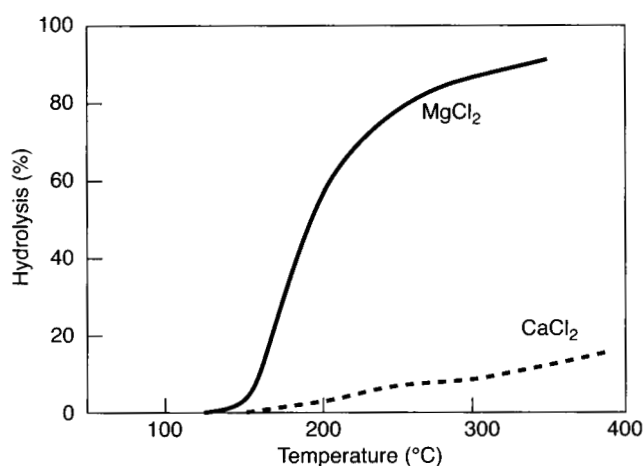
1.7.2 Mechanisms and parameters governing corrosion

Chlorides come from various sources [84; 150]:

- Mineral salts present in crude oils which were not eliminated in the desalting unit. These mineral salts are generally composed of 75% NaCl, 15% MgCl₂ and 10% CaCl₂;
- Organic chlorides: when they are present in the crude at entry to the refinery, being insoluble in water they are not eliminated by the desalting treatment. These organic chlorides may come from:
 - solvents associated with the fracturing fluids injected to stimulate wells,
 - solvents used to dissolve the deposits of wax and tars in the crude transport pipes, storage tanks and other equipment,
 - anticorrosion additives used for upstream production water treatments, especially oil-soluble quaternary amine based additives,
 - additives present in lubrication oils recycled in the refining effluents,
 - spent catalysts and petrochemical by-products.

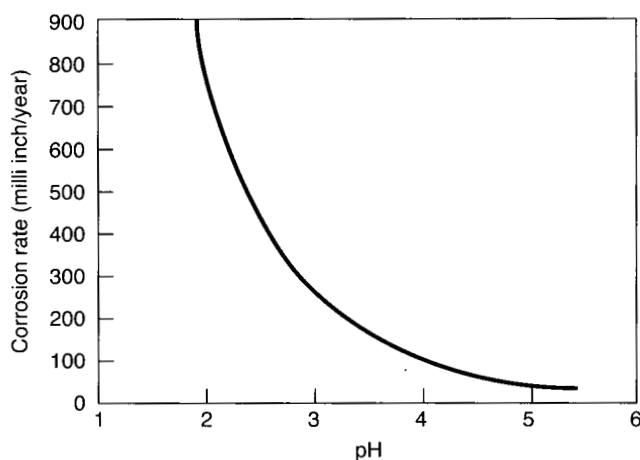
For inorganic salts, the reaction for the formation of HCl by hydrolysis starts from 130 °C, as shown on Figure 1.16, according to the following reactions:



**Figure 1.16**

Effect of temperature on the hydrolysis of magnesium and calcium chlorides [75].

In liquid state, and especially at its dew point, the hydrochloric acid formed causes, on all steels and some nickel alloys, serious uniform corrosion (see Figure 1.17) or localised pitting corrosion if HCl droplets condense on the metallic wall. The first droplets which condense are in fact highly acidic and very corrosive to all steels. The corrosion mechanisms are electrochemical ones, the anodic and cathodic reactions being respectively oxidation of iron and reduction of hydrogen ions (for further information on electrochemical corrosion, refer to paragraph 3.2.1).

**Figure 1.17**

Effect of dilute hydrochloric acid pH on rate of corrosion of carbon steel at 57 °C [82].

The main factors influencing corrosion by aqueous solutions containing hydrochloric acid are:

- HCl concentration and temperature, which accelerate this type of corrosion as long as the acid remains in liquid form (see Figure 1.17). The HCl concentration depends on the chloride concentrations in the feedstock;
- The presence of naphthenic acids in the crude may also increase the rate of hydrolysis of mineral salts [75];
- The presence of oxygen or oxidising agents (ferric and cupric ions) also has an accelerating effect.

The following metallic materials are sensitive to this type of corrosion:

- Carbon and low alloy steels when the pH is less than 4.5;
- Martensitic (AISI 400 UNS 4XXXX series) et austenitic (AISI 300 UNS 3XXXX series) stainless steels are not resistant, irrespective of the HCl concentration and the temperature, due to their sensitivity to pitting corrosion.

1.7.3 Example of corrosion by HCl formed by hydrolysis of chlorides

Plates made from martensitic stainless steel AISI 410 (UNS S41000) in a depropanisation unit column were totally corroded after two years service. The service conditions were:

T = 200 °C

Pressure = 15 bars

Feedstock = light gasoline contaminated by organic chlorides

As shown on Figure 1.18, uniform corrosion caused almost complete and regular loss of thickness of the plates.

A neutralising agent (ammonia in this particular unit) was injected to prevent this corrosion.

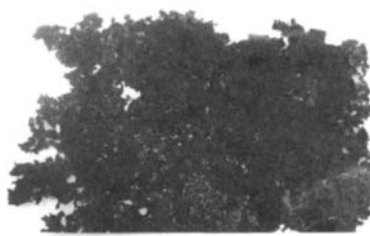


Figure 1.18

Corrosion of an AISI 410 stainless steel plate by hydrolysis of organic chlorides.

1.7.4 Prevention of corrosion by HCl formed by hydrolysis of chlorides

The main precautions to prevent this type of corrosion in distillation units are:

- Limit the chloride content in the refinery effluents to less than 20 ppm [10], and less than 1 ppm if possible [84]. Desalination must therefore be as efficient as possible and

all external contamination avoided. The residual magnesium and calcium chlorides can be converted into more stable sodium salts by injecting sodium hydroxide at the output of the desalinating unit, but this operation must not produce excessive quantities of salts which could block the preheat trains located downstream;

- Inject mixtures of neutralising and anticorrosion agents such as ammonia and film-forming amines, keeping the pH between 5.5 and 6.5 [131];
- Use corrosion resistant alloys including the nickel-copper alloys (Monel 400) used as coatings on the heads of vacuum distillation columns and titanium alloys for the exchanger tubes at column head.

For hydrotreatment and catalytic reforming units, apart from preventing external contamination, the hydrogen used must have low chloride and HCl contents. Installation of absorbent beds to remove the chlorides is recommended. In the absence of oxidising agents, steels can be replaced by nickel alloys containing chromium and molybdenum.

1.8 CORROSION BY CONCENTRATED ACIDS: HCl, H₂SO₄ OR HF

1.8.1 Corrosion by concentrated hydrochloric acid

Hydrochloric acid is sometimes used for well acidification during drilling operations. The corrosion products formed are highly soluble in the liquid phase, resulting in linear corrosion rates, constant over time.

In the refinery this acid may be formed at the head of the distillation, fractionation or stripper column (see paragraph 1.7).

It is corrosive in concentrated liquid state or when dissolved in a liquid aqueous phase. In gaseous state, it is not corrosive.

1.8.1.1 Equipment concerned by HCl corrosion

For refining, the equipments concerned are mentioned in paragraph 1.7.1.

For oil and gas drilling, the equipment conveying and injecting HCl to fracture the rocks must be resistant to this type of corrosion.

1.8.1.2 Mechanisms and parameters governing HCl corrosion

The corrosion mechanisms are electrochemical ones, the anodic and cathodic reactions being respectively oxidation of the metal and reduction of hydrogen ions (for further information on electrochemical corrosion, refer to paragraph 3.2.1).

For steels, the overall reaction is: $\text{Fe} + 3 \text{HCl} \longrightarrow \text{FeCl}_3 + 3/2 \text{H}_2$

The main parameters governing this corrosion are temperature, acid concentration and the presence of contaminants and oxidising agents.

1.8.1.3 Example of HCl corrosion

Figure 1.19 shows an example of corrosion of the inside of an aluminium bronze alloy valve conveying concentrated hydrochloric acid [87]:

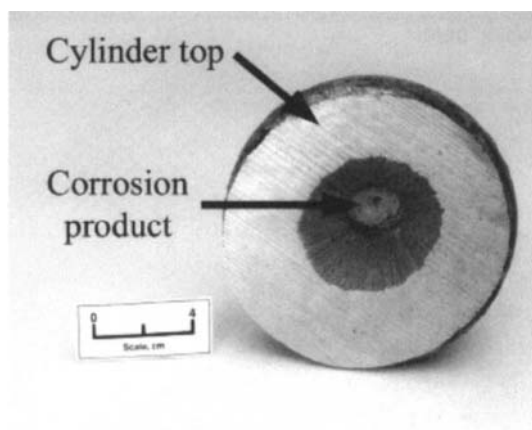


Figure 1.19

Corrosion of a aluminium bronze alloy valve by concentrated HCl [87].

1.8.1.4 Prevention of HCl corrosion

The materials offering the greatest resistance to concentrated and hot HCl corrosion (see Figure 1.20) [21; 65] are as follows:

- Monel 400 nickel-copper alloys (UNS N04400) for HCl concentrations less than 15% and in the absence of oxygen,
- Hastelloy nickel alloys of type B (UNS N10001) or C (UNS N10002) in the absence of oxidising elements such as oxygen, chlorine or ferric iron dissolved in the solution,
- Zirconium or tantalum,
- Vinyl ester based organic coatings,
- Inhibitors may also be used during well acidification.

1.8.2 Corrosion by concentrated sulfuric acid

Concentrated sulfuric acid is used as catalyst for some alkylation processes. In these units, olefins such as propylene or butylene react with isobutane to form iso-heptanes and iso-octanes.

Sulfuric acid may be formed during the condensation of sulfurous fumes and may also be present in wastewater treatment units.

It is generally corrosive in concentrated liquid state (under certain conditions it may nevertheless passivate steels) or dissolved in a liquid aqueous phase. In gaseous state, it is not corrosive.

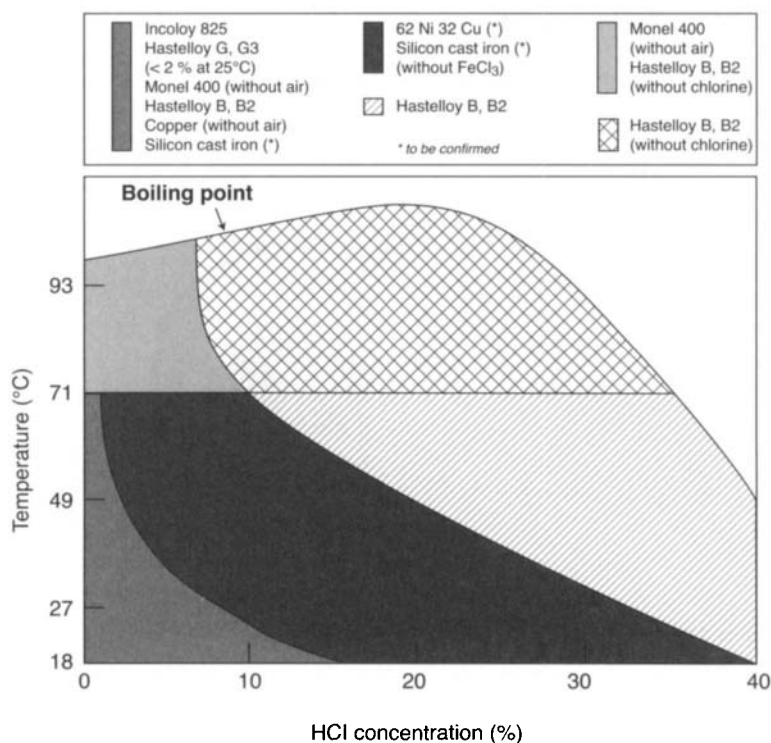


Figure 1.20

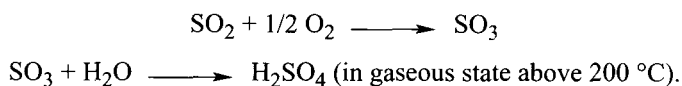
Graph showing the HCl corrosion resistance of various materials.

1.8.2.1 Equipment concerned by H₂SO₄ corrosion

For alkylation units, the following equipment is concerned:

- new and worn sulfuric acid storage tanks [6; 18],
- reactor effluent lines,
- reboilers,
- soda wash reactors,
- depropanisation column heads.

Sulfuric acid may be formed in the fumes output from furnaces by reaction of SO₂ and SO₃ with steam as follows:



1.8.2.2 Mechanisms and parameters governing H₂SO₄ corrosion

The corrosion mechanisms are electrochemical ones, the anodic and cathodic reactions being respectively oxidation of the metal and reduction of hydrogen ions (for further

information on electrochemical corrosion, refer to paragraph 3.2.1). For steels the overall reaction results in dissolution of the iron and formation of iron sulfate according to the equation: $\text{Fe} + \text{H}_2\text{SO}_4 \longrightarrow \text{FeSO}_4 + \text{H}_2$.

Uniform corrosion is observed if the acid covers the entire metallic part, localised corrosion if there is condensation of acid droplets.

The main parameters governing corrosion are temperature, acid concentration, the hydrodynamic flow rate and the presence of contaminants and oxidising agents. Increasing the temperature up to the boiling point increases the rate of corrosion. For alloys protected by the formation of a layer of metal sulfate, serious corrosion will occur if this layer is torn off by high flow rates. The rate of corrosion is increased by the presence of contaminants such as chlorine and oxidising agents such as O_2 , Fe^{3+} , Cu^{2+} in liquid sulfuric acid.

1.8.2.3 Example of H_2SO_4 corrosion

A carbon steel furnace tube in a boiler suffered uniform corrosion when the unit was stopped (Figure 1.21). The furnace was heated by a heavy crude with high sulfur content. During shut-down, the SO_3 compounds reacted with atmospheric water vapour, thereby forming sulfuric acid.

Neutralisation by injection of ammonia or carbonated water would have prevented this corrosion.



Figure 1.21

Example of H_2SO_4 corrosion.

1.8.2.4 Prevention of H_2SO_4 corrosion

In order of increasing corrosion resistance, the materials to be used are [48; 64; 124]:

- Carbon steel: it can be used for H_2SO_4 concentrations of at least 85% and temperatures below 38 °C when the flow rate does not exceed 0.7 m/s and in the absence of contaminants ($\text{Cl} < 200$ ppm) and oxidising agents (O_2 , Fe^{3+} , Cu^{2+}). In this case, the carbon steel is protected by a layer of iron sulfate. Figure 1.22 shows carbon steel corrosion rates for various temperatures and sulfuric acid concentrations;

- Stainless steel AISI 316 (UNS S31600) is used for flow rates less than 1.2 m/s and concentrations of more than 20% at ambient temperature;
- Alloy 20 (UNS N08020) can be used for weaker acid concentrations and temperatures below 50 °C. Figure 1.23 shows stainless steel 316 and alloy 20 corrosion rates for various temperatures and sulfuric acid concentrations;
- Nickel alloys Hastelloy B2 (UNS N01665) and C276 (UNS N10276) exhibit good corrosion resistance for severe temperature conditions. Figure 1.24 shows the corrosion rates of these two alloys for various temperatures and sulfuric acid concentrations.

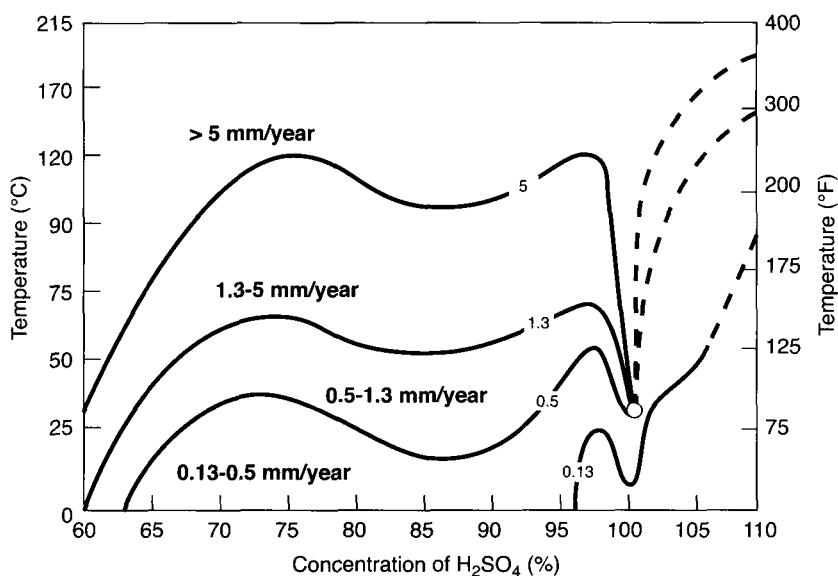


Figure 1.22

Carbon steel corrosion rate in concentrated H₂SO₄ medium.

1.8.3 Hydrofluoric acid corrosion

Hydrofluoric acid is used as catalyst for another alkylation process. In the presence of water, it reduces the thickness of some alloys but it also promotes penetration of hydrogen into steels, causing Hydrogen Induced Cracking (HIC), Stress Oriented Hydrogen Induced Cracking (SOHIC) and Hydrogen Stress Cracking (HSC). Hydrogen embrittlement of steels was discussed in detail in paragraph 1.3, when H₂S in aqueous solution is the hydrogenation promoter.

1.8.3.1 Equipment concerned by HF corrosion

All equipment of HF alkylation units transporting or in contact with hydrofluoric acid (pipes, HF regenerator) or vapour condensates containing this acid (exchangers, stripping columns, reboilers) is concerned. Numerous recommendations are provided in documents API 751 [28] and Nace 5A171 [23].

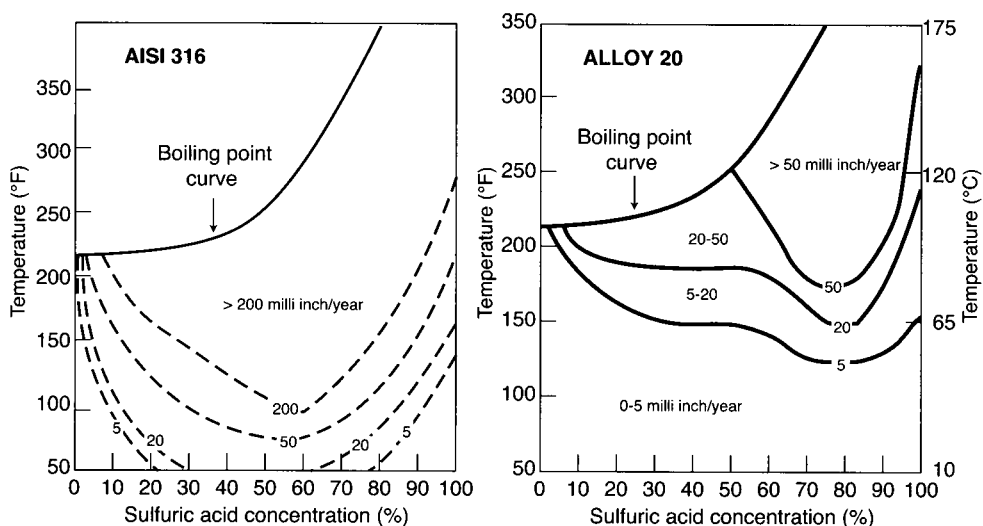


Figure 1.23

Stainless steel 316 and alloy 20 corrosion rates (milli inch per year) in H_2SO_4 medium.

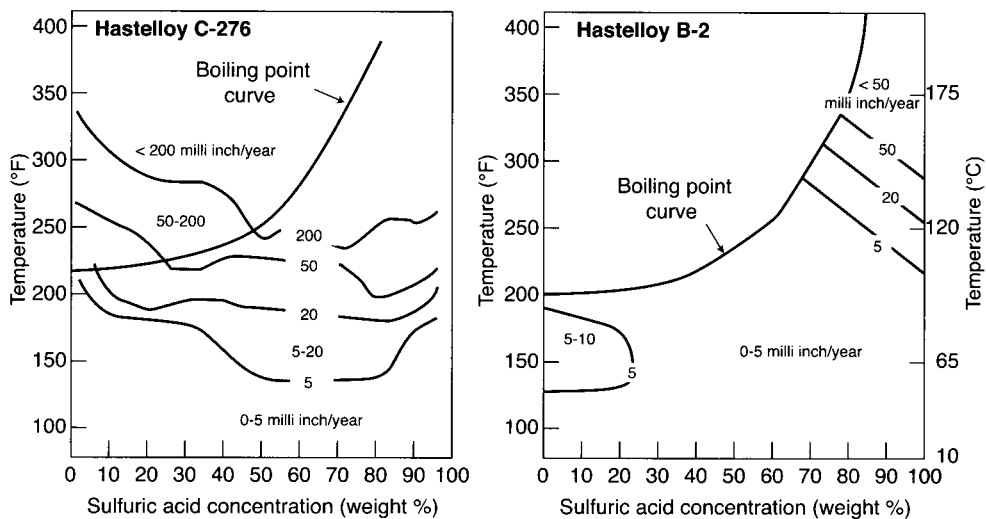


Figure 1.24

Nickel alloy B2 and C276 corrosion rates (milli inch per year) in H_2SO_4 medium.

1.8.3.2 Mechanisms and parameters governing HF corrosion

The thinning corrosion mechanisms are electrochemical ones, the anodic and cathodic reactions being respectively oxidation of the metal and reduction of hydrogen ions.

For iron and steels, this attack results in the formation of iron fluoride:



For steels, anhydrous or highly concentrated (> 65%) hydrofluoric acid flowing at rates of less than 1 m/s is not very aggressive due to the formation of a protective layer of iron fluoride when the temperature is below 66 °C.

The main parameters governing this type of corrosion are:

- the water content (HF concentration) which increases corrosion by destabilising the protective fluoride layer, as illustrated on Figure 1.25,
- the temperature, which also accelerates corrosion,
- the hydrodynamic flow rate which may destroy the protective metal fluoride layer,
- the presence of oxygen may accelerate the corrosion of carbon steel,
- for Alloy 400 (UNS N04400), a nickel-copper alloy, presence of oxygen may cause the formation of cupric fluoride and stress cracking [23].

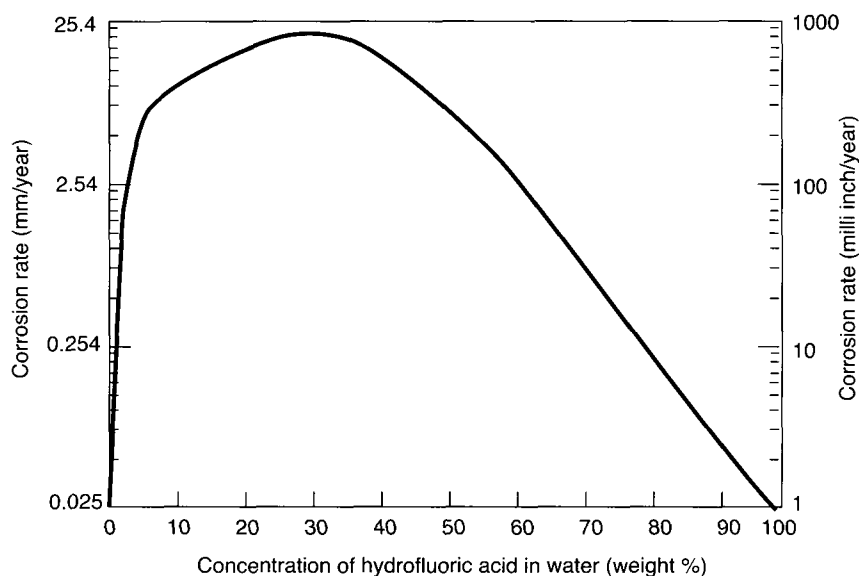


Figure 1.25

Influence of HF water content on carbon steel corrosion rate between 20 °C and 40 °C [6].

HF is also a steel hydrogenation promoter. The parameters governing hydrogen induced embrittlement are the same as those discussed in paragraph 1.3:

- steel composition and microstructure,
- steel mechanical characteristics (global or local mechanical characteristics – non stress relieved zones that favour hydrogen stress corrosion).

1.8.3.3 Example of HF corrosion

Figure 1.26 shows the influence of carbon steel composition on the HF corrosion rate. This example is a weld between two tubes of a depropaniser feed line in a HF alkylation unit ($T = 71\text{ }^{\circ}\text{C}$, the feed contained 0.3% HF and 0.001% water). The tube on the right part of the weld had copper, chromium and nickel contents far higher than those of the left part [85].

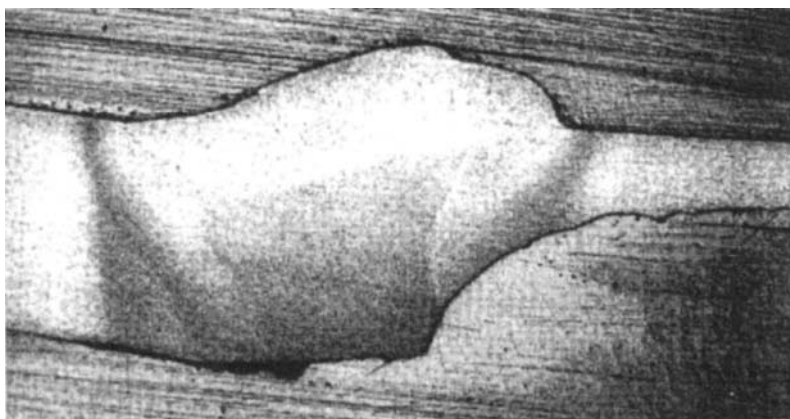


Figure 1.26

Example of HF corrosion [85].

1.8.3.4 Prevention of HF corrosion

Carbon steel is used for anhydrous or highly concentrated ($> 65\%$) hydrofluoric acid flowing at rates of less than 1 m/s when the temperature is less than $66\text{ }^{\circ}\text{C}$. Since the presence of some residual elements in the steel such as copper, nickel and chromium would seem to accelerate this type of corrosion, it is sometimes recommended to limit the contents on these elements according to the rule $\% \text{Cu} + \% \text{Ni} + \% \text{Cr} < 2.2\%$ [23; 28; 68; 135; 142]. In addition, the carbon steel must be resistant to hydrogen embrittlement (see paragraph 1.3).

For temperatures greater than $66\text{ }^{\circ}\text{C}$, the nickel-copper alloy “Alloy 400” is used. If oxygen is present in the hydrofluoric acid, this alloy may be sensitive to stress corrosion [23]: it is sometimes replaced by Alloy C276 to prevent this risk [10].

For some applications, a PTFE (polytetrafluoroethylene) coating may prove suitable.

1.9 STRESS CORROSION IN ALKALINE AND QUASI-NEUTRAL MEDIA

1.9.1 Caustic stress corrosion

Bases such as NaOH and sometimes KOH or LiOH are used in numerous refining and gas treatment processes. Even at low concentrations (50-100 ppm), these bases may cause stress corrosion damage in carbon steels, low alloy steels and austenitic stainless steel of AISI 300 series.

1.9.1.1 Equipment concerned by caustic corrosion

The main equipment concerned are located in areas where soda (or potash) is injected to neutralise acid effluents (HDS regeneration, reforming, isomerisation, etc.), LPG or light naphtha treatment processes and boilers and steam generators.

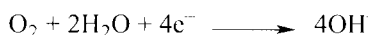
1.9.1.2 Mechanisms and parameters governing caustic corrosion

Caustic agents attack steel according to an electrochemical process:

anodic reaction:



cathodic reactions possible in the presence of oxygen:



or



Although propagation of this type of stress corrosion is mainly intergranular, transgranular paths have been reported in the literature [9].

The main parameters governing this type of corrosion are the caustic agent concentration, the temperature and the applied or residual stresses on the steel.

Figure 1.27 indicates the domains of resistance to caustic corrosion of various materials [143]. For temperatures below 50 °C, carbon steel is not sensitive to stress corrosion, irrespective of the soda concentration.

1.9.1.3 Example of caustic corrosion

Figure 1.28 is an example of stress corrosion cracks near a weld that was not stress relieved: this carbon steel plate is part of a soda wash tank used in a Merox process for sweetening FCC LPG. Under normal service conditions, the temperature is below 50 °C. Steam was injected to remove the plugs of solid soda, raising the temperature and generating stress that induced cracking of the carbon steel.

1.9.1.4 Prevention of caustic soda corrosion

The main prevention methods are given on Figure 1.27:

- Use of stress-relieved carbon steel (including areas where the steel has been welded or bent) up to 80 °C-100 °C depending on the caustic soda concentration. Heat treatments at 620 °C-650 °C are recommended [9];

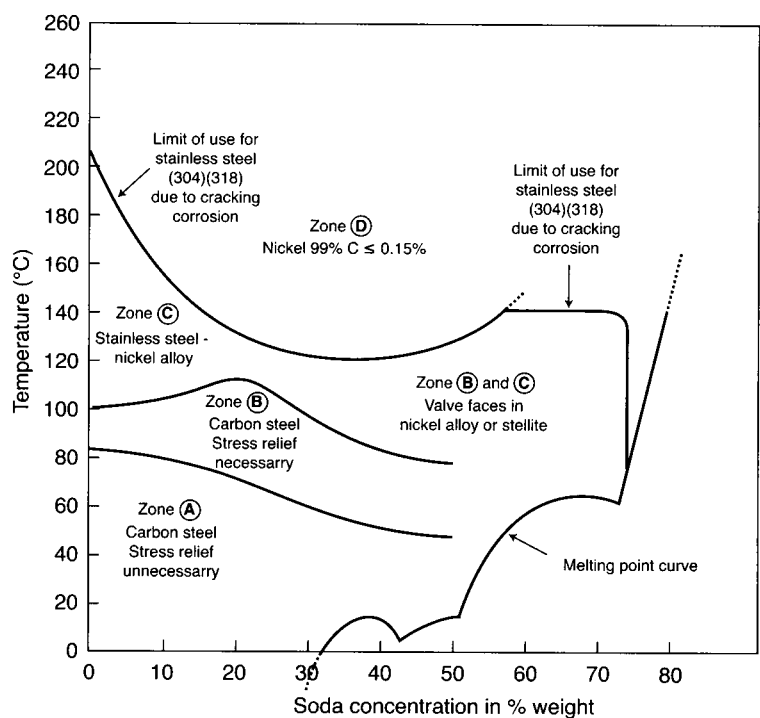


Figure 1.27

Graph showing the caustic corrosion resistance of various materials [143].

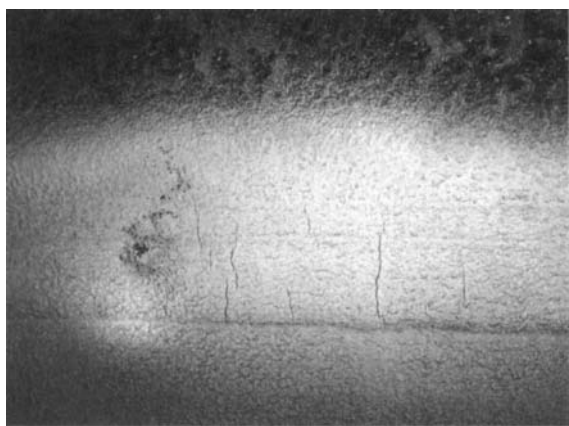


Figure 1.28

Example of soda corrosion in an LPG Merox unit.

- Use of austenitic stainless steels up to 120 °C-200 °C for low soda concentrations;
- Use of nickel alloys (Monel 400 UNS N0440, Inconel UNS N06XXX) for temperatures above 80 °C and high soda concentrations.

1.9.2 Carbonate stress corrosion

1.9.2.1 Equipment concerned by carbonate corrosion

Carbon and low alloy steels may suffer stress corrosion in FCC and coker units (and in the associated acid water treatment units) where free water containing carbonate-bicarbonate ions, H₂S and ammonia could be present [127]. The equipment (pipes and reactors) affected includes the fractionating column overhead condensers and accumulators, the wet gas compressor condensers and surge drums, the light cut fractionating columns and the residual water treatment units associated with this equipment.

Other processes involving a basic liquid phase loaded with carbonates (e.g. potassium carbonate): gas (e.g. hydrogen) decarbonation units may be concerned. Cases of stress corrosion have been reported for gas treatment units containing more than 2% CO₂ at temperatures exceeding 90 °C [10].

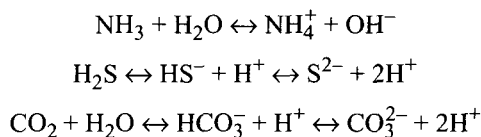
1.9.2.2 Mechanisms and parameters governing carbonate corrosion

This type of stress corrosion follows an intergranular path of fine cracks filled with oxides. It develops in stressed zones; for welds, cracks propagate parallel to the weld in the residual stress zones but also in the heat affected zones [101; 115; 120; 127].

The main parameters governing this type of corrosion are:

- the pH of the residual free water (due to ammonia),
- the water composition (concentration in carbonates, H₂S, cyanides),
- the residual stresses,
- the steel abandon potential.

The water composition is governed by the following chemical equilibria:



Carbon and low alloy steels are sensitive to this type of stress corrosion in alkaline medium for the following free water acidity domains [29; 101; 127]:

- pH ≥ 7.6 above an H₂S concentration of at least 50 ppm,
- 8 ≤ pH ≤ 9 above a carbonate concentration of at least 400 ppm,
- pH ≥ 9 above a carbonate concentration of at least 100 ppm.

This corrosion generally occurs at a potential between – 500 mV/ECS and – 650 mV/ECS. For aqueous solutions containing H₂S, the presence of CN[–] ions limiting the formation

of the iron sulfide layer could affect the abandon potential by bringing it into the domain of sensitivity to stress corrosion.

1.9.2.3 Example of carbonate corrosion

The example shown on Figure 1.29 concerns a carbon steel acid water storage tank of an FCC unit [19]. The cracks were found at the bottom of the tank near a weld bead. Propagation is intergranular.

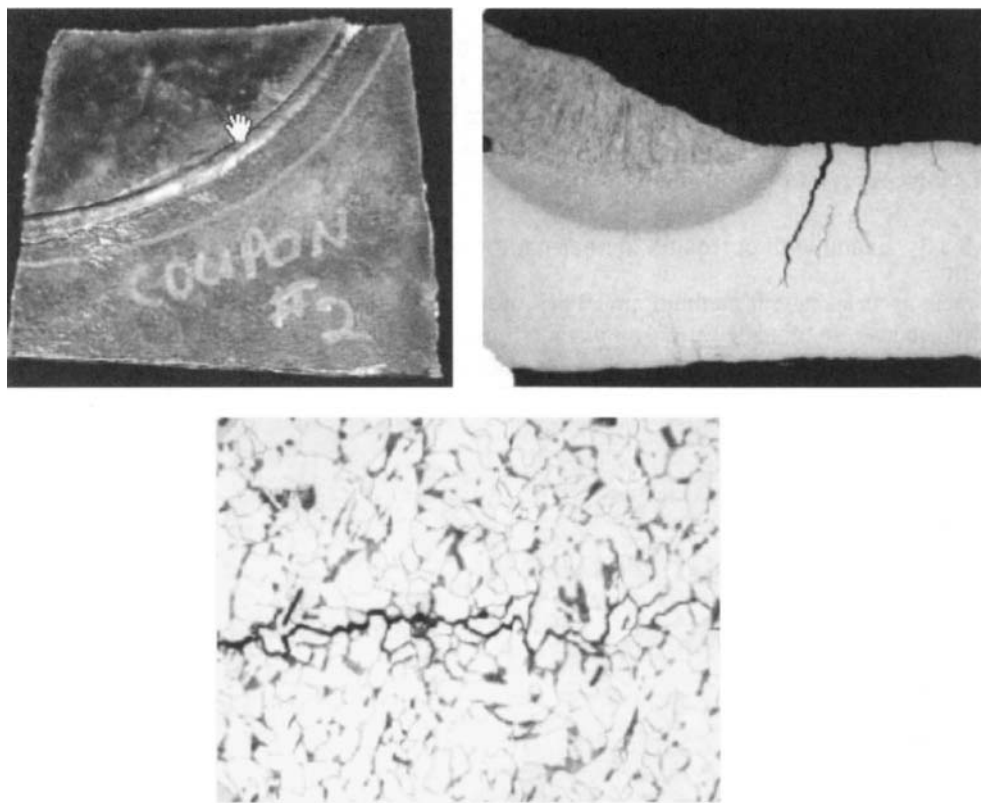


Figure 1.29

Example of carbonate stress corrosion [19].

1.9.2.4 Prevention of carbonate corrosion

Post weld heat treatment reduces the probability of stress cracking. Temperatures of at least 625 °C are recommended for this heat treatment [143].

Protecting the carbon or low alloy steel with austenitic stainless steel (AISI 300 series), nickel alloy (alloy 625 UNS N06625) or nickel-copper (alloy 400 N04400) cladding may also be effective [10; 29]. A corrosion inhibitor (e.g. metavanadate) is sometimes added [19].

1.9.3 Stress corrosion in near neutral medium

1.9.3.1 Equipment concerned by corrosion in near neutral medium

Most stress corrosion of carbon steel is encountered on the outside of gas and petroleum pipelines (Canadian [67], Russian and Argentinean pipelines, Jura pipeline). This type of corrosion is also sometimes associated with disbonding of the external protective coatings.

1.9.3.2 Mechanisms and parameters governing corrosion in near neutral medium

Unlike those generated in more alkaline media, the cracks developing in near-neutral solution of pH about 6.5 follow a transgranular path and their initiation and propagation mechanism is relatively independent of the temperature between 5 °C and 50 °C. These transgranular cracks are wider due to anodic dissolution of the side edges. Hydrogen penetration phenomena are associated with the anodic dissolution reactions [121].

1.9.3.3 Example of corrosion in near-neutral medium

Cracks in near-neutral medium have been observed in particular on carbon steel pipelines protected on the outside by polyethylene strips and less frequently by a bitumen coating. These cracks are attributed to a lack of cathodic protection under disbonded coatings. Figure 1.30 illustrates a transgranular path observed under disbonded coating.

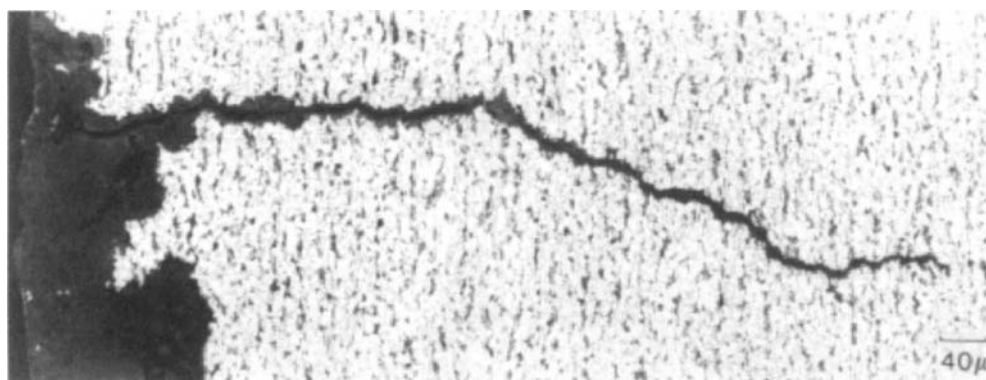


Figure 1.30

Example of stress corrosion in near-neutral medium [121].

1.9.3.4 Prevention of corrosion in near-neutral medium

The main factors to limit steel corrosion in near-neutral medium are:

- limitation of the mechanical characteristics of the steels,
- reduction of welding stresses by post weld heat treatment,

- selection of microstructures with small ferrito-bainitic grains rather than ferrito-pearlitic structures [109],
- protection with a coating (three-layer polyethylene as described in paragraph 2.2.1).

1.10 ALCOHOL (METHANOL AND ETHANOL) CORROSION

Short-chain alcohols such as methanol and ethanol may cause stress corrosion in carbon steels.

Methanol may also generate stress corrosion cracking in titanium and its alloys (in particular alloy Ti-6Al-4V UNS R56400).

1.10.1 Equipment concerned by alcohol corrosion

Methanol is used in petroleum production as thermodynamic agent to prevent the formation of gas hydrates. Methanol storage and transport equipment made from carbon steel and titanium alloy is therefore concerned.

Refrigerated methanol-water mixtures are used as solvent for extraction of acid gases (CO₂, H₂S) in some gas treatment processes. Carbon steel tanks and transport lines are potentially concerned.

In the chemical and refining industries, methanol is used to manufacture MethylTertButylEther (MTBE) by reaction with isobutylene. The carbon steel tanks of these units may be affected.

Ethanol is used as a substitution fuel: carbon steel reservoirs, tanks and pipes are more especially concerned.

1.10.2 Mechanisms and parameters governing methanol corrosion

The main cause of stress cracking in *carbon steels* is the presence of water and some chemical compounds (formic acid, chlorides) in methanol [15; 40; 77; 93; 95]. Cracking generally follows an intergranular path.

Electrochemical mechanisms are responsible for this corrosion. In the presence of certain quantities of water, the oxide film which forms naturally in air would not be stable and decomposes, forming Fe²⁺ ions (anodic attack) which react with the methanol and water according to the reactions:



The main parameters responsible for stress corrosion of carbon steels by methanol are [95], [15]:

- Water content: the corrosion conditions are reported in the literature for water contents below 1%, the sensitivity of cracking being strongest in the range 0.05% to 0.5%;

- Formic acid (methanol degradation product) when present up to 300 ppm, accelerates stress corrosion;
- When present, chloride ions destabilise the initial protective oxide layer;
- Presence of oxygen may increase the risk of stress corrosion by bringing the steel into a potential range where it is sensitive to stress corrosion. Moreover, the role played by oxygen in the degradation of alcohols into corrosive agents (formic acid) should not be ruled out.

For *titanium alloys*, methanol stress corrosion follows an intergranular path which is favoured by the presence of halide ions (chloride, bromide, fluoride). A sufficient quantity of water (between 2% and 20%) would prevent stress corrosion of titanium alloys [22; 137; 139].

1.10.3 Mechanisms and parameters governing ethanol fuel corrosion

The mechanisms involved in stress corrosion of carbon steels in the presence of ethanol fuel seem to be similar to those mentioned in the previous paragraph: anodic attack of the oxide layer associated with mainly intergranular stress cracking [15]. Cracks may develop within less than a year. Currently, the main parameters governing this type of corrosion are:

- the water content, increasing the water content favours stress corrosion,
- the high ethanol acidity (low pH determined according to standard ASTM D6324) would seem to be an aggravating factor,
- the chloride, sulfide and sulfate contents of ethanol fuel would seem to be major parameters [15].

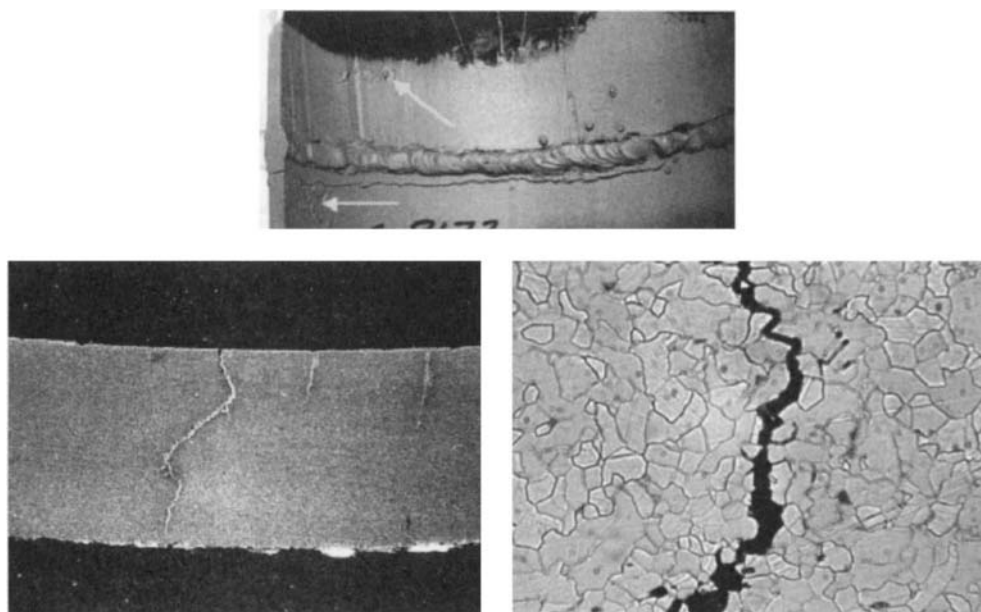
1.10.4 Example of ethanol corrosion

Figure 1.31 is an example of stress corrosion of a carbon steel ethanol fuel tank [93]. Intergranular cracking has propagated parallel to the weld bead, a few millimetres from the heat affected zone.

1.10.5 Prevention of alcohol corrosion

The main method used to prevent methanol or ethanol stress corrosion of carbon steels is to carry out post weld heat treatment on the welds and all zones subjected to shaping stresses (folding, bending, etc.). The use of metallic (stainless steel) or organic coating, as well as the addition of inhibitors (e.g. in ethanol fuel) may sometimes prove efficient.

Titanium alloys should never be used with methanol, unless its minimum water content is known: the minimum water content must be between 2% and 20%, depending on the titanium alloy composition [137]. Applying cathodic protection seems effective in preventing stress corrosion phenomena [22]. Replacing titanium alloys by stainless steels or nickel alloys is also a possibility.

**Figure 1.31**

Example of ethanol fuel stress corrosion of a tank [93].

1.11 CORROSION BY ACID GAS CHEMICAL SOLVENTS

1.11.1 Introduction: principles of acid gas removal by chemical solvents

Throughout the petroleum chain, the treatment steps are nearly always designed to purify the fluids, separate various components and eliminate undesirable species, in particular the two acid gases carbon dioxide and hydrogen sulfide. Treatments to remove CO_2 and H_2S from natural gas are often implemented as soon as the gas leaves the well. At the other end of the chain, the refinery gases may also need to be stripped of these acid gases. Lastly, these separation treatments are becoming increasingly important in the fight against greenhouse gas emissions and might be used in a near future for the postcombustion capture of CO_2 in fumes from industrial processes.

The most widely used process in all these applications uses alkanolamine-based chemical solvents (MEA, DEA, MDEA, AMP) capable of reacting preferentially with CO_2 and H_2S . The first paragraph provides a simplified description of this type of treatment unit (Figure 1.32). The main components and the operating principle are the same in the three broad domains concerned: treatment of production acid gases, treatment of refinery gases and postcombustion CO_2 capture treatment plants.

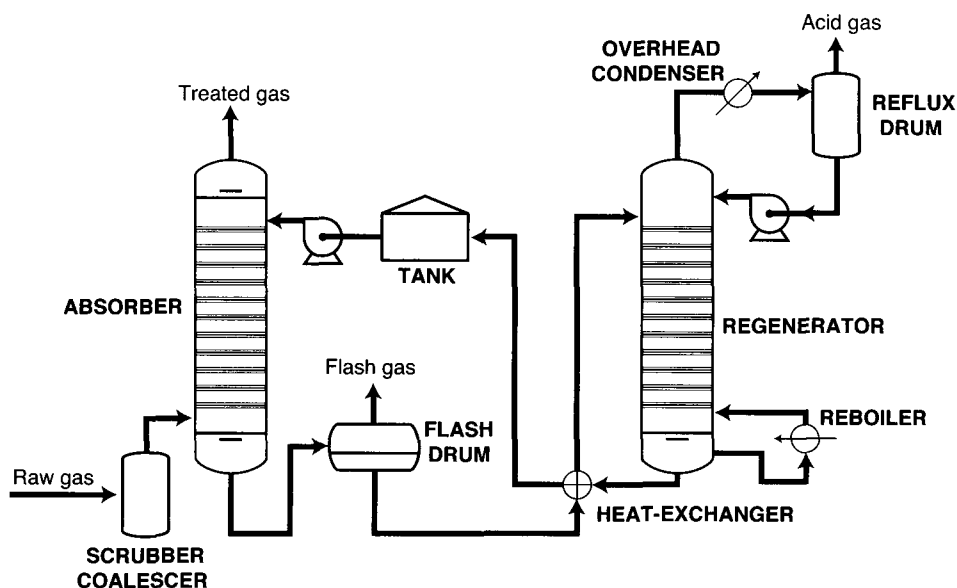
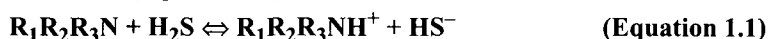


Figure 1.32

Simplified diagram of an alkanolamine acid gas removal unit.

The gas to be treated is introduced in the unit at the bottom of the absorber where it comes into contact with the solvent. The acid gases (CO_2 and/or H_2S) react and are absorbed by the solvent according to reactions 1.1 to 1.6 below.

The reaction with H_2S , which is the same irrespective of the type of amine considered, consists of direct proton transfer (Equation 1.1).



The reaction with CO_2 is slightly more complex. Two different mechanisms may be involved. A first reaction may occur, involving the successive formation of carbonic acid and bicarbonate (Equation 1.2 and Equation 1.3), followed by direct proton transfer identical to that observed for H_2S (Equation 1.4).



This mechanism may occur for all types of amine. The global kinetics is slow, however, since it is limited by dissociation of carbonic acid into bicarbonate (Equation 1.3).

For the primary and secondary amines, which have hydrogen bond to the nitrogen, a second mechanism is possible.



Prevention of corrosion and degradation of metallic materials used in the petroleum industry

This second section of the book discusses the various techniques implemented to protect the materials most frequently used in the petroleum industry against corrosion. Protection consists of two aspects, firstly appropriate selection of the metallic material and secondly proper design of the equipment to control the various corrosion risks. If this first approach does not guarantee the overall integrity of the unit or equipment or if the resulting investment is too high (CAPEX), protection must be provided by applying a coating (inorganic or organic), injecting chemical formulations inhibiting corrosion into the corrosive medium, or applying cathodic protection (even anodic for a limited number of applications).

The last paragraph of this section deals with corrosion detection, control and monitoring. The choice of corrosion control, evaluation and inspection methods used to set up possible corrective actions is of vital importance to guarantee the reliability and safety of the equipment.

2.1 CORROSION PREVENTION BY APPROPRIATE SELECTION AND DESIGN OF MATERIALS AND EQUIPMENT

Several interdependent criteria are involved when choosing the material that will be used to manufacture equipment (or part of equipment) operating in corrosive environment whose main operating parameters are known (e.g. concentration or pressure of the corrosive agents, temperature, flow rate, mechanical stresses in service) and for a planned service lifetime of the equipment.

2.1.1 Data concerning the corrosion type and propagation rate

The first aspect taken into account is the corrosion type: localised or uniform. Localised corrosion is taken to mean damage affecting only part of the material: pitting, crevices, craters, cracking, blistering, galvanic coupling. Uniform corrosion damages the entire surface and leads to a more or less homogeneous reduction in wall thickness. The various signs of corrosion are described in more detail in section 3 of this book. The reader may also refer to the ISO standards defining the various corrosion categories [160].

- Risks of localised corrosion: the material (chemical composition, mechanical characteristics, microstructure, welding modes, heat treatments) is chosen to minimise or prevent this corrosion. For example (non-exhaustive list):
 - choice of a stainless steel composition not sensitive to pitting corrosion,
 - choice of a carbon steel composition (with controlled sulfur and phosphorus contents) not sensitive to blistering and hydrogen-induced cracking,
 - choice of a low alloy steel not sensitive to high temperature hydrogen attack (with a proper chromium and molybdenum content),
 - choice of a stainless steel composition not sensitive to a chromium depletion of grain boundaries (sensitisation) during operation at high temperature (low carbon or stabilised stainless steel) and heat treatment for chemical stabilisation of stabilised stainless steels in order to prevent intergranular cracking corrosion,
 - application of heat treatment to relax internal stresses (produced during welding or when shaping the part) to prevent stress corrosion,
 - coupling of materials of similar electrochemical potential to avoid galvanic corrosion if they are immersed in an electrolyte,
 - etc.
- Risks of uniform corrosion: an estimate of the corrosion rate (CR) is required at design stage to determine a corrosion allowance thickness (CA) which ensures that the material is sufficiently thick at end of life (D) to withstand the various mechanical service stresses (pressure, etc.).

$$CA \text{ (mm)} \geq CR \text{ (mm/year)} * D \text{ (year)}$$

As a general rule the corrosion allowance CA is no more than 6 mm. When $CR > 0.25$ mm/year, the conclusion of the financial analysis is generally either to change the material grade or, depending on the media, apply cathodic protection or a corrosion inhibition treatment or coating. For some equipment, the 6 mm corrosion allowance may prove too expensive, in which case it may be necessary to review the metallurgical choice.

The data used to assess uniform or localised corrosion are obtained from:

- Curves and models validated by the profession. Numerous examples and references used in the petroleum and process industries are provided in the first section of this book;
- Results of specific corrosion tests conducted in laboratory or full scale tests. In this case, it is essential to ensure that the test conditions are representative of the industrial operating conditions;
- Feedback from field experiences obtained under the same operating conditions.

2.1.2 Control of operating parameters

It is essential to control the operating parameters in order to prevent corrosion risks. In the first section of this book, we examined the influence of the main operating parameters on the corrosion mechanisms encountered in the petroleum and process industries. In service, it is vital to set up instrumentation and regulation as well as corrective action plans to avoid any slips which could be disastrous for the equipment integrity. These corrosion detection,

monitoring tools and methodologies are described in paragraph 2.3 of this second section. The main critical operating parameters are:

- Temperature of the corrosive fluids and the equipment (in particular furnaces, boilers, heat exchangers, etc.) since most corrosion processes are thermally accelerated. Temperature (and pressure) also govern the thermodynamic state of the corrosive compounds. For example, following an accidental temperature rise, solid alkaline salts may change to highly corrosive liquid state (as described in paragraph 1.18). Inversely, following a temperature drop, inorganic acids such as HCl may change from gaseous to liquid state: the non-corrosive gas is now a highly corrosive liquid, resulting in metal wastage in just a few hours;
- Concentration and partial pressure of the corrosive agents: increasing these parameters generally increases corrosion rates;
- Mechanical stresses (hydrostatic pressure, stress cycles, etc.) applied on the metallic materials. Even if these variations do not affect the physical integrity of the equipment, the materials may become sensitive to stress corrosion or corrosion fatigue;
- Fluid flow hydrodynamic conditions. Increasing the flow rate may cause erosion-corrosion and cavitation phenomena. The opposite is true for some materials, where conditions under which corrosive products stagnate may generate increases of the sensitivity to localised corrosion (e.g. pitting corrosion caused by chlorides on stainless steel surfaces);
- Presence of solid particles likely to cause attacks by erosion-corrosion, by continuously removing the natural surface layer protecting the metallic material.

2.1.3 Equipment design

Well-designed equipment with suitable geometry may prevent some forms of attack such as crevice corrosion, galvanic coupling and corrosion-erosion damage.

Figure 2.1 provides some examples of bad configurations creating liquid retention zones which may result in crevice corrosion:

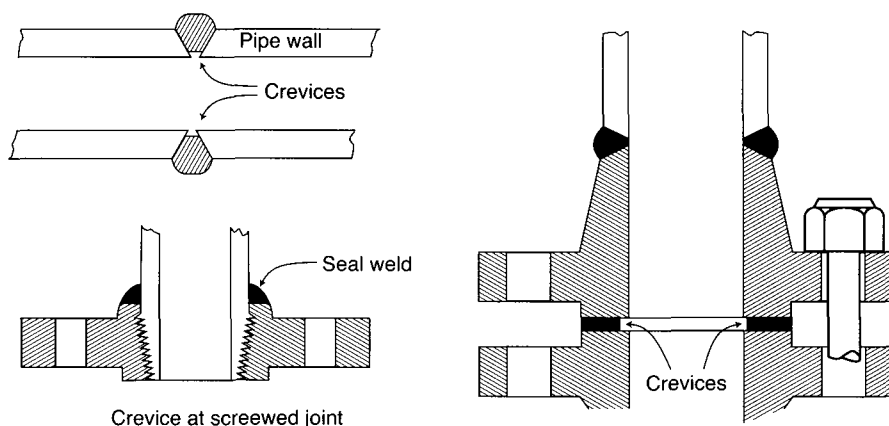


Figure 2.1

Examples of designs resulting in crevice corrosion (source: [269]).

Assemblies where metallic alloys of different corrosion potentials are placed in direct contact are possible sources of galvanic corrosion, as shown on Figure 2.2. This type of corrosion risk is generally prevented through the use of electrical insulation with a non-conducting polymer gasket (as long as electrical shunting via external components such as brackets does not make the insulation ineffective):

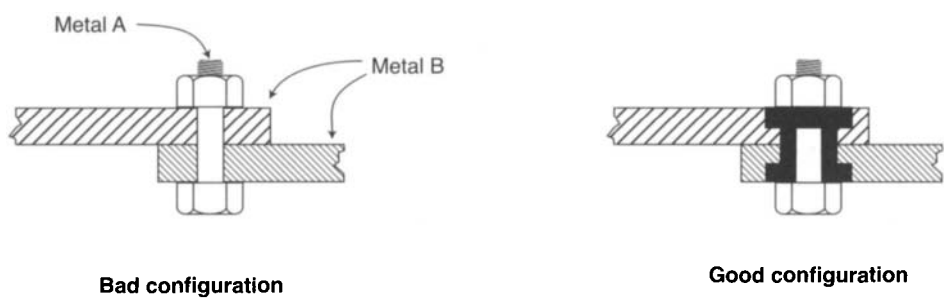


Figure 2.2
Example of design resulting in galvanic coupling corrosion.

To avoid erosion phenomena, bottlenecks or sudden obstacles on the pipes should be avoided, such as an overlap seam weld as shown on Figure 2.3 or a radius of curvature which is too small.

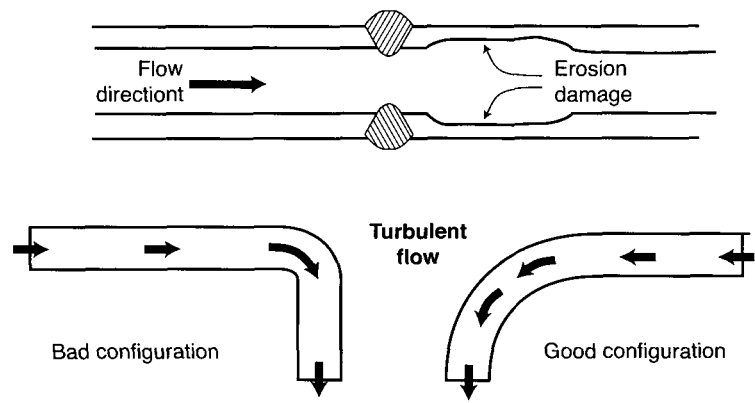


Figure 2.3
Examples of design resulting in corrosion-erosion (source: [269]).

In environments where stress corrosion cracking could occur, stress-relieving heat treatment should be performed to zones with high internal stress such as welds or zones which were highly strain-hardened during the manufacturing the equipment.

2.2 USE OF COATINGS, CORROSION INHIBITORS OR CATHODIC PROTECTION

When control of operating parameters or equipment design fails to provide efficient corrosion protection, other solutions must be considered, such as use of coatings, inhibitors or application of cathodic protection. These protection modes can be used alone or combined. Anticorrosion protection can be applied before the equipment is put into service (by applying a coating or cathodic protection) or when it is in service (by applying cathodic protection or injecting inhibitors), depending on operating conditions and costs. Coatings may also provide resistance to erosion or abrasion and act as thermal insulation.

2.2.1 Protection by coatings

The term coating generally refers to the class of organic coatings and paints, including the composite liners, and the class of inorganic coatings, including metallic and cement-based coatings. Before describing each class of coating, we will summarise the main principles governing the anticorrosion protection provided by coatings [168; 202; 203; 206].

2.2.1.1 Principle

A coating acts as a physical barrier isolating the metal from the corrosive medium and, theoretically, preventing the transfer of corrosion promoters (water, ions, chemical agents, etc.). The success of this type of protection depends to a large extent on the choice of materials forming the coatings and the quality of application. Protection by coating is fully efficient if the coating has no defect and is perfectly impermeable to the corrosive media. Unfortunately, it is impossible to achieve these conditions with an organic coating and penetration of the corrosive medium through to the metal must be considered. Note, however, that organic coatings are generally far less permeable to ionic species than to water. The resistance of the electrolyte penetrating the coating is therefore much higher when it reaches the metal surface than the resistance of the external electrolyte and the corrosion current is reduced accordingly.

Another type of protection is based on the use of sacrificial coatings. Placed in electrical contact with metal, these coatings form an anode. As a result, the metal becomes totally cathodic and is therefore protected against corrosion. This is the case with zinc, for example, for galvanised steel. This is also the principle of zinc or magnesium-rich organic primers.

Lastly, some coatings may inhibit corrosion reactions on the metal surface through the action of active compounds in the coating capable of dissolving and reacting with the substrate to form a protective oxide film on the metal surface. This is the case of traditional chromate or lead-based anticorrosion primers, recently prohibited on massive scale due to their toxicity. New anticorrosion primers, based on phosphate, silicate, titanate or molybdate are now commercialised.

Apart from coating formulations and traditional paints, involving the above-mentioned anticorrosion mechanisms, recent studies have led to the class of smart coatings, generally formulated with encapsulated active agents [201]. When a smart coating cracks, the

encapsulated anticorrosion active agents or polymerisation agents are released as the crack propagates, inhibiting corrosion or protecting the bottom of the crack. This will possibly heal the crack, thereby attenuating the corrosion effects [222; 260].

2.2.1.2 Organic coatings and paints

Numerous publications have described organic coatings and paints in detail: their chemistry and composition, surface preparation methods and application methods. The reader is recommended to refer to the books mentioned as references [171], [205; 223] on the subject. Paints, characterised by conversion of a liquid product when applied on a substrate into a solid film after drying, generally form a class separate from coatings. The main definitions are detailed below.

A. Definitions

Organic coatings are composite materials consisting of an organic matrix (polymer) loaded with pigments and fillers. Applied on a metallic substrate, they adhere to the support, in principle due to chemical and mechanical phenomena. Several coatings may be applied one after the other to get the various functions required. For example, a three-layer coating system for external protection of buried or underwater pipelines consists of a highly adherent primer in contact with the steel, a mechanically resistant product on the outside and an intermediate adhesive product to bond the outer layer to the adherence primer.

Organic coating products include paints, liquid, paste or powder substances which, applied on a support, form a solid and adherent film after drying. For more information, especially on the vocabulary of paints, the reader can refer to European standard ISO EN NF 4618 [AFNOR T36-001, October 1999 edition, "Paints and varnishes – Terms and definitions"]. In terms of raw materials, a paint is a mixture of fillers and pigments in suspension in a non-volatile liquid binder, possibly containing solvents and other specific substances. The binder, the essential element of a paint, consists of macromolecular products (polymers or prepolymers) which will form the film. Solvents are organic or aqueous liquids (pure or a mixture) which generally dissolve the binders. They help to adjust the viscosity of the product to be applied. A wide variety of fillers and pigments is incorporated in the formulations to reduce the cost and/or adapt the properties of paints. For example, it is recommended to add lamellar pigments such as micaceous iron oxides, glass flakes and nanocomposite clays to improve the barrier properties of coatings and paints. The average length of the path taken by molecules (water, oxygen, etc.) diffusing through the coating is increased and the permeability reduced, provided that there is good adherence between the fillers and the matrix.

Over the last few years, numerous studies have been dedicated to replacing organic solvents by water to reduce the Volatile Organic Compound (VOC) content of paints, in response to new regulations. Similar efforts are also underway to reduce the quantity of solvents in traditional paints. Low-solvent paints, known as "high solids" due to their high dry extract, are formulated with this aim in mind. The field of application of powder paints, which are absolutely solvent-free, is therefore developing [187].

Paints are classified according to how the liquid product is converted into a solid: evaporation of solvents, oxidation or polymerisation. They are applied using different methods, depending on the paint viscosity. Fluid products are generally applied by brush, roller,

immersion or spraying. Powder paints are applied using two methods, fluidised bed powder coating (where the part heated to a temperature above the powder melting point is dipped in the paint) and electrostatic powdering followed by curing.

B. Main polymers

Numerous polymers are used in the composition of coatings and paints. The thermal stability of coatings and paints under continuous exposure, which is generally limited to well below 200 °C, is due to the fact that the polymers are organic, i.e. based on carbon chemistry. The short-term resistance is higher, but rarely exceeds 350 °C.

Polymers can be classified into two categories depending on their response to temperature increase [241]. Thermoplastic polymers generally consist of more or less interpenetrating linear or branched macromolecular chains. They soften reversibly when heated until they become liquid, and are generally soluble in solvents. Note that semicrystalline thermoplastics exhibit locally structured crystalline zones (crystallites), as opposed to the disorganised amorphous zones. The elastomer and thermosetting polymers have a covalent three-dimensional network architecture composed of chemically cross-linked macromolecular chains. The networks are infusible and insoluble. They are obtained by the formation of a chemical bond between high molecular weight linear or branched polymers, or by polymerisation of low molecular weight prepolymer components having functionalities greater than or equal to two.

Thermoplastic polymers frequently used as coatings include polyolefins (polyethylene, polypropylene, etc.) and polyamides. The more expensive fluorinated polymer coatings are much appreciated for their chemical and temperature resistance. The thermosetting plastics which include epoxy resins, acrylic resins, polyesters and polyurethanes are frequently used in the composition of anticorrosion coatings. Silicone-based high temperature paints are also used when the other coatings are no longer efficient.

C. Surface preparation

Surface preparation of the support is extremely important, since it governs the wetting and the adherence of the coating on the substrate. The adherence mechanisms, detailed for example in the books [170; 245] are based on chemical and mechanical phenomena highly dependent on the degree of cleanliness of the substrate (elimination of solid deposits, rust, dust, grease and soluble salts) and its roughness (surface structure). The surfaces are prepared by projecting abrasive particles (sand or grit blasting) or stripping with ultra-high pressure water (several hundred bar). These operations are designed to increase the number of reactive sites between the metal entities (oxides and hydroxides) and those of the coatings (acid groups, hydroxyls, etc). They also prevent pollution of the interface which impairs the efficiency of the coating protection mechanisms and leads to blistering [203; 273].

D. Application examples

Organic coatings and paints are generally applied on the outer surface of metallic infrastructures (protection against the ambient environment). Anticorrosion protection is particularly important for buried structures (pipelines) and underwater structures (pipelines, ships and offshore production platforms). Organic coatings may also be applied, however, inside tanks

dedicated to the storage of corrosive effluents and inside transport pipelines (especially for purposes other than anticorrosion). Concerning gas transport pipes, the internal coating may yield a substantial benefit in terms of reduced internal losses at the walls [179].

The example of external protection of petroleum effluent transport pipelines will be developed below in greater detail, since numerous types of coating have been used for this purpose. Pipe anticorrosion external coatings have evolved over the years as new organic materials and application methods have become available. Note that this protection mode is always accompanied by a cathodic protection system (see paragraph 2.2.2) for buried or underwater pipelines. Despite the precautions taken during surface preparation and application, pipe coatings may have local defects, due for example to mechanical damage of the coating during transport or when laying coated tubes.

Originally, hydrocarbon coatings (based on coal-tar pitch from distillation of tars and on bitumens from distillation of oil) were widely used for outer protection of buried pipelines, and especially parts of structures not visible or buried. These coatings were generally applied hot in thick layers (about 5 mm). Oil bitumen coatings are still used for offshore pipelines at temperatures below 60 °C when they are weighted down by a layer of concrete. Research studies have been conducted on the ageing mechanisms of these coatings, still in use on sections of the oil and gas effluent transport network [200]. Currently, epoxy resins which polymerise when mixed with, typically, amine or amide hardeners form paint binders widely used for external protection of pipes, due to their high adherence on metallic supports. Readers can refer to the specialised book [FBE: Foundation for pipeline protection, Kehr] [214] which deals with this subject in detail, providing numerous applied examples. In the United States, the United Kingdom and the Anglo-Saxon countries, epoxy resins are applied in a single-layer coating of several hundred microns thick. In Continental Europe, epoxy paints, used as adherence primers for three-layer type external coating systems, are applied in thinner coats (between 60 µm and 150 µm), generally as a powder paint, so called fusion bonded expoxy (FBE) [214].

E. Problems encountered

Anticorrosion protection provided by coating is generally impaired if defective (areas with no or very thin coating). Coatings such as epoxy resins are brittle and easily damaged. Singular points (corners, edges, etc.) and zones where coated parts are joined together are also potential problem sites, especially if another application method is involved or even another coating technology. Defects are likely to develop at cutbacks of coated pipes, where the corrosive agents in contact with the metal tend to diffuse laterally along the metal-coating interface. To limit these defects, apart from careful selection of the welded joint system with respect to the type of coating, the quality of support surface preparation and the quality of the coating application are crucial and must be certified by a recognised inspector [191].

The long term performance of the organic coatings (even fault-free) is also critical. Exposed to harsh environments, these coatings are expected to last for several decades. Coatings in service on overhead pipes must be inspected regularly, whenever possible, to limit the risks of collateral damage. For example, cases of massive disbonding of undamaged three-layer coatings have been observed during inspections on pipes in service, without generating corrosion however, since the rate of renewal of the corrosive species is too low thanks to the fact that the coating remained pressed against the steel [246; 255; 256].

Diffusion of water to the interface through the undamaged three-layer coating system, which occurs relatively rapidly with respect to the pipe lifetime (Figure 2.4), could be responsible for the loss of adhesion of the primer epoxy resins [226; 259]. Reversible phenomena such as plasticisation of the resin by water and differential swelling between the resin and the metal may be put forward, as well as irreversible phenomena such as hydrolysis of the epoxy resins, which occurs above temperatures of 50 °C for some compositions [262]. The effect of residual stresses in the three-layer coating, related to application process by extrusion of the polyolefin-based layers, has also been put forward [178].

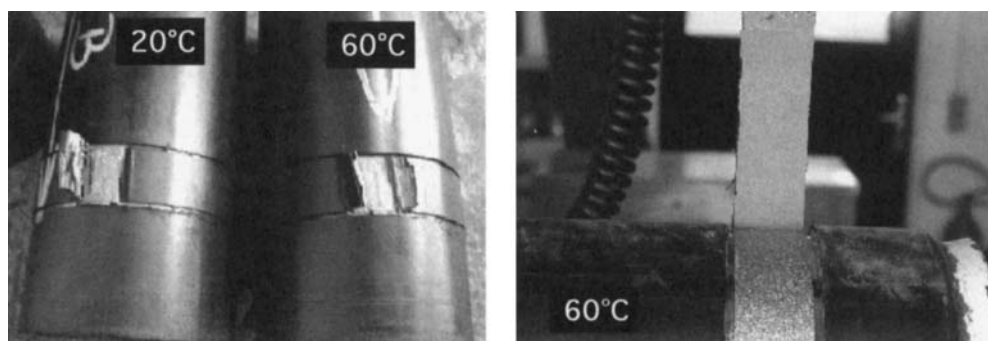


Figure 2.4

Results of peeling at 21 °C obtained on undamaged three-layer coatings aged in deionised water and scarified just before peeling: (a) cohesive failures in the adhesive after 10 days at 20 °C and 60 °C (mean peeling forces = 36 kN/m); (b) steel/epoxy primer adhesive failure after 49 days at 60 °C (mean peeling force = 6 kN/m) [261].

In conclusion, the performance of a coating (applied correctly on a properly prepared surface) depends on several criteria:

- Adhesion of the coating on the metallic substrate in initial state;
- Barrier properties of the coating with respect to the molecular species to which it is exposed. Note that the permeability of a material to a molecular species is an intrinsic property, product of the diffusion coefficient and the solubility. The rate of permeation through the coating is proportional to the permeability and inversely proportional to the coating thickness (case of a thermally activated, traditional diffusion process);
- Durability of the coating and of the coating-substrate adhesive bonds, in particular resistance to chemical damage such as hydrolysis. It is also an intrinsic property related to the chemical nature of the materials;
- Resistance to mechanical damage, such as that caused by accidentally dropping a tool onto the coating during an inspection, and during service under the effect of differential substrate-coating swelling (due to temperature cycling or plasticisation/deplasticisation of the organic coating).

We must also point out that it is extremely difficult to estimate the long-term performance of a coating system, especially since the contents and specifications of coating products and paints

change permanently, which limits feedback. Returning to the above example of three-layer coatings, the qualification tests include dry adhesion measurements as well as cathodic disbonding resistance measurements, but the adhesion properties of undamaged three-layer coatings plasticised by water are generally not evaluated [259]. The qualification tests must be adapted to the service conditions, in terms of environment and duration. These qualification tests must also meet industrial constraints, however, hence the notion of accelerated ageing. This remark raises the question of the accelerated ageing tests representativity. These tests are relevant if they implement the ageing mechanisms of a coating in a given application, but this assumes that the ageing mechanisms, which are often complex, have been identified [234]. While the debate on the issue continues, the best way to guarantee that a coating is efficient is to involve and train all the various players: suppliers/manufacturers/customers/inspectors/scientists.

2.2.1.3 Composite liner

Consisting of a resin, fillers and reinforcing materials, a composite liner is a thick coating (at least 1 mm) applied to protect the inside of tanks against corrosion or contamination [158]. This type of protection is similar to that provided by organic coatings, since it prevents contact between a corrosive medium and a metallic structure.

We will take the example of the wash tank of a catalytic reforming regeneration loop in refineries. In the wash tank partially filled with Raschig rings, acid vapour (just neutralised with excess soda) from the reforming unit comes into contact with mineralised water at ambient temperature injected in counter-current. The operating conditions (temperature/pressure) in the tank are typically 60 °C/4 bar. The design conditions are 80 °C and 10 bar. The acid vapour composition may nevertheless reach a molar CO₂ content of about 20%, the HCl content remaining less than a few ppm. Under the design conditions, the partial pressure of CO₂, which is a highly corrosive species for iron (see paragraph 1.2 in this book), may reach 2 bar. According to the literature [188], the CO₂ corrosion rate (at 2 bar) of unprotected carbon steel is 3 mm/year at 40 °C, reaching 9 mm/year at 60 °C. In view of the high carbon steel corrosion rates under the tank operating conditions, it is essential to use a coating which acts as an efficient, long-term barrier against the corrosive species. According to feedback, the epoxy paints (thickness < 1 mm) traditionally used as anticorrosion coating for reforming wash tanks do not protect the steel efficiently over long periods of time. One explanation put forward is their brittleness during maintenance phases, resulting in damage to the coating (numerous cracks in the paints during inspection). The damaged zones of the tank steel represent zones of preferential attack by CO₂.

A Stratified Glass fibre/vinyl ester Resin (SGR) of total thickness approximately 4 mm has been recommended, comprising an anticorrosion primer, various resin coated glass reinforcements and a final resin layer about 2 mm thick. The main factors governing the performance of an anticorrosion coating in the short and long terms have been considered: surface preparation and application quality, durability of the component materials under the exposure conditions, resistance to mechanical damage and barrier properties. Due to the similarities between epoxy resin and vinyl ester families, the annual flow rate of CO₂ through a 4 mm thick epoxy-amine coating was calculated under the tank design conditions, i.e. $7.5 \cdot 10^{-5}$ g/cm³ on the basis of CO₂ solubility and diffusion coefficients measured on epoxy resins [192]. This flow rate induces an acceptable carbon steel corrosion rate of 0.8 µm per year.

2.2.1.4 Inorganic coating

Inorganic coatings include those made from metals, heat-resistant compounds (oxides, carbides, nitrides) and cement.

Metallic coatings, consisting of a metal layer resistant to corrosion in the medium considered often provide additional mechanical resistance (against abrasion or against friction). They are said to be cathodic or anodic due to their protection mechanism, which depends on the position of the protective metal in the corrosion potential scale (refer to paragraph 3.2 for further information). The difference in behaviour of these two protection mechanisms is very important in case of defects (such as pores) in the coating. With a coating which is more noble (cathodic) than the substrate with an open porosity, the substrate (anode) will locally corrode; this damage cannot generally be observed on the surface of the coated part. This type of attack is therefore very insidious. In contrast, when the deposit is less noble than the substrate, the opposite phenomenon is observed, with the deposit acting as an anode in this case: it corrodes (acting as sacrificial anode) while the substrate is protected.

Metallic coatings can be applied using techniques classified into the following categories: thermal spraying, physical or chemical vapour deposition techniques, electroless plating, immersion in liquid metal and electrodeposition.

A. Thermal spraying

Thermal projection refers to deposition by detonation, deposition by flame spraying and deposition by plasma spraying, which produce very similar microstructures. Ideally, the particles of a pulverulent material melt completely during spraying (but do not sublime), then flatten and solidify on striking the substrate surface. The solidified particles are more or less flat depending on the state of fusion and the surface wettability, while their microstructure depends on the rate of cooling. The coatings, built up by stacking lenticular particles, contain cavities due to degassing, contraction of the material or topographic effects.

B. Vapour deposition [225]

Cathodic sputtering, which is a Physical Vapour Deposition (PVD) technique, can be used to deposit a large number of metals, alloys and heat-resistant compounds. In a vacuum chamber containing a gas such as argon under low pressure, a voltage of about 2000 V is applied between the target (negative pole containing the chemical elements to be deposited) and the substrate (positive pole). A plasma is formed. The electric field accelerates the plasma ions (Ar^+ if argon is used) which will collide with the target: these collisions eject atoms from the target which are then deposited on the substrate.

In Chemical Vapour Deposition (CVD) techniques, a mixture of gases containing a volatile chemical compound of the metal to be deposited is used in the presence of a reducing gas such as hydrogen or methane. As this mixture of gases is introduced into the reaction chamber, the volatile compound is reduced on the surface of the substrate to be coated, forming a deposit. These CVD techniques, which generally require high temperatures (800 °C to 1 000 °C), can be used to deposit heat-resistant compounds (oxides, carbides, nitrides, borides).

C. Electroless plating

During electroless plating, the metallic ions to be deposited, dissolved in the solution, are reduced by a reducing agent on the surface of the substrate which acts as catalyst. Unlike electrodeposition, electroless plating also applies to insulating substrates such as ceramics and polymers. The example of electroless plating most frequently implemented in the petroleum industry is chemical nickel plating (also known as the Kanigen process): Ni^{2+} ions are reduced in aqueous solution by hypophosphite ions H_2PO_2^- . An Ni-P coating is formed. Heat treatment (in the region of 500 °C) applied to this type of coating may considerably increase its hardness and adhesion due to the formation of Ni-P-Fe intermetallic compounds at the internal coating-steel interface.

D. Immersion in a liquid metal

This technique is used to coat steels with zinc: the substrate is immersed in a bath of molten zinc (above 420 °C); a zone of Zn-Fe interdiffusion also forms, ensuring good adhesion of the deposit.

E. Electrodeposition

This technique is used to deposit metals such as nickel, copper, chromium and zinc, as well as their alloys, on a conducting substrate which is then placed as cathode in an electrolyte cell containing the ions of the metal to be deposited (together with various complexing agents and buffers).

2.2.1.5 Cladding

Cladding is the combination of two metallurgies. It is applied by roll bonding, weld overlay or explosion technique. This type of solution offers a compromise between different properties. One provides chemical inertia, for example, the other mechanical strength. This technology is typically applied to pipes to protect specific parts against erosion (surface attack due to impact of debris) or abrasion (surface attack due to friction of another moving part). In the refining industry, this technology is frequently used for hydrotreatment reactors to provide inexpensive protection against internal corrosion by sulfidation: stainless steel claddings are used to protect low-alloy steel ferrules, instead of making ferrules out of solid stainless steel which would exhibit lower mechanical properties.

A. Roll bonding

Roll bonding consists in feeding sheets of the base metal and the plating metal simultaneously through the rolling mill.

B. Weld overlay

In the weld overlay technique, the noble metal is deposited as continuous weld seams over the entire surface of the base metal. The main welding techniques used are Submerged Arc Welding (SAW), Electro Slag Welding (ESW), Gas Tungsten Arc Welding (GTAW) and Shielded Manual Arc Welding (SMAW). Two layers of different types are generally

specified to create the overlay required for hydrotreatment reactors. The first layer, made from high-chromium stainless steel (AISI 309L, UNS S309003), reduces the effects of chromium dilution from the overlay to the base metal during welding. The second layer, in contact with the process fluid, consists of stabilised austenitic stainless steel [niobium in grade AISI 347 (UNS S34700), or titanium for grade AISI 321 (UNS S321000)]. The ferrite content is an important parameter in this second layer: it must be greater than 3% to avoid hot cracking and less than 8% to prevent loss of ductility, reduce hydrogen accumulation and avoid low cycle fatigue cracking.

C. Explosion cladding

The energy required to bond the two sheets is obtained by the shock wave and pressure (several GPa) generated by detonation of an explosive. This technique does not generate a temperature increase in the centre of the metal or any metallurgical conversion which would impair the corrosion resistance (e.g. chromium depletion of the grain boundaries).

2.2.1.6 Anticorrosion cements

Cements can be used to protect the metallic walls against corrosive attack. Cement coatings are generally sprayed on and secured by metal anchoring points welded to the wall. The cement coating is generally about 50 mm thick. They are virtually impermeable to water and hydrocarbons. In addition, they generally offer excellent erosion and abrasion resistance. This type of coating is used for example to protect carbon steel tanks against wet H₂S corrosion.

2.2.1.7 Surface treatments

Surface treatments are used to obtain a conversion layer by reaction of the metal with a chosen medium. Chemical modification of the surface increases the corrosion resistance.

A. Anodising

Anodising is carried out to increase the natural metal oxide by anodic oxidation. For aluminium alloys, the metal is immersed in a suitable solution (e.g. sulfuric acid) and a voltage of 10 V to 20 V is applied for a few minutes. Anodising is also used to increase the thickness of passive films on the surface of metal parts benefiting from this natural protection (stainless steels, titanium, tantalum, zirconium). For stainless steels, the treatment – which is also known as passivation – consists in dipping the metal into a solution of nitric acid.

B. Phosphating

Phosphating is applied to low alloy and carbon steels. The metal is immersed in a solution of phosphoric acid causing corrosion of the iron and precipitation of iron phosphates on the surface. This type of protection is used, for example, to protect carbon steel equipment during transportation. Protection is only efficient up to 120 °C, since the iron phosphates formed decompose above this temperature.

2.2.2 Cathodic protection of structures

2.2.2.1 Principle

Since electrochemical corrosion is due to flow of a current between anode and cathode, it is sometimes beneficial to cancel this current and completely convert the metallic structure to be protected into a cathode, thereby protecting it against attack. This technique is known as cathodic protection. The current applied can be produced by a DC generator and supplied by more or less consumable anodes (scrap steel, ferrosilicon, graphite) or inert anodes (platinum-plated titanium, mixed metal oxide coated titanium Ti/MMO), which is, for example, generally the case for onshore pipelines. The dissolution current of a sacrificial magnesium, aluminium or zinc alloy anode may also be used to provide cathodic protection. Offshore pipelines, for example, are protected by sacrificial anode clamps connected every 100 m to 200 m during laying. Cathodic polarisation of the metal lowers the metal/solution potential so as to bring it within the immunity zone (Figure 2.5).

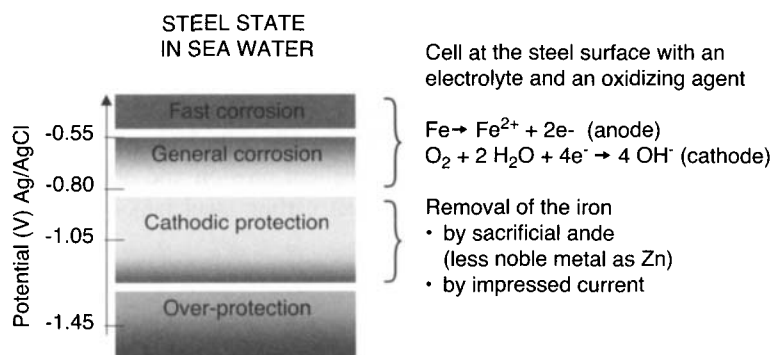
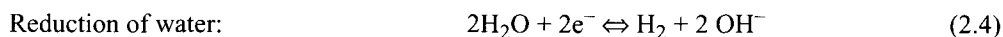
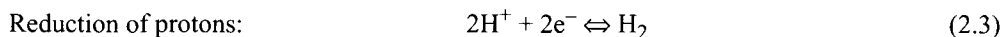
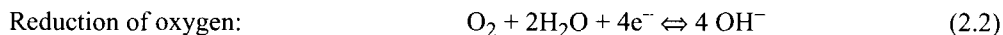
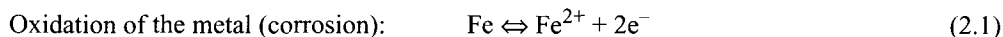


Figure 2.5

States of steel in seawater according to the potential scale.

When Cathodic Protection (CP) is applied on a metallic structure, the substrate oxidation reaction (Equation 2.1) is unfavoured. In this case, the reduction reactions occur at the metal (cathodic zone): reduction of oxygen (Equation 2.2) and/or reduction of protons (Equation 2.3). At very low potential, reduction of water occurs (Equation 2.4).



2.2.2.2 History of offshore and onshore applications

Cathodic protection of metallic structures, whose history has been documented and described in detail by M. Roche [254], dates back to the 19th century. Cathodic protection is now systematically applied to metallic structures, both buried (pipelines, tanks) and

submerged (pipelines, offshore infrastructures, ships, etc.). The reader can refer to a specialised document [243]. Cathodic protection is also implemented, though less frequently, to protect internal seawater circuits and steel in concretes.

Cathodic protection can be combined with an anticorrosion organic coating, which considerably reduces the current required for cathodic protection or the weight of the sacrificial anodes, compared with the cathodic protection necessary to protect the entire area of the uncoated structure. Use of a coating will therefore be taken into account when designing cathodic protection under given service conditions. It is essential to ensure, however, that the coating, if damaged and exposing the metal, is not too sensitive to cathodic delamination phenomena. The consequences of these phenomena, whose mechanisms have been extensively studied in the literature [176; 219; 258], are to increase the cathodic current demand or the rate of consumption of the sacrificial anodes over time. As for coatings used without cathodic protection, adhesion is a key parameter when choosing a coating to be applied on a structure which will be placed under cathodic protection; adhesion must be evaluated under conditions – potential, exposure medium, dissolved oxygen, electrolyte flow and duration – simulating the service.

2.2.2.3 Problems encountered (design, checks of cathodic protection and cathodic overprotection, shielding, monitoring)

To ensure that the entire installation is at the correct potential, the cathodic protection voltage must actually reach all bare steel surfaces exposed to the surrounding medium. The installation must therefore be properly designed and maintained to limit failures of the impressed DC power supplies and replace the sacrificial anodes on proper time. Design of cathodic protection must be carefully studied, especially for a complex structure, since the distribution of potentials at each point on the structure may vary considerably. The risk is that certain zones where the IR drop with the groundbed is too significant would be under-protected. This may be the case for example in soils, when the land dries, increasing the electrolyte resistivity and reducing the range of the cathodic protection. Cathodic protection design models have been developed as support during the initial design phase.

Another risk associated with the combined use of an organic coating and a cathodic protection system is the shielding of the cathodic protection current, if the organic coating exhibits high electrical resistivity, which is the case of polyolefins, for example, and if it is thick. This risk may lead to highly critical situations in case of substantial disbonding of the coating from the steel if the locally damaged coating allows electrolyte to come into contact with the metallic substrate in a zone remote from the defect, where cathodic protection is no longer effective [209; 270; 271].

Application of the cathodic protection must be monitored during service in order to avoid situations where there is no more protection, but also situations of overprotection. In practice, it may be difficult to check the potential applied: cathodic overprotection may occur when the potential is too negative for impressed current systems using a magnesium electrode. Cathodic overprotection is accompanied by the production of hydrogen, which exposes the steel to a risk of hydrogen embrittlement. Overprotection also increases the risk of cathodic disbonding of coatings near the defects, exposing the metal. For onshore facilities, cathodic protection

efficiency is generally controlled by periodic checks at the potential measurement points, together with records of potential measured using permanent electrodes distributed in the critical zones, possibly transmitted to a remote monitoring system. Cathodic protection measurement techniques are continuously being improved, to eliminate the problem of IR drop between the reference electrode and the structure controlled. The measurements taken when cathodic protection is applied are in fact subject to error, due to the IR drop between the reference electrode and the structure controlled. The higher the land resistivity, the greater the distance between the reference electrode and the point to be controlled, and the greater the cathodic current density (e.g. at coating defects), the greater the error. The most well-known means of correcting the IR drop is to take measurements using the on/off method. Cathodic protection monitoring is a major issue and improvements are made on a regular basis: to check the true effectiveness of cathodic protection on buried structures, in particular, intensive methods operating with stray or telluric currents as well as remote monitoring and the use of cellular and satellite telecommunication are being developed [254]. The best way of guaranteeing the effectiveness of cathodic protection is to rely on qualified personnel whose skills have been demonstrated by a certification system, complying with standard EN 15257 for example.

2.2.3 Corrosion inhibitors

2.2.3.1 Principle

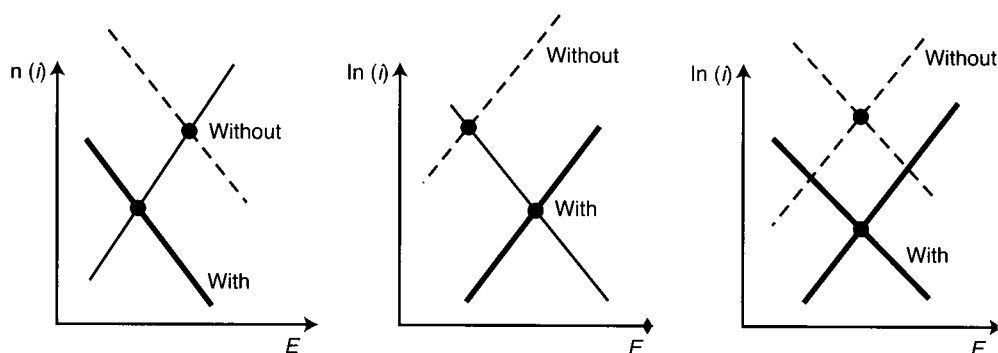
Added to the corrosive medium in small doses, corrosion inhibitors are compounds which modify the electrochemical reactions without taking part themselves in the reactions. There are numerous types of inhibitors and inhibition mechanisms. The main reaction mechanisms used to classify inhibitors include adsorption, passivation, film precipitation (precipitation of complexes on the metal surface), elimination of a corrosive agent (applicable in closed systems such as elimination of oxygen using scavengers). A given inhibitor is often associated with several action mechanisms. Inhibitors are in fact specific to a type of alloy and a type of medium. In liquid media, they are said to be cathodic, anodic or mixed, depending on whether they act more especially on the cathodic reaction, anodic reaction, or both at the same time by reducing the current density of the reaction(s) concerned, as indicated on Figure 2.6 (see paragraph 3.2 for more detailed information).

Some anodic inhibitors may have a passivating effect, i.e. participate in the formation of a passive, protective surface layer. The effect of this type of passivating inhibitor is illustrated on the simplified polarisation curves shown on Figure 2.7.

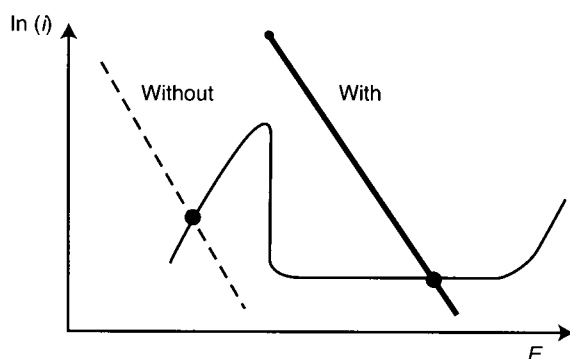
Inhibitors can also be added in gas phase: adsorption and/or formation of protective surface layers govern their action mechanisms.

The degree or efficiency of inhibition characterises the decrease in corrosion rate due to the presence of the inhibitor. It depends on the inhibitor concentration (*c*) and is generally expressed by:

$$\% \text{ efficiency} = 100 \times \frac{(\text{corrosion rate in absence of inhibitor} - \text{corrosion rate in presence of a quantity } c \text{ of inhibitor})}{\text{corrosion rate in absence of inhibitor}}$$

**Figure 2.6**

Influence of an anodic, cathodic or mixed inhibitor on simplified polarisation curves and on the corrosion potential.

**Figure 2.7**

Influence of a passivating anodic inhibitor on the simplified polarisation curves and on the corrosion potential.

In petroleum production, the aim is to achieve efficiencies of at least 80% [239]; efficiencies of more than 99.9% can be obtained if the inhibitors are correctly selected.

2.2.3.2 Liquid phase inhibitors

We have seen that these inhibitors affect either one or both of the corrosion reactions.

A. Anodic and passivating inhibitors

These inhibitors are mainly used in neutral medium to form or promote the formation of a protective film which inhibits anodic dissolution of the metal. These inhibitors must be injected in sufficient concentrations since otherwise, they may accelerate anodic dissolution.

Anodic inhibitors can be classified according to their corrosion inhibition action mechanism:

- Oxidising inhibitors such as chromates CrO_4^{2-} , nitrites NO_2^- or the less efficient molybdates MoO_4^{2-} and nitrates NO_3^- . Due to their toxicity, however, these inhibitors are only recommended for systems and circuits with no discharge to the exterior (e.g. closed cooling water circuits);
- Inhibitors acting as buffers to maintain a high pH near the surface, to facilitate passivation. Basic salts such as silicates, borates, carbonates or phosphates can be used to stabilise the pH in neutral or alkaline medium.

B. Cathodic inhibitors

Cathodic inhibitors control corrosion by reducing the cathodic reaction by adsorption of chemical compounds (cathodic poisons) or by formation through precipitation or polymerisation of a film-forming a layer preventing diffusion:

- Sulfide or selenide type cathodic poisons adsorb onto the metallic surface whereas compounds containing arsenic, bismuth and antimony are reduced, forming a metallic layer. Adsorption of these compounds may also favour hydrogen penetration in steels, causing Hydrogen-Induced Cracking (HIC) or Stress Corrosion Cracking (SCC), as described in paragraph 1.3 of this book;
- Precipitation or polymerisation agents generate the formation of a protective film which reduces the cathodic reaction rate. In neutral and alkaline media, this occurs when scale deposits of calcium and magnesium carbonates precipitate on the metallic surface. Inorganic salts such as silicates, borates or phosphates may also have this cathodic effect. Polyphosphates $(\text{NaPO}_3)_n$ and organophosphates are also included in this category.

C. Mixed inhibitors

Numerous inhibitors, mainly organic formulations, are capable of reducing the rates of anodic and cathodic corrosion reactions. Their efficiency is closely related to their ability to adsorb onto and cover metallic surfaces. Their adsorption depends on their structure, the charge of the metallic surface and the type of electrolyte.

The organic inhibitors are composed of numerous formulations: aromatic molecules, linear or branched chain macromolecules, etc. They contain a non polar, hydrophobic part consisting mainly of carbon and hydrogen atoms and a polar hydrophilic part consisting of one or more functional groups such as amines ($-\text{NH}_2$), mercaptans ($-\text{SH}$), hydroxyls ($-\text{OH}$), carboxyls ($-\text{COOH}$), phosphates ($-\text{PO}_3$) or their derivatives (addition information on the functional groups is provided in Table 2.1). The inhibitor is attached to the surface by its hydrophilic functional group, while its larger non polar part partially blocks the active surface, as shown on Figure 2.8.

a. Examples of basic compounds used to inhibit corrosion in petroleum production .

The inhibitors have a long hydrocarbon chain (12 to 18 carbon atoms) and a nitrogen- and oxygen-based functional group, as indicated in Table 2.2. The hydrocarbon chain makes these additives partially soluble in crude oil: the chain also attracts hydrocarbons in the

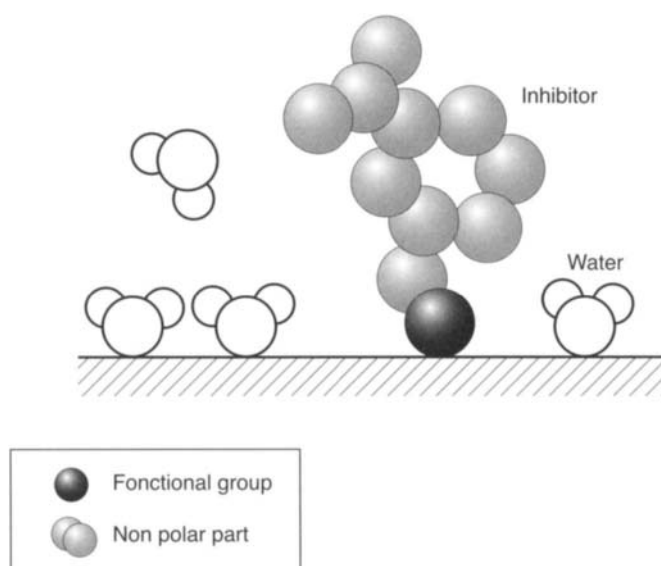


Figure 2.8

Adsorption of an organic inhibitor in aqueous medium [225].

Table 2.1 Chemical compositions of the functional groups of organic inhibitors (source: [240]).

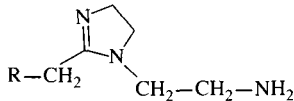
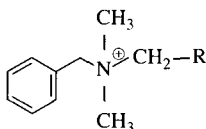
Structure	Name	Structure	Name
—OH	Hydroxy	—CONH ₂	Amide
—C≡C—	-yne	—SH	Thiol
—C—O—C—	epoxy	—S—	Sulfide
—COOH	Carboxy	—S=O	Sufoxide
—C—N—C—	Amine	—C=S—	Thio
—NH ₂	Amino	—P=O	Phosphonium
—NH	Imino	—P—	Phospho
—NO ₂	Nitro	—As—	Arsano
—N=N—N—	Triazole	—Se—	Seleno

fluid; the film formed by these hydrocarbons on the metallic wall may also play a role in inhibiting corrosion.

In petroleum production, inhibitors are also classified according to their solubility, dispersibility in water and/or in crude oil:

- water-soluble inhibitors quaternary amines, amine salts, imidazoline salts,
- crude oil-soluble inhibitors: for example long chain primary amines, imidazoline, fatty acids, phosphate esters.

Table 2.2 Basic chemical compositions of some inhibitors used in petroleum production (source: [239]).

Chemical compound	Structure
Primary amine	$R-CH_2-NH_2$
Amide	$R_1-CH_2-\overset{\overset{O}{\parallel}}{C}-NH-R_2$
Imidazoline	
Quaternary ammonium ion	
Polyethoxylated amines	$R-N\begin{cases} (O-CH_2-CH_2)_n OH \\ (O-CH_2-CH_2)_n OH \end{cases}$

b. Examples of inhibitor injection modes in petroleum production

Inhibitors can be added by continuous injection, batch injection or a mixture of both:

- Continuous injection: after several hours of pretreatment with an overconcentration of products, a constant quantity of inhibitors is injected throughout the lifetime of the equipment;
- Batch injection: a larger quantity of inhibitor is injected periodically, with no continuous injection. A pig is generally run through to clean the pipe walls before injecting the batch. The batch injection frequency depends on the concentration of the inhibitor which desorbs, this quantity being determined by analysing the product in the effluent at the exit of the effluent and by monitoring the corrosion rates;
- Mixed treatment: periodic batch treatment is carried out, together with maintenance by continuous injection of a small quantity of inhibitor.

c. Other associated functions in anticorrosion formulations

Corrosion inhibition additives are often associated in formulations with other chemical compounds, for example to limit deposits, to break up emulsions and to neutralise acid compounds:

- Antimineral deposit additives to prevent clogging of wells, oil tubings and water cooling circuits. These additives prevent precipitation of calcium and magnesium carbonates and barium sulfates. They are based on film-forming fatty amines, condensed phosphates, organophosphates, organic polymers and polyaspartates. Sometimes they also have corrosion inhibiting properties;

- Antideposit and antifouling: refining processes may be particularly affected by deposits from side chemical reactions (polymers, coke), especially in heat exchangers. Antideposit additives are often based on antipolymerising and oxygen scavenging compounds;
- Neutralising agents to reduce corrosion by increasing the pH of the aqueous solution which may condense, for example in atmospheric distillation column heads. Although ammonia has been widely used and remains an inexpensive solution, it may cause ammonium chloride deposits, as well as fouling and under deposit corrosion. Organic liquid neutralisers have been developed to prevent the formation of ammonium chlorides.

Table 2.3 illustrates the anticorrosion, antideposit and neutralising functions sought for various refining processes.

Table 2.3 Applications of anticorrosion, antideposit and neutralising formulations in the refining industry [204].

Unit	Process flow	Anticlogging	Corrosion inhibitor	Neutralising
Distillation	crude feedstock	X		
	atmospheric column head		X	X
	vacuum column head		X	X
	steam injection	X		
Coker	coker feedstock	X		
Alkylation	debutaniser column head		X	X
	depropaniser column head		X	X
FCC	fractionation column head		X	
	compressed wet gas		X	
	debutaniser column head		X	
	depropaniser column head		X	
Catalytic reformer	hydrodesulfurated feedstock	X		
	hydrodesulfurated effluent	X	X	
	light product stripping column head		X	X
	prefractionation column head		X	X
	hydrogen feedstock stripper		X	
Hydrocracker	reactor feedstock	X		
	debutaniser column head		X	

2.2.3.3 Gas phase inhibitors

These inhibitors are conveyed by gas pathway up to the metallic walls to be protected. Amongst the gas phase inhibitors used, two types of additive can be identified depending on the temperature range of the application.

A. Inhibitors providing temporary protection against atmospheric corrosion

They are generally organic compounds with high vapour pressure which, after transport in gas phase, adsorb onto the metallic surface and protect it against atmospheric corrosion. The various chemical compounds used include amines (triethylamine, hexylamine, dibenzylamine, isopropylamine, etc.) and organic carbonates (monocyclohexylamine, ethylamine carbonate, etc.). Amine-based compounds vaporise without molecular dissociation and only dissociate on the surface of the metal to be protected when they come into contact with liquid water [164].

B. Inhibitors to avoid some types of high temperature corrosion

Most film-forming amine-based inhibitors are used to solve problems of liquid-phase corrosion up to their stability limit of about 175 °C. For applications at higher temperatures, inorganic or organometallic formulations are used to transport protective alkaline earth and/or metal sulfides, phosphates or oxides, for example, to the metallic walls. The following examples concern applications of corrosion inhibitors during high temperature refining operations. These inhibitors form, for example, a phosphate or sulfide ester-based protective layer on the metal surface:

- Inhibition of corrosion by the naphthenic acids present in some crudes during distillation operations (a more detailed description of naphthenic acid corrosion is provided in paragraph 1.12). Phosphate ester or thiophosphorated compound-based additives are proposed to limit this type of corrosion [232; 238];
- Inhibition of corrosion by metal dusting and clogging by catalytic coking. (also refer to paragraph 1.17): injecting small quantities of sulfur compounds (H_2S , DiMethylDi-Sulfide) in the feedstocks blocks the activity of iron particles which catalyse coking and metal dusting of steels [257].

2.3 CORROSION DETECTION, CONTROL AND MONITORING

2.3.1 Introduction

In the oil and gas industry, corrosion control tools and inspection strategies are required to guarantee equipment integrity and reliability.

To prevent catastrophic failures, optimise inspection activities and limit repair costs, significant effort has always been invested in the development of corrosion monitoring tools [217; 248]. For example, inspection practices have become much more efficient through, in particular, the use of risk evaluation strategies, which lead to improved inspection planning. Thanks to continuous progress in inspection tools, the data obtained to assess corrosion is now more useful and more accurate, e.g. reduction in wall thickness and *in situ* conditions (temperature, pH, etc.). This type of information provides a means of evaluating the overall condition of the equipment or the various parts and predicting lifetime via corrosion models, when available.

In total interaction with the process conditions, corrosion evaluation must be considered as input data for global management of industrial equipment and installations. On-line corrosion monitoring, i.e. permanent, real-time recording [213], firstly prevents unplanned stoppages and, secondly, the data collected can be merged or correlated with process variables [195; 213] in order to take decisions more rapidly. Due to the progress made in the fields of automation and computer technologies as well as recent improvements in the corrosion monitoring tools themselves, it is now possible to meet most of these new corrosion measurement requirements.

This paragraph provides a non-exhaustive overview of the various tools available for corrosion detection and monitoring in the oil and gas industry, from the simplest tools to the most recent developments and trends.

The first section is dedicated to real-time monitoring techniques, i.e. those requiring no process interruption. We will make a distinction between techniques requiring intervention, e.g. recovery of coupons, and those which can be carried out completely on line, since they can be installed permanently, automated or even managed remotely.

The techniques in this category can also be classified according to their relations with corrosion:

- electrochemical means are available to record the actual corrosion taking place, due to electronic transfers,
- specific tools are also available to determine the corrosive power, i.e. the severity of the conditions faced by the structure; these measurements generally concern the corrosive medium, but measurements may also be taken with galvanic probes.

These two types of monitoring provide instantaneous corrosion data, either directly on the phenomenon or indirectly, i.e based on the potential risks. Although some electrochemical methods are essentially qualitative, they are nevertheless valuable to identify the active corrosion mechanisms, especially in case of local attack.

Some techniques also provide quantitative corrosion measurements based on property-induced variations (weight loss, electrical resistance), but only cumulatively; as a result, they can only be used to monitor damage over a relatively long period, since the corrosion intensity can only be appreciated through the rate of variation of the variable recorded or in reference to a previous value.

The second section describes the methods used for inspection and, in particular, tools belonging to the family of non-destructive methods. A subsection will be dedicated to pipeline inspection, a very special activity due to the use of pigging. The last subsection will deal with Risk-Based Inspection (RBI).

2.3.2 Corrosion control methods

This category includes all the techniques which do not necessarily require shutdown of the installations concerned (even if this may be the case), as opposed to inspection methods which, by definition, are employed during scheduled shutdowns.

We will make a distinction between direct methods, used to detect corrosion as it is actually happening, and indirect methods generally based on the cumulative effects of corrosion,

either due to modification of a property (weight, electrical resistance) or of an induced consequence (e.g. hydrogen production).

In the first case, corrosion intensity can be monitored in real time and expressed as a corrosion rate, provided that prior calibration has been carried out. This is essentially the case with electrochemical methods, which take direct measurements of the electronic transfer responsible for metal consumption: they will be discussed in paragraph 2.3.2.2 on direct methods.

The response time of cumulative methods is much longer, since the property concerned must be modified sufficiently with respect to the accuracy of the sensors used. Consequently, the measurement taken is necessarily an average, which means that trends can be monitored but not short-term effects, induced for example by occasional modification of the installation operating conditions.

2.3.2.1 Indirect methods

A. Corrosion coupons [189; 217]

This is the oldest and most widely used method of monitoring corrosion in industrial installations. In the petroleum industry, it is still the basic tool to evaluate corrosion for all accessible equipment. The principle, which is extremely simple, consists in placing coupons made from the same alloy as the equipment in contact with the aggressive medium (as a comparison, coupons made from more or less resistant alloys can also be inserted). The coupons are inserted for a specific period, typically several months, after which they are removed and examined. They are generally inserted on simple devices (Figures 2.9 and 2.10), with the following considerations:

- firstly the need to access the chosen location, which may involve adapting the installation (e.g. a special flange),
- secondly, the need to minimise the impact on operation of the installation and on the corrosion phenomenon itself, especially by galvanic coupling or geometric confinement problems.

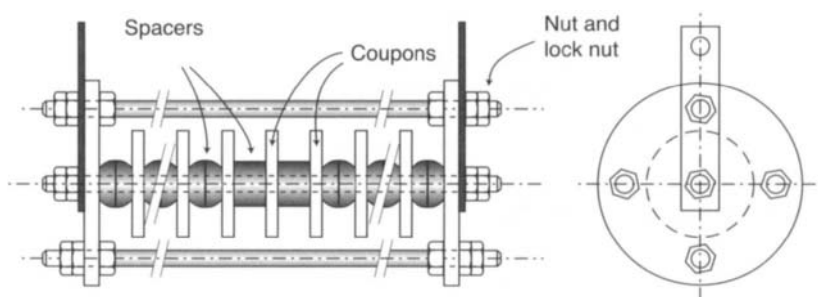


Figure 2.9

Example of corrosion coupon rack [159].

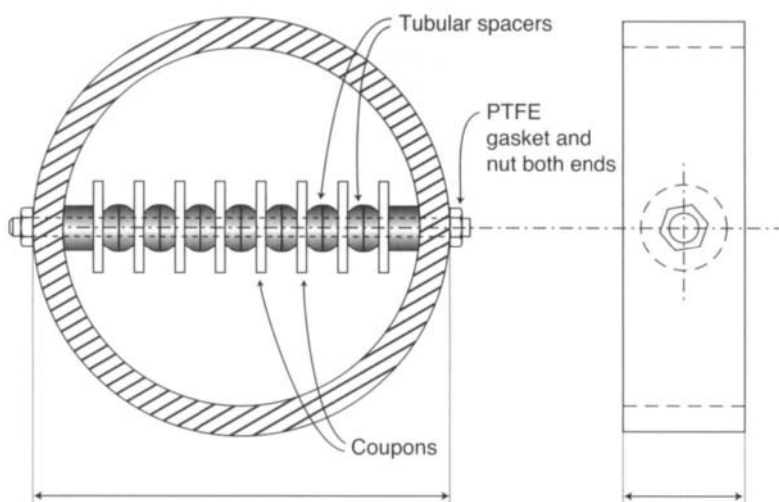


Figure 2.10

Example of Dutchman corrosion coupon rack [159].

An equivalent uniform corrosion rate can then be calculated from the sample weight loss, using a simple analytical formula:

$$V = - (K \cdot \Delta M / (\rho \cdot S \cdot t))$$

where: V: corrosion rate ($\mu\text{m}/\text{year}$)

ΔM : sample weight variation (mg)

ρ : alloy density (g/cm^3)

S: area of the sample exposed to the medium (cm^2)

t: exposure duration (h)

K: adimensional coefficient ($= 8 \cdot 76 \cdot 10^6$, with the units used for the other terms)

This formula is included in standard ASTM G1-03 [161] which also describes the sample cleaning and weighing procedures.

Metallographic examination may confirm the presence of uniform corrosion and, otherwise, reconsider the corrosion rate calculated. Physico-chemical analyses (e.g. X-ray diffraction analyses of the corrosion products, analyses of chemical elements present in the cracks) are then conducted on the coupons to identify or corroborate the mechanisms responsible for metal attack.

Some coupons are specifically designed to study certain forms of localised corrosion, such as crevice or pitting corrosion.

Apart from its simplicity, the main advantage of this technique is the fact that the coupons are highly representative of the installation material, since they can have the same composition and metallurgy and even similar surface condition, if necessary. The coupons may also include portions of welded joints produced using a suitable process.

The composition of medium is also the same as that actually seen by the equipment monitored and there is no limitation to its electrical conductivity. In addition, good representativeness is obtained, both as regards the corrosion deposits and more generally the degradation process seen by the installation.

There are also numerous restrictions:

- The coupons can only be installed in accessible locations, making them unsuitable for underwater applications and, unless a removable rack is used, the equipment must be shut down to remove them;
- The corrosion measurement may be biased not only by localised corrosion but also by the positioning of the coupons and by the possible effect of disturbing factors such as multiphase flow, turbulence, and areas of aqueous phase condensation, which may lead to incorrect interpretations;
- The coupons are unable to indicate changes in corrosion over time; consequently, they are of no use to solve problems requiring operator reactivity;
- Lastly, due to their small size, corrosion coupons are unable to take into account the effects of solid-liquid heat transfer, which may bias their behaviour compared with the more massive metal walls.

Coupons have been developed to evaluate specific types of corrosion. The variants produced for specific degradation problems include:

- Crevice corrosion coupons: the various geometries available [155; 157] (ASTM G48 and G78) are based on different principles to initiate a crevice (differential aeration, local pH, anode/cathode surface area ratio). The choice must be made in view of the actual risks involved; coupons used on oil fields are generally installed on electrically-insulated supports whose geometry is adapted to the equipment (reactor or pipeline: Figures 2.3.1 and 2.3.2);
- Galvanic corrosion coupons composed of different electrically-coupled metals [156] (ASTM G71) with variable anode/cathode surface area ratios; apart from dissolution of the anode, this type of coupon can be used to study the risk of cathode embrittlement by the hydrogen produced during the corrosion reaction;
- Stress corrosion coupons: the devices used to produce the stress (C-ring, U-bend) are small and relatively simple so that they remain easy to handle and insert; the drawback, however, is that failure rarely occurs since the stress tends to relax spontaneously as corrosion develops, and careful examination is required to detect the cracks.

B. Electrical resistance probes [207; 215; 217]

These probes monitor metal consumption by measuring the electrical resistance, which increases as the cross-section of the consumable coupon decreases [265]. These coupons can provide remote, instantaneous information on corrosion development, upon request [242]. Most of the strong and weak points of this technique are the same as those of traditional corrosion coupons, but since the corrosion rate can be measured, corrosion can be monitored on a far more regular basis.

The main limitation concerns temperature, which affects electrical resistivity. Compensation is therefore required in case of significant temperature variations.

Provided that this precaution is taken, the technique exhibits relatively good sensitivity, typically 0.1% on the thickness variation detected. This accuracy nevertheless remains insufficient to monitor highly fluctuating corrosion conditions, and electrical resistance probes must be considered primarily as long-term monitoring tools designed to measure the cumulative effect of corrosion.

In addition, this type of device requires a power supply, which may represent a significant limitation for some applications involving explosion or flammability risks. Anti-deflagration devices are necessary in this case, possibly incurring substantial extra costs.

Moreover, the “coupon” is not examined afterwards (since it is consumable) and therefore provides no indication on the corrosion mechanism involved: it is therefore essential to ensure beforehand that the active phenomenon is uniform corrosion, since otherwise the information collected will be worthless.

The information collected will be highly representative since the coupon is subjected to the actual process conditions, and the technique imposes few limitations on the electrical conductivity of the medium (except for highly conducting media such as molten salts or liquid metals). Care must nevertheless be taken to keep the coupon electrically insulated to avoid problems of galvanic corrosion due to accidental contact with a metallic part.

Although the geometry of the “consumable” part of the electrode may vary, long products suitable for resistivity measurements are often used (wires, tube, thin strip). Numerous products are available to carry out this type of measurement, to suit the application conditions or specific monitoring requirements. For example, flush probes are used to monitor corrosion related to thin films in pipes with two-phase flows [162; 189].

For some applications, where access is difficult or impossible (e.g. deep offshore), several probes of different characteristics can be used, some with higher sensitivity, others with longer lifetime [196].

Despite the disadvantages described above, corrosion measurement by electrical resistance probes is one of the most widely used techniques on oil fields [194].

Different versions, marketed since the mid-1990’s, have contributed to this continued success. The most well-known are:

- FSM™ (Field Signature Method) intended for pipelines [221]: suitable for a wide range of applications, this method can be used to produce an electric potential map, while offering the enormous advantage of being non-intrusive [263; 274]. Capable of operating at temperatures up to 400 °C, its use can be extended to refinery installations [165]. Dedicated software calculates the corrosion rate and produces a 3D profile of the metal loss [166; 167];
- High-sensitivity tools such as the Microcor™ system by Cortest Inc. [215-217] and the CEION™ system by Cormon [172; 173; 184], which can calculate corrosion rates over shorter periods thanks to more advanced electronics. For temperature compensation, the first system uses a relative measurement (by comparison with a reference sample), while the second proposes numerical correction.

Research conducted by Li *et al.* [227] aims at further improving the sensitivity of resistive sensors, in order to install instruments on equipment operating under moderate corrosion

conditions. The special geometry of these Thin Film Electrical Resistance (TFER) sensors involves a highly sophisticated manufacturing process. A secondary advantage of this increased sensitivity is faster response time than for current products. Lastly, it may be possible to adapt the method to detection of localised corrosion using a multiple-line pattern configuration.

C. Chemical analysis [189; 242; 278]

Although highly indirect, global and requiring “off line” analyses, this method is worthy of attention being based on a simple principle. It is relatively easy to implement since no instrumentation is required, apart from a sampling valve. It can be used for all types of equipment containing or conveying aqueous fluid (tanks, transfer lines, treatment units, distillation units, various utilities, etc.), especially in petrochemical plants and refineries where it is considered as an additional but valuable technique to obtain semi-quantitative corrosion information.

The principle consists in analysing the metallic ions solubilised in the fluid following corrosion. In practice, the element considered is nearly always iron, the majority component in most metal alloys: more reliable results can be obtained since the analyses are conducted on high content values.

The disadvantage with iron is that precipitates form under certain pH or temperature conditions frequently encountered in the petroleum industry. These precipitates will not be taken into account in the analysis and the corrosion will be underestimated. Determination of manganese content has therefore been proposed, especially for applications in the presence of H_2S [233].

The ion content measured is directly proportional to the weight of metal consumed. Consequently, knowing the area of metal affected and provided that there is no other source for the metallic ion considered, it is theoretically possible to calculate a corrosion rate. The main application of this technique is more global, however, to monitor corrosion trends, detect anomalies (sudden variations) or check the efficiency of a protective measure (addition of inhibitors, coating, etc.)

Samples are sent to the laboratory where a number of analysis methods are available to determine the metallic ion contents:

- atomic absorption spectroscopy,
- atomic emission spectroscopy, used more and more routinely, in particular ICP-MS (inductively coupled plasma mass spectroscopy),
- colorimetry, using light absorption by metallic complexes formed using reactants (this method can also be applied on the field).

This technique has two main limitations: it provides global, essentially qualitative information and the corrosion rate estimation is not obtained immediately (time must be allowed for analysis).

D. Hydrogen probes [189; 242; 265]

Dating back to the 1990's, this non-intrusive technique provides continuous information and offers a vast potential for petroleum equipment.

Its principle is based on the fact that the quantity of hydrogen produced during corrosion is proportional to the intensity of the reaction and that the hydrogen can be collected and measured to calculate the corrosion rate.

Hydrogen is generated by the cathodic component of the electrochemical corrosion reactions occurring in non-oxidising acid medium. The method is therefore ideal for sour service applications (presence of H_2S) especially pipelines and pressurised containers.

Since the hydrogen produced penetrates steel rapidly and diffuses easily through the metallic walls, this property can be used to monitor from the outside the intensity of the corrosion occurring on the inside.

This is not the only configuration since intrusive use is always possible, with in this case the probe consisting of a thin steel tube, immersed in the medium (or flow). This tube contains a cylindrical rod to form an annular space. Molecular hydrogen, recombined after atomic diffusion into the tube from the outside, builds up in this annular space, raising the pressure which can then be measured easily with a sensor. The rate of pressure increase provides an indication of the corrosion intensity on the outer surface of the tube.

The same pressure measurement principle is applied for non-intrusive use in refining [190], with in this case a patch being attached to the outer wall of the equipment (Figure 2.11). This patch creates a volume where hydrogen produced by corrosion on the process side builds up. The method is extremely simple, but the drawback is that the actual area concerned by the corrosion producing the hydrogen collected is unknown. It is even possible that this area could change over time (formation or disappearance of corrosion deposits). The information collected is therefore primarily qualitative: it can be used to detect substantial modifications in corrosion intensity (change of slope on the pressure curve) but not to determine a corrosion rate directly.

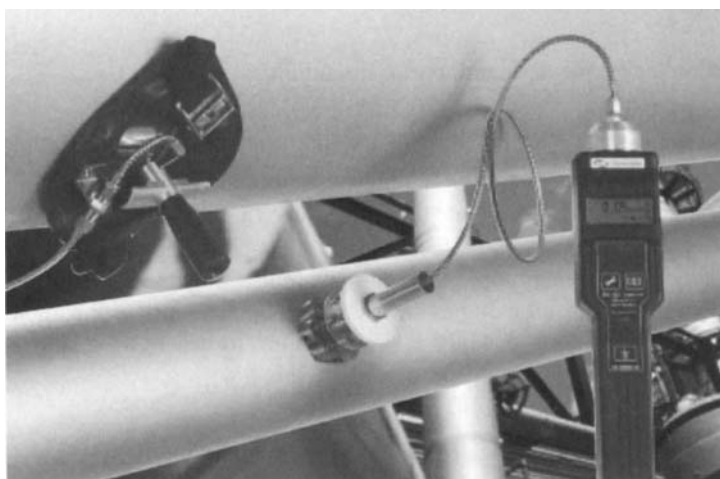


Figure 2.11

Hydrogen patch probe [190].

Other external hydrogen probes are based on an electrochemical principle to quantify the hydrogen collected (Figure 2.12). After diffusing through the wall, the hydrogen is quantified by the intensity of the current required for its oxidation. An electrolytic cell is used (the electrolyte is an acid solution) fitted with electrodes, one being a stainless steel working electrode which produces the oxidation current. A sheet of palladium (inert material) is inserted between the equipment wall and the electrolytic detection cell to normalise the flow of hydrogen, like the permeation cells used in laboratory (Devanathan type).

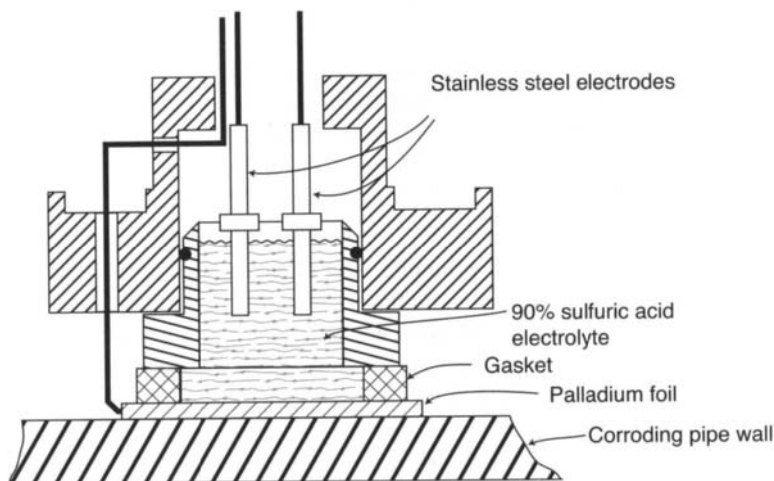


Figure 2.12

Diagram of a hydrogen patch probe [190].

This detection technique has a number of limitations:

- temperature limitation, especially for the electrolytic version,
- complexity of the system for this version and limitation inherent to extended use on equipment in service (reliability, maintenance, infrastructure, cost),
- need for high rate of diffusion into the wall, which rules out the use for austenitic alloys,
- for the quantity detected to be representative of the corrosion intensity, a sufficient proportion of the hydrogen produced by corrosion must penetrate the steel instead of being released on the inside; this assumes the existence of poisons preventing molecular recombination on the steel surface, which in practice limits its benefit in situations with H_2S .

E. Optical sensors

These methods [169] take advantage of the progress made in the field of optical fibres, for telecommunication applications, and they are worthy of interest since they represent a useful addition to the range of existing techniques. In addition, they solve many of the electricity supply problems encountered with traditional methods, a significant advantage for installations which are remote, difficult to access or subject to special safety constraints (ATEX).

Optical fibres also offer extended lifetime under special conditions (humidity, fluctuating pressure and temperature) or aggressive conditions (chemical inertia) and good insensitivity to electromagnetic interference.

These optical methods are all indirect since they detect a consequence of corrosion as opposed to the actual phenomenon. The property most frequently monitored with optical fibres is their strain under the effect of corrosion. There are several possible configurations. Optical fibres, especially Fibre Bragg Gratings (FBG), behave as strain sensors capable of detecting strain or curvature variations.

Developed by the Canadian company FOX-TEK [235] the system, which consists of a spiral-wound optical fibre strain gauge attached to the outside of the equipment, can detect very small wall thickness variations. The system is therefore non-intrusive, a big advantage for numerous applications, whether in petroleum production (buried pipelines) or refining installations [235].

The strain is measured with respect to an internal reference not exposed to the aggressive environment. Development of corrosion can therefore be monitored, provided that temperature correction is made (for HT processes, limited to about 250 °C) since the thermal expansion of the fibre must be taken into account.

Like all non-distributed control systems, the main disadvantage with this strain gauge is that it provides local information.

Distributed measurement systems for corrosion detection based on fibre optical measurement are also available [174; 224; 250]. They may involve several principles, but the most widely used consists in coating the fibre with a corrosion-sensitive metallic layer. When the metallic layer has been corroded away, some of the light injected down the fibre escapes from the point considered, reducing the intensity of the reflected light. In addition, this point can be located by analysing the travel time of the light signal.

Another possibility is to use a fibre Bragg grating, stressed by the coating (or plating). The strain induced is detected when the coating has thinned down or completely disappeared. The zone concerned along the fibre can be located.

These systems are used mainly as alarms since, once corrosion has been detected, the device provides no further information. Since the metallurgy of the material forming the coating is different from that of the installation, the main problem with this device is that it could react differently with respect to corrosion.

Warning signals on damage to pipeline networks, in particular the appearance of leaks, can be obtained by installing distributed optical measurement devices. For example, special coatings (concept proposed by the company Luna Innovations) can be used to detect chemical species or variations (in humidity or pH for example) around the fibre, located near the pipe. The company SensorTran has designed a leak location system based on detection of very slight temperature variations, but the principle still relies on induced strain measurement.

IFP has also developed a system called CODA (Corrosion Optical Detection and Alarm) [198], which provides a local indication of corrosion progress based on a measurement of the refractive index of light at the end of the optical fibre. The end of the fibre is placed in a sealed cavity which is closed by a corrosion coupon. When the coupon disappears or starts to leak, liquid enters the cavity, causing a sudden change in the local refractive index. The

change of index can easily be detected by inexpensive, traditional optical measurement means (laser diode, photo-diode, coupler). The robustness of the concept and its ability to detect corrosion from a distance of several hundred metres, via the optical fibre, were validated through an industrial demonstration carried out on large-size equipment.

The system has several limitations: local measurement, intrusive device (contact with the corrosive medium necessary) and single-use alarm type operation, although the corrosion coupons can be replaced to a certain extent.

In addition to its simplicity, the associated reliability and low cost, there are numerous advantages:

- Versatility: suitable for numerous configurations (including a standalone version with built-in, high-autonomy power supply) and a wide range of equipment, even when access is difficult;
- Adaptability: the coupon material can be chosen to be fully representative of the installation, including its metallurgical composition and surface roughness;
- Safety: no electrical components are required near the instrumented equipment;
- Ability to monitor corrosion progress, by installing several sensors with coupons of different thicknesses (different alarm levels).

F. Acoustic emission (AE) [175]

This well-known technique consists in recording and analysing the acoustic signals emitted by active degradation phenomena, by interpreting them with respect to the cause. Ceramic piezo-electric sensors are used, which convert the elastic waves received into recordable electric signals. In principle therefore, this technique would appear highly suited to detection during service, especially due to its high sensitivity. This is also its main drawback however, since it is strongly disturbed by all the background phenomena, always abundant in an industrial environment. This makes it difficult to identify the relevant signals and extract any information that could be used for preventive monitoring.

Consequently, the technique is not implemented permanently and is mainly reserved for control and inspection purposes, generally during installation shutdown phases. In this case, it is often combined with hydraulic or pneumatic testing, during which the external noise sources can easily be controlled or filtered from the acquired signal [175]. The principle consists in stressing the equipment and recording the signals emitted by any emissive phenomena, for example crack initiation or propagation. The method is widely used for closed equipments (storage tanks, pressurised devices) since it is non-intrusive: sensors positioned on the outer wall record signals emitted by phenomena occurring either on the inside or within the thickness of the material. The technique can be used not only to detect but also to locate evolving defects, in order to produce maps of localised corrosion or leaks, for example at the bottom of storage tanks. The main emission sources (due to corrosion) are located by triangulation between several sensors.

In the field of corrosion, Acoustic Emission (AE) is generally employed as an external preinspection method intended for equipment which are difficult to open or dismantle, such as storage tanks or process units [183]. In the latter case, installations are not shut down systematically, provided that the relevant signal can be extracted from the background noise.

Higher frequency sensors can be used to identify the signal due to corrosion, but their range remains limited to a maximum of about 1 metre.

Although acoustic emission is primarily used for inspection, it can also provide warnings of active corrosion [249] – including localised corrosion (pitting, crack) – and may be included in an integrated monitoring approach as a tool for early detection of corrosion [177].

G. Measurement of factors leading to corrosion

Instead of monitoring the progress of corrosion through its effects, one method widely used in the petroleum industry for aqueous medium consists in measuring the factors promoting corrosion, especially the corrosivity of the solution in contact with the equipment [242].

Measurements can be taken on samples, as with chemical analysis described above: they should preferably be taken on line, not only to obtain a fast measurement but also and above all to avoid disturbing the medium.

Measurement of temperature is also important since the processes responsible for corrosion are thermally activated. This is also true for pressure which has a major impact on the acidity of process aqueous solutions. Pressure affects the pH via solubilisation of acid gases such as CO_2 and H_2S , present at sometimes high concentrations in oil and gas products. The concentration of these gases depends on the origin of the crudes and the treatments carried out to eliminate them: it is therefore especially critical for equipment located upstream (on oil and gas fields, well equipment, petroleum pipes, processing units) where these gases are in contact with production water. Probes capable of operating under severe conditions of temperature (100 °C or more) and pressure (up to several tens of bars) are available for continuous pH measurement. When the conditions are too severe, sampling remains a valid solution. In this case, the pH measurement is corrected using formulae based on thermodynamic equilibria: $\text{pH} = f(T, P, \% \text{CO}_2, \% \text{H}_2\text{S})$.

Salinity and oxygen content are also important parameters when determining corrosion risks, especially for passivable alloys such as stainless steels. The stability of protective passive layers composed of oxides is sensitive to the presence of chlorides and to the electrochemical nature of the medium (reducing or oxidising).

With pipes, the erosive action of the fluids transported must also be taken into account. This effect, which increases with the rate of flow, amplifies the corrosion risks due to two mechanisms (see also paragraph 3.3.7):

- synergy between chemical and mechanical effects, during the corrosion process,
- degradation of the protective layers formed by corrosion, since some deposits may provide good protection.

This is particularly important for materials protected by a passive layer or by coatings since, once this protective surface layer has been eliminated, consumption or perforation of the wall may occur rapidly in some critical zones which are subjected to high forces by the fluids (bends, nozzles, regions of turbulence). Pressure sensors or flow sensors measuring the fluid speed or flow rate should therefore be positioned in the immediate vicinity of these zones.

These measures are all relatively straightforward to implement and the data produced can be read immediately, allowing action to be taken rapidly in case of potential problem. In

Fundamentals on metallic alloys and corrosion

The first paragraph in this third section deals with the basic information concerning the main metallic materials used in industrial processes and in the petroleum sector: alloy structures, mechanical behaviour and the main alloy families which find application in the petroleum industry. The second paragraph describes the various corrosion modes and mechanisms discussed in the first section of this book. Lastly, other damage modes are mentioned: metallurgical transformations due to high temperature ageing. The chapters in this section will provide the non-specialist reader with basic information on metallurgy (structure, families of metallic alloys used in the petroleum industry) and corrosion, making the first chapters of the book easier to understand.

3.1 BASIC INFORMATION CONCERNING THE METALLIC MATERIALS USED IN THE PETROLEUM SECTOR, THEIR STRUCTURE AND PROPERTIES

To obtain a better understanding of the reactivity of metallic materials with respect to corrosion, we will first examine the metallurgical structure of alloys, then the resulting mechanical properties before describing, in the last paragraph, the main families of metallic materials used for industrial processes and in the petroleum sector. For more information, the reader may also refer to the bibliography indicated at the end of the chapter [316; 320; 321; 330; 333; 350; 352].

3.1.1 Structure of metallic alloys

Due to their chemical, physical or mechanical properties, most pure metals are unsuitable for industrial applications. Deliberate or accidental addition of one or more elements to a pure metal may significantly modify its properties. Metallic elements (Cr, Ni, Mo, Cu, etc.) as well as other inorganic elements (C, S, N, O, P etc.) may be added. The mixtures obtained are known as metallic alloys.

The properties of alloys depend mainly on:

- their overall chemical composition,
- their physico-chemical constitution: the type, composition and proportion of the constituents,

- their microstructure (distribution of constituents),
- their mechanical state characterised by some specific constraints related to crystalline defects at atomic scale (dislocations, macles, etc.) and to chemical heterogeneities.

Depending on their manufacturing process and their subsequent treatments (mechanical, thermal, chemical), alloys are in equilibrium or non-equilibrium state.

3.1.1.1 Crystallographic structures of alloys

In solid state, metallic alloys consist of numerous small crystals (grains) that have a diameter of a few microns. These crystals can be oriented in all spatial directions (isotropic medium) or have preferential orientations (anisotropic) due for example to the solidification or forming (rolling) conditions: in this case, the alloy has a texture and its properties are also no longer isotropic (Figure 3.1).

The crystals are characteristic of the alloy structure: they may all have the same composition (single-phase alloys) or correspond to different phases. Each crystal consists essentially of metallic ions forming a pattern periodically repeated in all three spatial directions. The crystal can be defined as a regular stack of cations which can be considered as hard spheres tangential to each others. The unit cell is the elementary structure repeated infinitely throughout the crystal, forming a lattice. A crystal system is defined by the parameters of the unit cell (length of edges, angles) and the arrangement of the metallic ions (Figure 3.2).

Nearly all metallic alloys crystallise in one of the following three systems:

- Body-Centred Cubic system (BCC): the unit cell is a cube (edge of length a) with the centres of the metallic ions not only at the corners but also at the centre of each elementary cube (Figure 3.3). The coordination number (number of first neighbours) of each ion is 8. α -iron, chromium, tungsten, molybdenum and vanadium crystallise with this structure. Other ions can fill two types of interstice in this system. The largest interstices are the tetrahedral holes [centres located in the faces, coordination numbers ($a/2$, $a/4$, 0)]

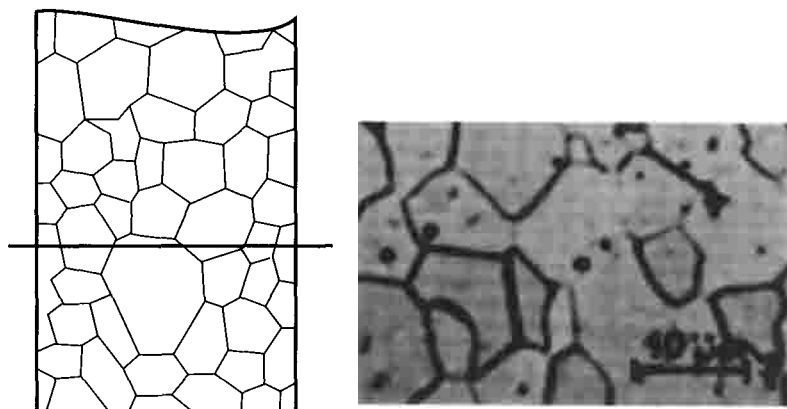


Figure 3.1

Metallic alloy crystals.

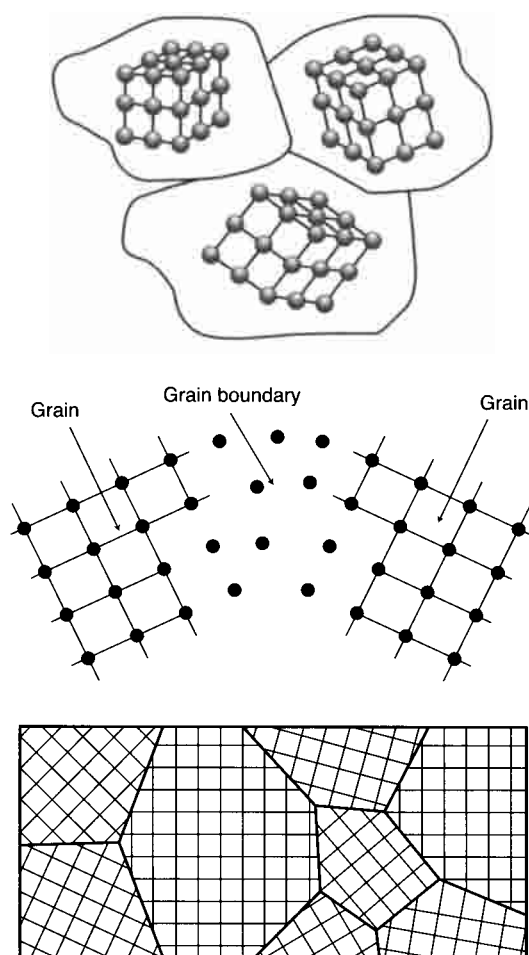


Figure 3.2

Metallic alloy crystals and unit cells.

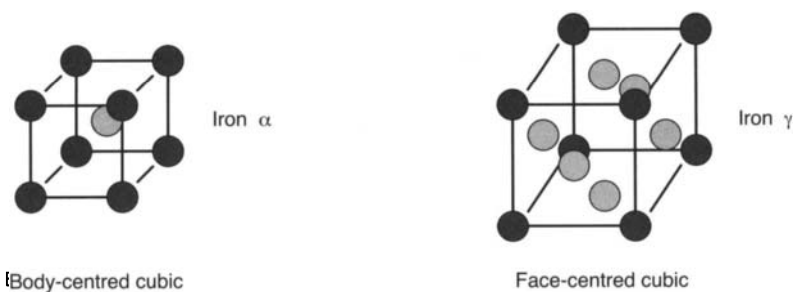


Figure 3.3

Cubic structures.

which can be occupied by atoms of radius $0.126a$. There are 12 tetrahedral interstices per unit cell (Figure 3.4). The smallest interstices are the octahedral holes (centres located in the middle of the edges and in the centre of the faces) which can be occupied by atoms of radius $0.067a$. There are 6 octahedral interstices per unit cell;

- Face-Centred Cubic system (FCC): the unit cell is a cube (edge of length b) with the centres of the ions at the corners and the centres of the faces (Figure 3.3). The coordination number of the FCC system is 12. Examples of elements with this crystal system include γ -iron, nickel, copper, aluminium and lead. The largest interstices are the octahedral holes (centres located in the middle of the edges and in the centre of the cube) which are surrounded by 6 atoms arranged at the corners of a regular octahedron. There are 4 per unit cell, which can be filled by spheres of radius $0.146b$. The smallest interstices are tetrahedral since each centre is surrounded by 4 atoms located at the corners of a tetrahedron: their centres are in the middle of each of the 8 small equal cubes into which the unit cell can be divided. There are therefore 8 per unit cell, which can be filled by spheres of radius $0.08b$;
- Hexagonal Close-Packed arrangement (HCP): the unit cell is a rhombus-based right prism, but the hexagonal-based right prism which is three times bigger is generally considered as the conventional cell (Figure 3.5). The centres of the metallic ions are organised in three layers, the top and bottom layers containing six ions at the corners of a hexagon and one atom at the centre of each hexagon, the middle layer containing three ions at the centres of the 3 non-adjacent equilateral triangles at half way between the top and bottom layers. The coordination number is 12. Magnesium, titanium, cobalt, zinc crystallise with this lattice. The interstices of the hexagonal close-packed arrangement are the same as those of the FCC system: there are 6 octahedral interstices (the largest) per hexagonal prism.

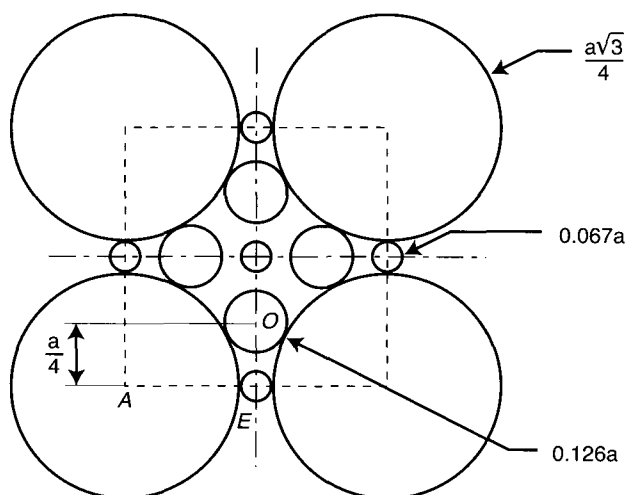


Figure 3.4

Interstices of the body-centred cubic structure.

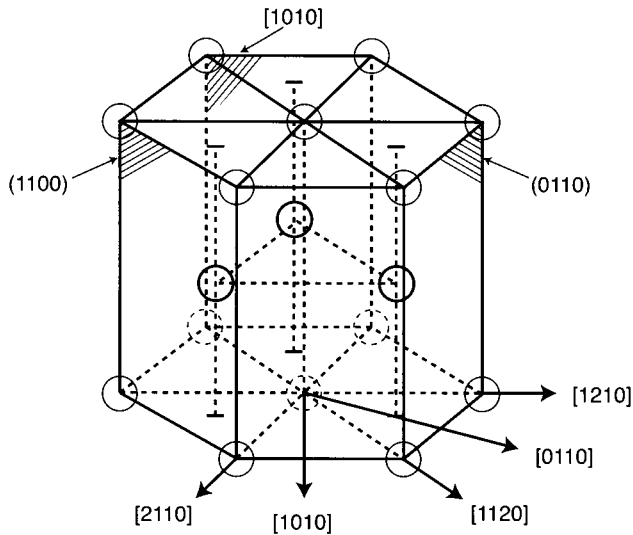


Figure 3.5

Hexagonal close-packed structure.

In alloys, metals can be found:

- In pure state: when alloying two metals without any combination taking place, the atoms of one metal may be too large with respect to those of the main metal: the large atoms cannot penetrate the lattice of the base metal and the metals separate;
- In combination: the metal (or sometimes non-metal) added is generally incorporated into the crystal lattice of the base metal, resulting in a solid solution (Figure 3.6) which is an intimate mixture where the atoms of the alloyed metals are assembled in a unique crystal lattice. There are three types of solid solution: in substitution (the solute ions are similar in size to those of the solvent metal and are distributed randomly in the nodes of the lattice, such as for example nickel in the γ -iron lattice and chromium in the α -iron lattice); ordered (the solute ions replace those of the solvent

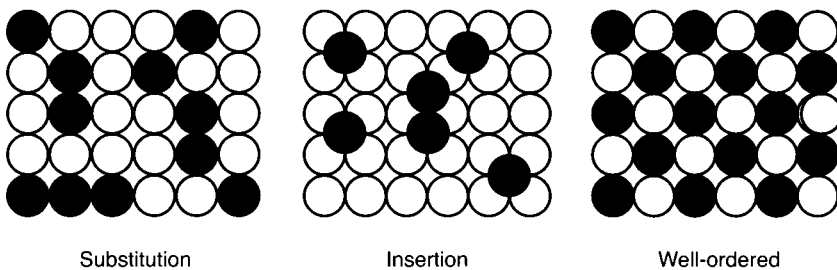


Figure 3.6

Types of solid solution.

metal and are distributed in an ordered manner in the nodes of the lattice); and insertion (the solute atoms such as carbon, hydrogen, nitrogen are small enough to fill the empty interstices between the atoms in the unit cell).

The alloys may also contain definite compounds, whose atoms are present in relatively simple and well-defined proportions. Examples of definite compounds include carbides (e.g. cementite Fe_3C), nitrides and sulfides (MnS).

Compared with the crystallography models which have just been described, real crystals contain imperfections which have beneficial or negative impacts on some of their properties (Figure 3.7):

- point imperfections such as impurities (foreign atoms which deform the network by substitution or insertion) and vacancies (holes created when the normal position of an atom is not occupied),
- line imperfections such as dislocations (screw, edge or mixed) which are disturbed regions of a crystal situated between two parts which fit perfectly but have been shifted relative to the other,
- planar imperfections such as grain boundaries, interfaces between two phases or twin boundaries.

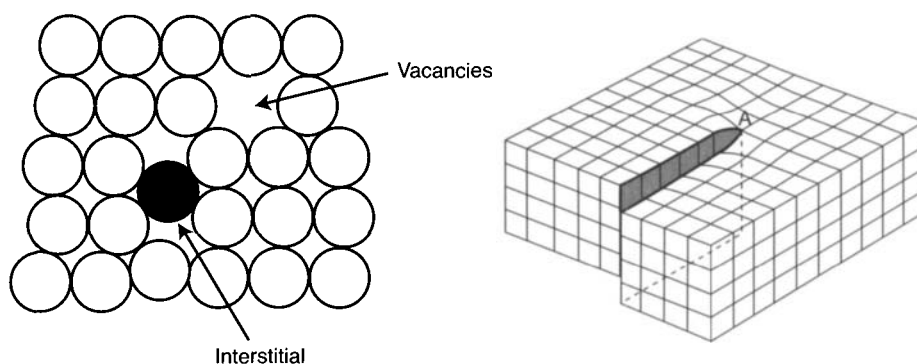


Figure 3.7

Lattice imperfections: vacancies and screw dislocation.

3.1.1.2 Alloy equilibrium diagrams

Alloys do not generally solidify at a specific temperature: under fairly slow cooling, solidification starts at temperature T_1 and finishes at temperature T_2 : there is no solidification point but a solidification interval. The solidification diagram is the area bounded by temperatures T_1 and T_2 which depend on the alloy composition. The line of temperatures T_1 when solidification starts is called the liquidus and that when solidification ends is called the solidus. In solid state, the physico-chemical constitution of an alloy may undergo changes revealed by sudden variations in one or more of its properties. The transformation points and their positions depending on the alloy composition form the transformation lines. An equilibrium diagram includes the following information: liquidus, solidus and transformation lines.

Equilibrium diagrams form the basis of all rational studies of alloys. Given the chemical composition of an alloy, the diagram indicates its constitution at all temperatures, provided that the alloy is in its *equilibrium state*: this assumes extremely slow heating or cooling. However, the equilibrium diagram provides no indication concerning the micrographic structure.

To produce the equilibrium diagrams of an alloy, we must know the Variance (V) of the chemical system in equilibrium, i.e. the number of equilibrium factors that can be arbitrarily varied without varying the number and type of the system phases:

$$V = C + 2 - \phi$$

- C is the number of independent constituents (number of pure simple bodies present in the alloy),
- ϕ is the number of phases (homogeneous parts of the system).

Number 2 represents the two factors, pressure and temperature, but since the effect of pressure variations is imperceptible, we consider a reduced variant V_r :

$$V_r = C + 1 - \phi$$

Application to a Binary Alloy (BA) formed from two solid solutions with eutectic:

The alloys of metals A and B will form solid solution α if they have a high content in A and a solid solution β if they have a high content in B. The liquidus and solidus corresponding to the solid solution α start from the melting point of pure A and the liquidus and solidus corresponding to the solid solution β start from the melting point of pure B (Figure 3.8). The two branches of the liquidus intercept at E. Three phases exist at this point: the liquid and two solid solutions $\alpha(e_1)$ and $\beta(e_2)$. The reduced variance is then zero $V_r = 2 + 1 - 3 = 0$ and equilibrium can only exist at a specific temperature. The triple point E is called the eutectic point.

For this alloy composition, corresponding to point E, at temperature T_1 we obtain equilibrium: $\text{Liq } E \leftrightarrow \text{solid solution } \alpha(e_1) + \text{solid solution } \beta(e_2) \pm n \text{ calories}$.

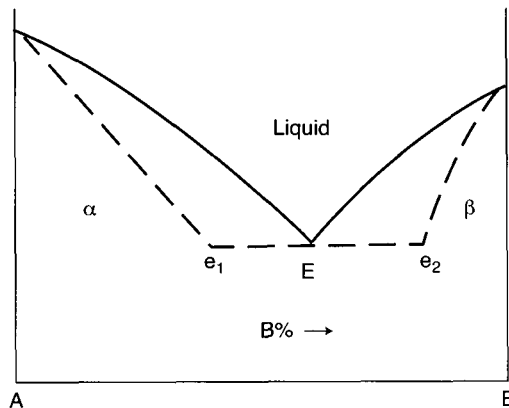


Figure 3.8

Transformation diagram of a Binary Alloy (BA) formed from two solid solutions with eutectic.

Solidification occurs at constant temperature T_1 by simultaneous formation of two solid solutions $\alpha(e_1)$ and $\beta(e_2)$. The eutectic alloy is therefore a mixture of these two solutions, the ratio of their masses being given by the inverse segments rule:

$$\text{mass } e_1 / \text{mass } e_2 = Ee_2 / Ee_1$$

Solidification for other compositions of the alloy BA:

- a) alloys for which $0 < B (\%) < e_1$: the solid solution α is the only constituent,
- b) alloys for which $e_1 < B (\%) < E$: the two constituents of the solid solution $\alpha(e_1)$ and the eutectic,
- c) alloys for which $E < B (\%) < e_2$: the two constituents of the solid solution $\beta(e_2)$ and the eutectic,
- d) alloys for which $e_2 < B (\%) < 1$: the solid solution β is the only constituent.

A eutectic triple point may also be found in transformation lines of the alloys (in the solid domain): this is the eutectoid point.

3.1.1.3 Application to the Fe-C diagram

We will apply the notions discussed in the previous paragraphs to the iron-carbon equilibrium diagram (steels sufficiently annealed) which is the basis of metallurgy and heat treatments for steels. There are two Fe-C diagrams: an iron-cementite (Fe_3C) diagram, which corresponds to a metastable state, and an iron-graphite diagram, which corresponds to a stable state: the two diagrams partially overlap.

A. Iron-cementite diagram

A simplified diagram is given on Figure 3.9 for carbon contents below 6.7%. We observe the presence of a eutectic (called ledeburite) at 1145 °C for 4.3% C and a eutectoid (called pearlite) at 725 °C for 0.85% C. The various zones are:

Zone I: liquid + austenite mixture (γ -iron with carbon inserted in the FCC unit cell)

Zone II: liquid + proeutectic cementite mixture

Eutectic line at 1145 °C

Zone III: austenite with variable carbon content in insertion

Zone IV: austenite + cementite

Zone V: austenite + ledeburite + proeutectoid cementite

Zone VI: primary cementite + ledeburite + proeutectoid cementite

Zone VII: ferrite (BCC α -iron which dissolves little carbon) and austenite

Eutectoid line at 721 °C. The following domains lie below this line:

- $0 < C < 0.85\%$: proeutectoid ferrite + pearlite (hypoeutectoid steels),
- $0.85\% < C < 1.7\%$: proeutectoid cementite + pearlite (hypereutectoid steels),
- $1.7\% < C < 4.3\%$: proeutectoid cementite + eutectic cementite + pearlite (hypoeutectoid white cast irons),
- $4.3\% < C < 6.7\%$: proeutectic cementite + proeutectoid cementite + eutectic cementite + pearlite (hypereutectoid white cast irons).

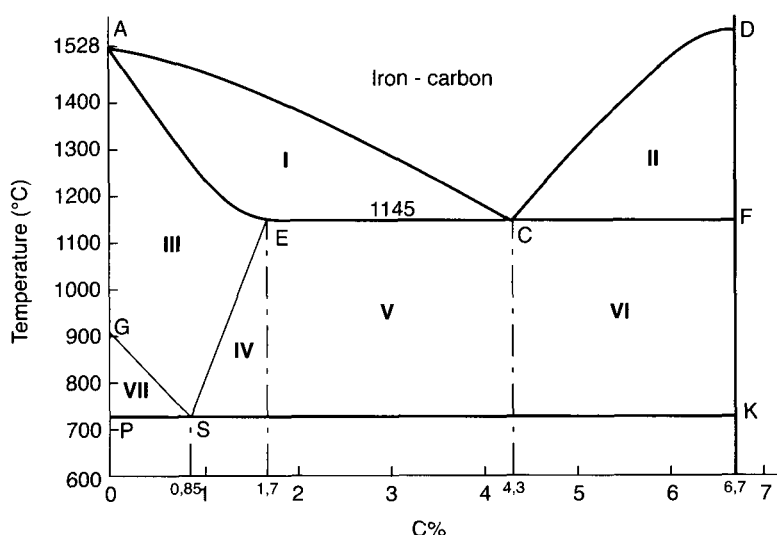


Figure 3.9

Simplified iron-cementite diagram.

B. Ordinary annealed steels

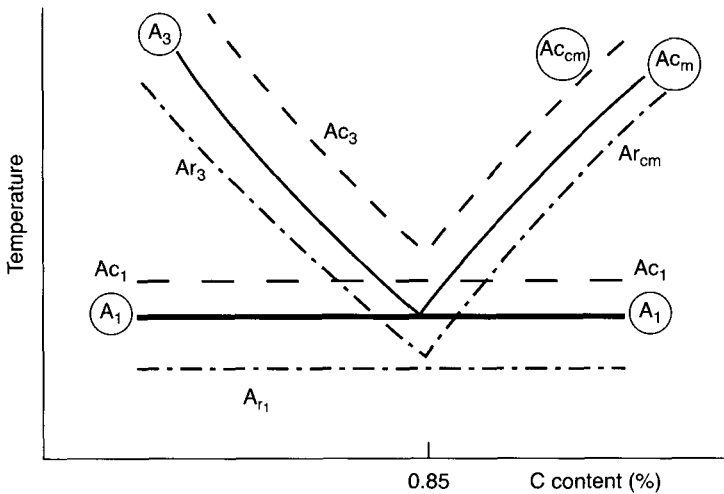
These are Fe-Fe₃C alloys which also contain small quantities of other elements (including Mn, S, P) as combinations or inclusions. They are composed of ferrite + hypoeutectoid pearlite or pearlite + hypereutectoid cementite. Pearlite has a two-phase lamellar structure (alternating lamellae of ferrite and cementite).

The transformation points of ordinary steels correspond to the intersection of the vertical representing the steel composition with the transformation lines on the diagram. In practice, the transformations are very slow. These points are extremely important for heat treatments (Figure 3.10).

Ac₁ corresponds during heating to the start of the reversible pearlite (ferrite + Fe₃C) ↔ austenite reaction. Transformation occurs progressively from Ac₁ to Ac₃. When cooling, austenite starts to transform at Ar₃; transformation of eutectoid austenite ends at Ar₁. For hypereutectoid steels (C > 0.85% C) point Ac₃ is replaced by point Ac_{cm}. The transformation interval is Ac₁-Ac₃ or Ac₁-Ac_{cm}.

3.1.1.4 Steel heat treatments: time-temperature transformation diagram

Heat treatments, which consist of heating and cooling operations, are carried out to change certain properties (mechanical, corrosion resistance, etc.) of an equipment to make it more suitable for its purpose. Traditional heat treatments include quenching, tempering and annealing.

**Figure 3.10**

Transformation points of ordinary annealed steel.

A. Quenching

Quenching is carried out to improve steel toughness (this property is described in more detail in paragraph 3.1.2). It consists of:

- heating the steel to a temperature θ_t , known as the quenching temperature, when austenitisation occurs,
- maintaining the part at temperature θ_t : the temperature is maintained long enough to ensure thermal homogeneity throughout the equipment,
- cooling by immersion in a suitable medium, rapidly enough to avoid transformation corresponding to the constitution predicted by the equilibrium diagram. The quenched state is characterised by the presence of non-equilibrium constituents (martensite, troostite or austenite).

Continuous Cooling Transformation (CCT) diagrams have been developed to indicate the composition of the steel after quenching: they can be used to monitor the austenite decomposition mechanism as a function of the cooling rate.

Figure 3.11 is an example of a cooling diagram for steel 42C4 (AISI 5140). The transformation (start and end) temperature ranges are given as a function of the logarithm of the time during cooling at various rates from an austenitisation state. The CCT diagrams also provide indications of the steel hardness obtained after these cooling operations:

- Very fast cooling (lines 1 to 3): from 310 °C, we observe exclusive but not necessarily complete transformation of the austenite into martensite (lines M50 and M90 correspond respectively to a transformation of 50% and 90% of the austenite into martensite). Martensite is an oversaturated solution of carbon in ferrite with expanded lattice whose unit cell is not cubic but tetragonal;

C %	Mn %	Si %	S %	P %	Ni %	Cr %	Mo %	Cu %
0.44	0.80	0.31	0.013	0.03	0.46	0.96	0.05	0.18

Austenitised at 850°C, 30 min., grain size: 9

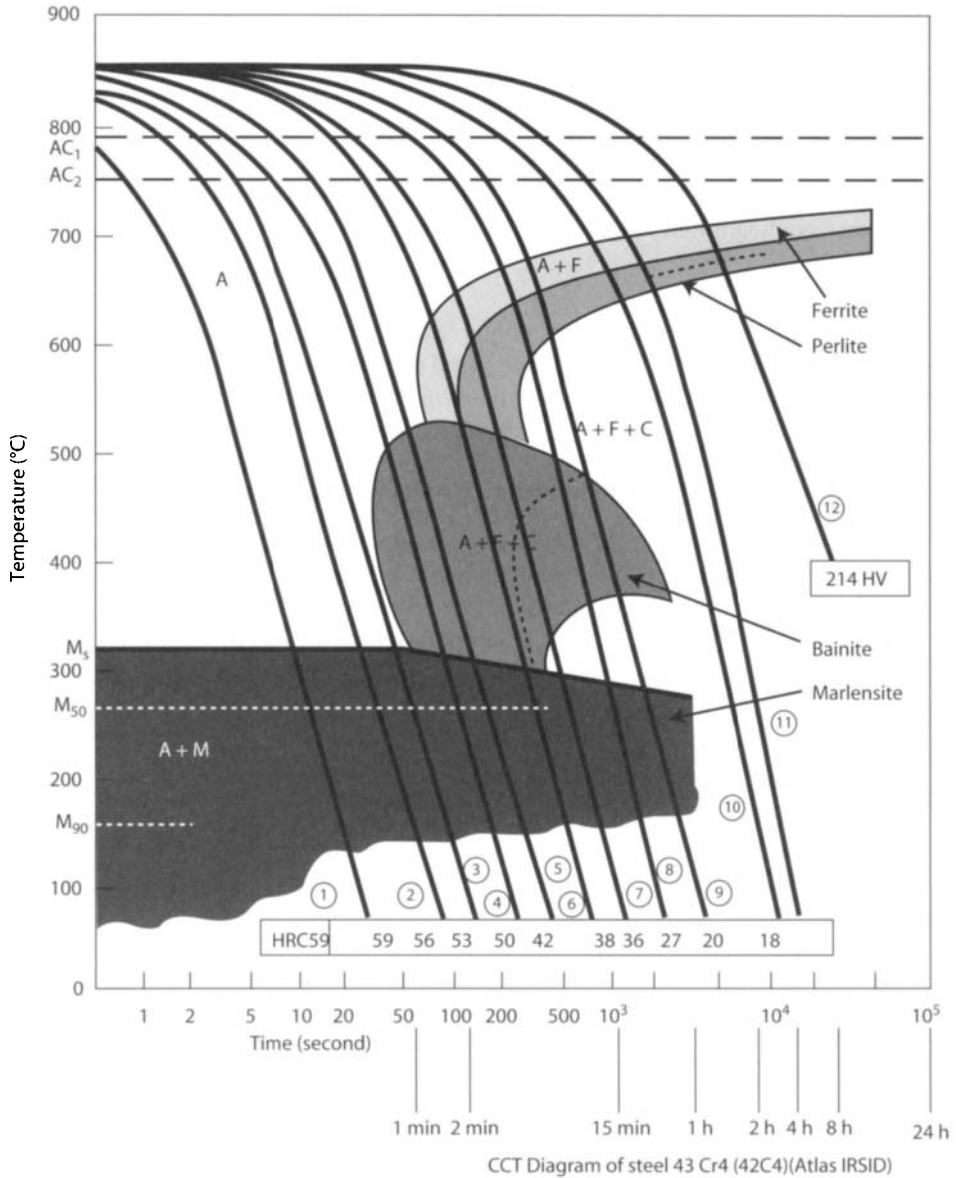


Figure 3.11

Cooling transformation diagram for steel 42C4 (AISI 5140) (Atlas IRSID).

- Relatively fast cooling (lines 4 to 9): we observe the formation of an intermediate structure, bainite, which has the same phases as pearlite (ferrite and cementite), but a fine morphology, often in the form of needles. After cooling, we observe the presence of martensite and bainite (lines 4 to 6) for fast intermediate rates and the presence of bainite and ferrite for slower rates (lines 7 to 9);
- Slow cooling (lines 10 to 12): we obtain a ferrite-pearlitic structure with lamellar pearlite (equilibrium structure) and low hardness.

B. Tempering

After the hardening treatment, steel is often harder than needed and generally too brittle for its application. Hardening is therefore followed by tempering, which consists in heating the steel to a temperature below A_{c1} , holding it at that temperature for the required length of time, and then cooling it fairly quickly.

C. Annealing

This treatment consists in heating the steel to a temperature generally above A_{c3} (or A_{cm}) then cooling it slowly at a rate less than the critical quenching rate. The metal is brought to a state of physico-chemical and structural equilibrium. The non-equilibrium states resulting from previous heat or mechanical treatments are removed.

3.1.1.5 Metallurgical transformations during steel welding operations

Steel welding operations involve heat cycles which generate different microstructures in the heat-affected zones. As shown on Figure 3.12 below, various structural transformations may occur in the weld, affecting its mechanical properties and corrosion resistance.

Taking the example of steel 42C4 (AISI 5140) whose CCT transformation diagram was detailed in the previous paragraph, we obtain the following microstructures after welding:

- Zone 1: base metal which has the initial steel structure depending on the heat treatments applied (ferrite-pearlitic, bainitic or martensitic structure);
- Zone 2: the temperature remained below A_{c1} (760 °C). The microstructure remains unchanged but precipitation of carbides and coalescence of the precipitates may occur;
- Zone 3: the steel temperature has been raised to between A_{c1} (760 °C) and A_{c3} (790 °C). Austenite has formed and has retransformed into pearlite, bainite or martensite depending on the cooling rate;
- Zone 4: the steel temperature has been raised to between A_{c3} (790 °C) and 1 100 °C. Only austenite has formed: depending on the cooling rates, different structures may be obtained, as shown on Figure 3.11;
- Zone 5: the steel temperature was raised to between 1 100 °C and its melting point (about 1 500 °C), well above that of the standard austenitisation treatments. A high grain size can be obtained.

3.1.1.6 Influence of the various addition elements on steel properties

The steel properties (mechanical strength, corrosion resistance) can be modified and adapted by incorporating other elements in the iron-carbon mixtures.

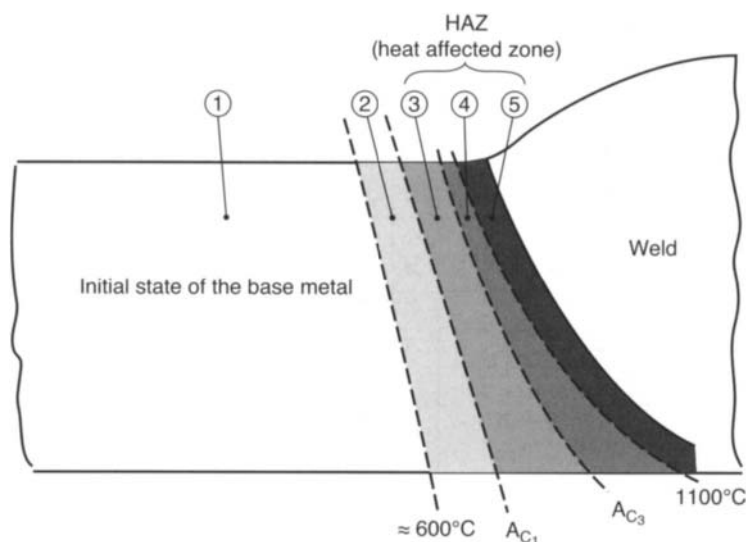


Figure 3.12

Microstructural modifications in a welded zone.

A. Influence on the equilibrium diagrams and the non-equilibrium states

Each element has a dominating tendency either to dissolve in the ferrite or combine with the carbon to produce a complex carbide replacing the cementite.

If we classify the main addition elements in the following order:

Ni – Si – Al – Mn – Cr – W – Mo – V – Ti

- the first three dissolve only in ferrite,
- from manganese, there is an increasing tendency for the elements to form carbides.

These elements are all soluble in austenite at high temperature and they modify the solid state transformation points of the steel.

Some elements reduce the range of austenite existence and increase the ferritic range: known as the *alphenous* elements, they include Cr, Si, Al, W, Nb, Mo, Ti and V.

Conversely, other elements widen the austenite range: known as the *gammagenous* elements, they include Ni, Mn, Co and Cu.

Elements W, Mo, Ni, Cr, V and Mn have an increasing tendency to lower the temperature at which martensite forms, while Co and Al increase this temperature.

B. Action of addition elements on steel properties

Table 3.1 below summarises the effects of the addition elements on the structural and mechanical properties.

Table 3.1 Influence of addition elements on steel properties.

	C	Mn	Si	Al	Ni	Cr	Mo	V	W	Co	Cu	S	P	Ti	Ta	Nb
Yield point	↗	↗	↗		↗	↗	↗	↗								
Tensile strength	↗	↗	↗		↗	↗	↗	↗	↗	↗	↗		↗	↗	↗	↗
Elongation	↘	↘	↘		↘	↘	↘		↘	↘	↘		↘			
R at high temperature	↗					↗	↗	↗	↗	↗			↗			
Creep resistance	↗	↗	↗	↘	↗	↗	↗		↗							
Hardness	↗	↗	↗		↗	↗	↗	↗	↗	↗	↗		↗	↗	↗	↗
Shock resistance	↘	↗	↘		↗	↗	↘	↘	↗	↘						
Fatigue resistance	↗					↗	↗	↗	↗	↗						
Ac ₁		↘	↗	↗	↘	↗	↗	↗	↗					↗		
Ac ₃		↘	↗	↗	↘	↗	↗	↗	↗	↘	↘		↗	↗	↗	↗
Austenitic range	↗	↗	↘	↘	↗	↘	↘	↘	↘	↗	↗					
Grain size	↗	↗	↗	↘	↘	↗		↘		↘			↗	↘		
Critical quenching rate		↘	↘		↘	↘	↘	↘	↘	↗						
Tempering stability			↗		↗	↗	↗	↗	↗	↗				↗	↗	↗
Carbide formation	↗					↗	↗	↗	↗					↗	↗	↗

Key: ↗ sharp increase ↗ increase
 ↘ sharp decrease ↘ decrease

3.1.2 Mechanical behaviour of metallic materials

3.1.2.1 Introduction

This aim of this section on mechanical behaviour is to provide a few basic notions to readers not familiar with this subject. These few pages will obviously not suffice to cover or explain in detail this vast domain, which is nevertheless fundamental in the use of materials.

In this section, we will first describe the *tensile test* which provides an introduction to the basic notions on mechanical characteristics and behaviour of metals (§ 3.1.2.2).

We will then give a an overview of the *strain, damage and fracture mechanisms* (§ 3.1.2.3 to 3.1.2.5).

The various types of *mechanical stress and behaviour* are discussed in § 3.1.2.6.

The *mechanical tests* most frequently used, after the simple tensile test, are discussed in § 3.1.2.7, especially *characterisation of creep, fatigue, hardness, resilience and toughness with some notions on fracture mechanics*.

Further knowledge on the behaviour and mechanical characterisation of metals can be obtained in several books [327-329; 332; 338].

3.1.2.2 Tensile test

We will describe the simple tensile test to illustrate fundamental mechanical behaviour and demonstrate the characteristics used to quantify this behaviour. This test, conducted on all materials and especially metals, has been documented in numerous standards. The test machines are said to be universal since they can be fitted with various assemblies and accessories in order to subject the materials to a wide range of mechanical stresses which will be described in this chapter. As first illustrations, Figure 3.13 shows diagrams and photographs of test machines (in tensile configuration) and Figure 3.14 shows photographs of test setups.

Tensile stress is obtained by vertical displacement of the crosshead or a hydraulic cylinder. A sensor records the displacement and a load cell records the stress applied to the specimen (the sensor is generally fitted on the crosshead above the upper grips holding the specimens). One or more *extensometers* can be fastened to the specimen to measure the strains more locally and more accurately.

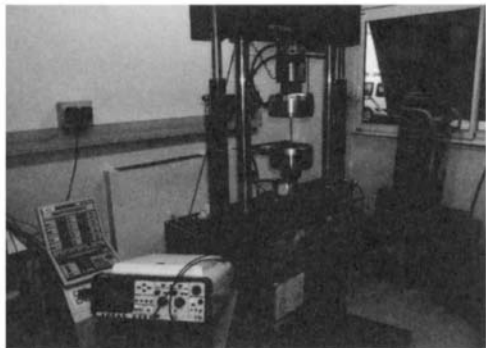
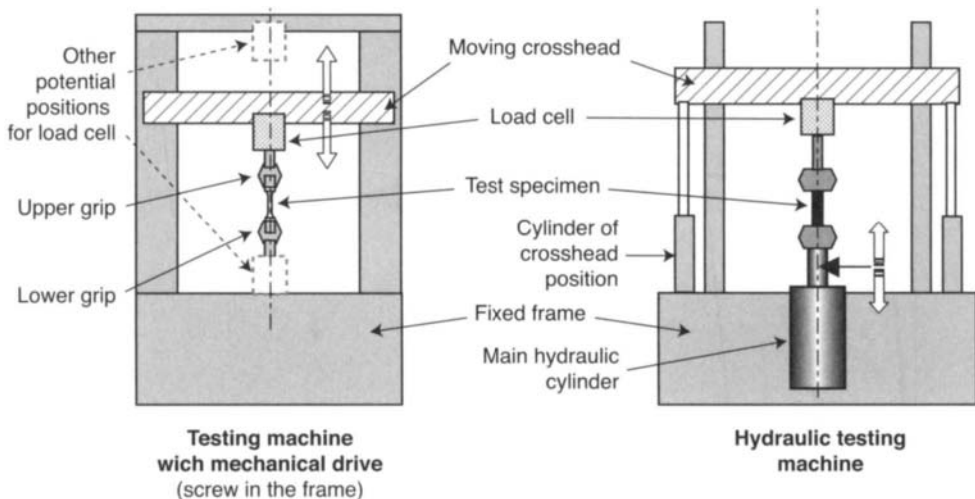


Figure 3.13

Universal mechanical test machines (shown here with tensile devices).

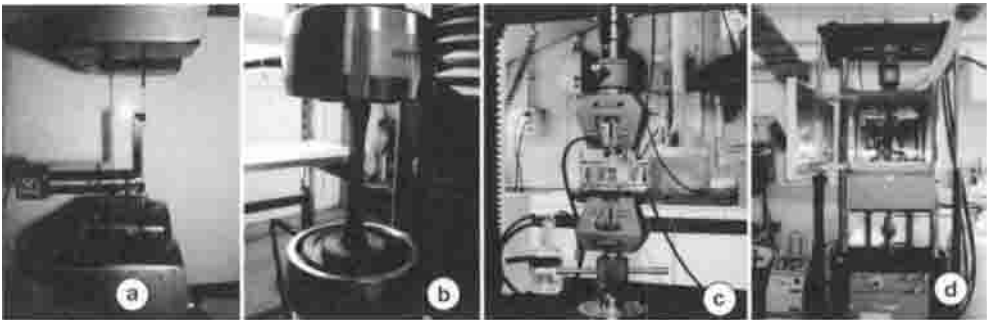


Figure 3.14

Tensile tests (a: on a steel cable with an extensometer, b: on a dumbbell prismatic specimen, c: on a steel specimen partially immersed in a corrosive environment – in this case $\text{H}_2\text{O} + \text{H}_2\text{S}$, d: temperature test in a chamber placed on the machine).

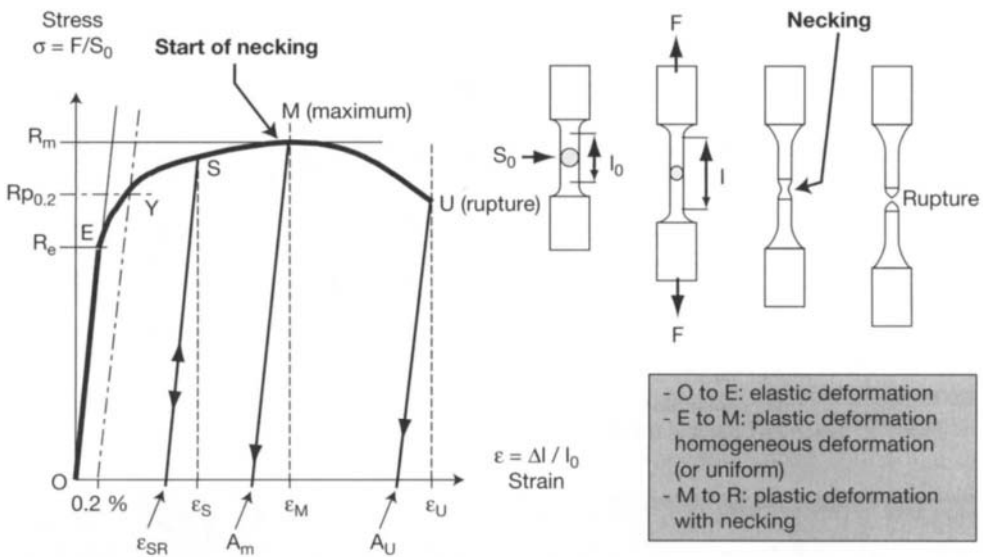


Figure 3.15

Typical tensile test (stress-strain curve and standard specimen).

The notions of elasticity, and therefore yield strength (also called elastic limit), as well as plasticity, necking and failure are illustrated on Figure 3.15 which shows a tensile stress-strain curve and a traditional specimen geometry. This test is generally interpreted by using the “engineering” curve (§ A below) but the notion of “true” curve (§ B below) may be employed for more in-depth studies.

Tensile tests have been described in numerous standards and vary depending on the materials and the standardisation organisations. We will only provide a few references

(specific to metals): European standards NF EN 10002 [314], NF EN 10319 [310]; international standards ISO 6892 [299], ISO 783 [313], ISO 15579 [312]; American standards ASTM E8M [286], ASTM E21 [288].

A. Engineering tensile curve (“engineering” characteristics)

The example of “*engineering*” or “*nominal*” *stress-strain curve* we provide here can be used to deduce the “*engineering*” or “*nominal*” *characteristics* (a “*true*” stress-strain curve deduced from this data will be explained below).

S_0 and l_0 correspond to the cross-section and length of the specimen at the start of the test. The tensile force F increases continuously and produces an elongation $\Delta l = l - l_0$. By definition, the **stress** (in MPa) and the **strain** (dimensionless but often expressed in%) are defined by: $\sigma = \frac{F}{S_0}$ and $\epsilon = \frac{\Delta l}{l_0}$.

We identify on this curve:

- the *elastic* region OE with *reversible* strains,
- the *plastic* region EM with *homogenous, permanent or irreversible* strains,
- the plastic region MU with propagation of *localised* strain called *necking*, U being the ultimate point corresponding to *failure* of the specimen,
- if *unloading* is carried out from point S, we follow a curve parallel to OE resulting into *permanent or irreversible strain* ϵ_{SR} .

Generally, *the total strain is the sum of the elastic (reversible) strain and the plastic (irreversible) strain*. The material reaching point S has therefore undergone a total strain $\epsilon_S = \epsilon_E + \epsilon_{SR}$ and retains the remanent strain ϵ_{SR} after unloading. On subsequent reloading, the material will exhibit elastic behaviour, with the same slope up to point S, then plastic behaviour along curve SM.

Other mechanical characteristics that can be obtained from this test:

- *The yield point (or proportionality limit):* R_e is given by point E which marks the end of the linear section where σ is proportional to ϵ , whose slope is *Young’s modulus* E . The constitutive law is the relation between stress and strain in this elastic region: $\sigma = E \cdot \epsilon$;
- Point E is therefore the end of *elastic strain* and the start of the *plastic flow or strain*. This point may be (especially with mild steels) followed by a plateau with a series of discontinuities (corresponding to the appearance of plastic deformation bands known as Piobert-Lüders bands), in this case the standard defines three additional elements (Figure 3.16):
 - an upper yield limit R_{eH} ,
 - a lower yield limit R_{eL} ,
 - and the length of the section A_p ;
- *The offset yield point* is given by point Y (Figure 3.15). Since point E is sometimes difficult to identify, a conventional limit has been defined, where a line parallel to OE (elastic section) shifted by 0.2% (generally, corresponding to a permanent or unrecoverable plastic strain of 0.2%) cuts the curve. This offset yield strength or proof stress is denoted $R_{p0.2}$;

- The maximum or ultimate strength: at point M the stress R_m (in MPa) or σ_{UTS} corresponds to the maximum load F_m supported by the specimen: $R_m = F_m/S_0$;
- The permanent set under maximum load is denoted A_m ;
- The total elongation under maximum load is denoted ϵ_m ;
- The permanent strain after fracture is denoted A_U ;
- The total elongation after fracture is denoted ϵ_U ;

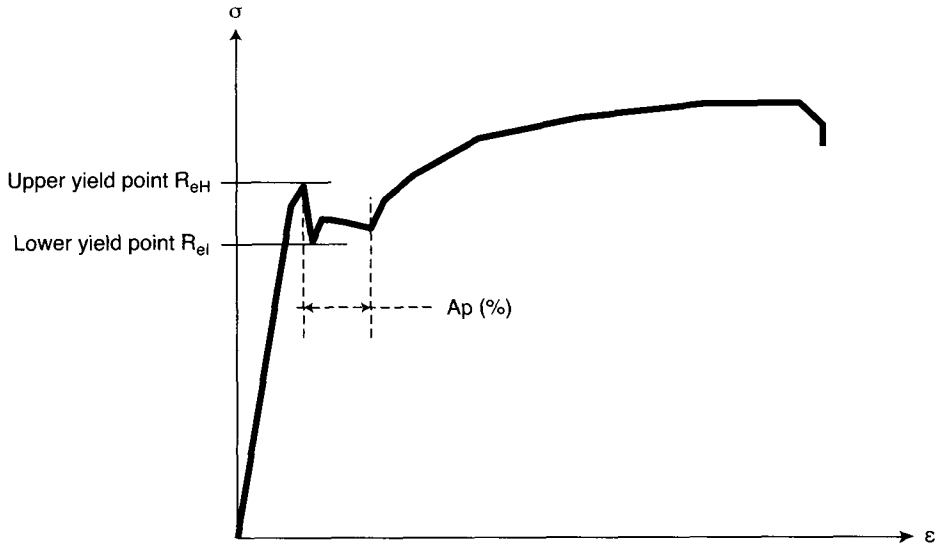


Figure 3.16

Upper and lower yield points.

- The necking Z (in%) is used to quantify the reduction in diameter (which does not always appear), knowing that S_U is the minimum ultimate cross-section of the specimen (at the fracture after necking): $Z = \frac{S_0 - S_U}{S_0} \cdot 100$;
- The Poisson's ratio ν is the ratio of the transverse strain ϵ_2 (in a plane normal to the load F) to the axial strain ϵ_1 (in the direction of the load F) $\nu = -\epsilon_2/\epsilon_1$ (see Figure 3.17).

Special extensometers are required to measure ϵ_1 and ϵ_2 .

Table 3.2 below compares the mechanical characteristics of various metallic materials.

B. True stress-strain curve

We observe that the definition of (engineering) stress $\sigma = F/S_0$, which is divided by the initial cross-section S_0 , does not correspond to the *true stress* in the cross-section S which is $\sigma_v = F/S$.

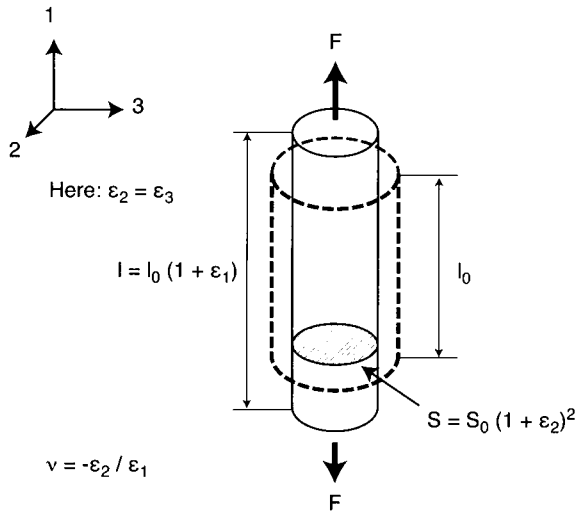


Figure 3.17

Tensile strain and Poisson's ratio ν (in this case $\varepsilon_2 = \varepsilon_3$).

Table 3.2 Examples of mechanical characteristics of metals.

Examples of mechanical characteristics of metals	Young's modulus E (GPa)	Yield strength (MPa)	Tensile strength Rm (MPa)	Failure elongation $\varepsilon_U\%$	Poisson's ratio ν
Steel	210	200-400	350-600	15-30	0.3
Special steels	210	500-1 300	700-1 800	10-15	0.3
Stainless steels	195	180-240	400-700	20-40	0.3
Aluminium alloys	70	100-500	200-600	5-30	0.35
Titanium and alloys	110	500-1 000	600-1 200	8-50	0.34
SG cast irons	100	200-600	350-900	2-25	0.29
Aluminium (annealed)	60	20	60	40	0.33
Copper (annealed)	130	20	200	30	0.34

Similarly, the (engineering) strain $\varepsilon = \Delta l / l_0$, which refers to the initial specimen dimension is not representative of the *true strain* of a volume element which is the sum of the elementary elongations undergone by the material and which can be written for a specimen

stretched from l_0 to l_1 : $\varepsilon_V = \int_{l_0}^{l_1} \frac{dl}{l}$ i.e. $\varepsilon_V = \ln \frac{l_1}{l_0}$.

The relation between true strain (ε_V) and engineering strain (ε) is therefore: $\varepsilon_V = \ln(1 + \varepsilon)$.

If we postulate *conservation of volume* during the plastic strain ($\nu = 0.5$), assuming that the transverse strains are equal, and if we consider the material before the appearance of necking, we obtain the following relation between cross-section and strain: $S/S_0 = 1/(1 + \epsilon)$ and between true stress and conventional stress: $\sigma_V = \sigma (1 + \epsilon)$.

The curve [true stress $\sigma_V = f(\text{engineering strain } \epsilon)$] shows the “*strain-hardening*” of the steel.

The curves have for example been described (at least partially) using the Ludwik $\sigma = \sigma_0 + \alpha \cdot \epsilon_V^n$ or Hollomon $\sigma = K \cdot \epsilon_V^n$ relation where “ n ” is called the *strain-hardening exponent* or *index*.

3.1.2.3 Elastic and plastic strain mechanisms in metals

A. Elastic strain in metals

Metals consist of an assembly of crystalline microstructures. “Elastic” strain occurs at atomic scale by deformation of the crystal unit cells, without the atoms actually changing neighbours. Consequently, only the distances between atoms or the angles may vary. This geometric phenomenon is therefore *reversible*. In metallic materials, however, little purely elastic strain is observed: about 0.2%.

As we saw during the tensile test, the elastic range (section OE on Figure 3.15) is characterised by a parameter intrinsic to each material called the modulus of elasticity or Young’s modulus E (E is the slope of the $[\sigma-\epsilon]$ curve and the elastic constitutive law is $\sigma = E \cdot \epsilon$). The other important characteristic is the yield point or elastic limit (point E on Figure 3.15).

B. Plastic or permanent strains

Beyond the elastic limit, *irreversible* (permanent) *strain* mechanisms develop. We are now in a region of “*plastic flow*”. While elastic strains of materials are generally very low, this is not true of “plastic” strains which may reach several tens or even hundreds of %.

Plastic strains only occur if flaws are present in the (poly)crystalline structures. For examples, flaws at atomic level (substitution, insertion or vacancies which distort the crystalline network), at grain boundaries or at twinned crystals, and especially the presence of *dislocations* which, due to their motions, represent the main mechanism of intragranular plastic strain.

Dislocations are the result of atom stacking faults naturally present when the crystals form. There are two types of dislocation, *edge dislocation* and *screw dislocation*, which are *schematised* in the crystal lattice on Figure 3.18. The number of dislocations may increase dramatically during high strain, making their motions more difficult and causing “hardening”. The dislocation density varies from about 10 km/cm^3 to 10^7 km/cm^3 in highly strain-hardened metals.

The above diagrams show that the faults are created by translation of the upper part of the crystal in case of edge dislocation, or a local rotation in case of screw dislocation. Through highly localised movements around the dislocation line, the *motion of dislocations* allows the entire structure to deform. These motions, which can be broken down into two components: glide and climb (see diagrams below on Figure 3.19), allow high plastic deformations in crystalline structures.

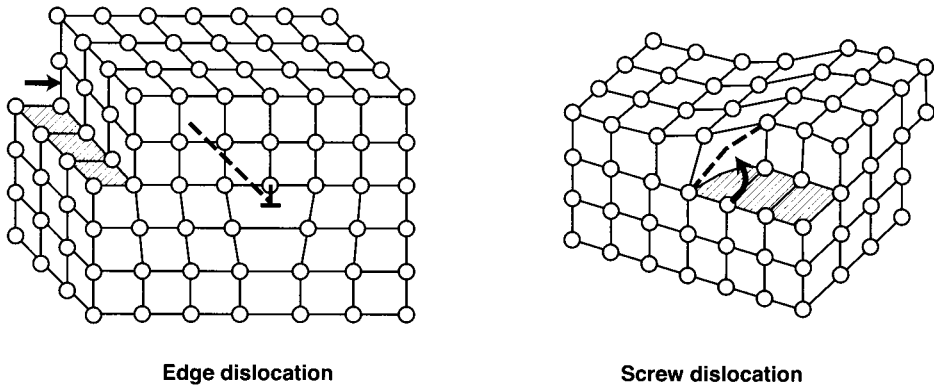


Figure 3.18

Schematic views of edge and screw dislocations (shown here in a simple cubic lattice).

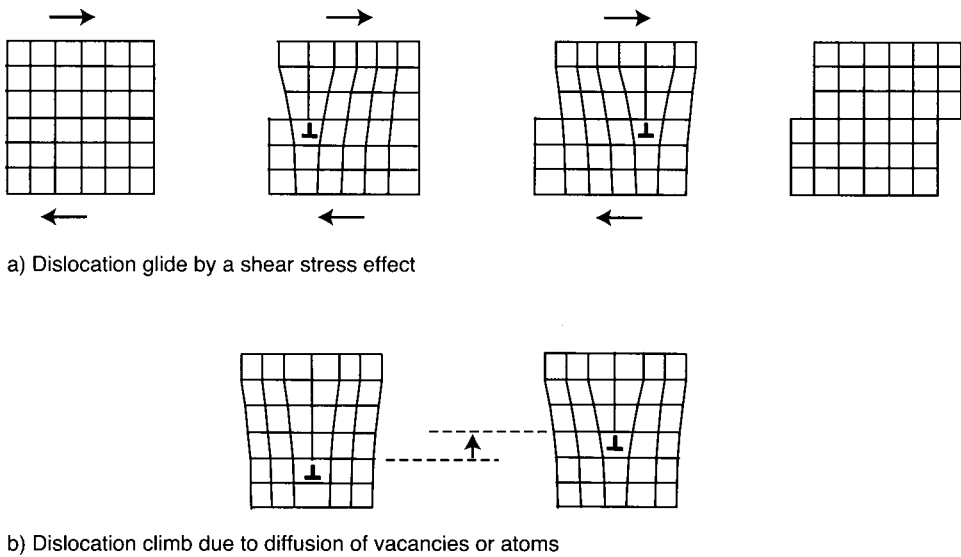


Figure 3.19

Diagrams showing the glide (a) and climb (b) motions of edge dislocations.

3.1.2.4 Damage and failure mechanisms

During plastic deformation, irreversible phenomena appear in multiphase and polycrystalline structures. Creation and motion of dislocations inside grains are the main mechanisms, even though they are accompanied by more macroscopic phenomena such as crystallographic slips and shears in the grains or at the grain boundaries.

Defects initiation may for example be attributed to dislocation stacks which create a *microcrack* in a previously homogeneous medium. *Inclusions*, however, form the most frequent initiation sites. These inclusions and the metallic matrices surrounding them have a wide range of shapes and properties. Decoherions may be observed at the interfaces as well as fragmentation of inclusions which are too brittle. We might then expect that these decoherions and fragmentations lead to the opening of *microcavities* or creation of *microcracks* (see Figure 3.20). By *propagation* and/or *coalescence*, these damage initiation sites may lead to macroscopic flaws which can propagate and cause total failure.

Apart from inclusions, grain boundaries and boundary junctions, irregularities and *external surface defects* (scratches, roughness, sharp edges, corrosion, etc.) also represent preferential damage initiation points.

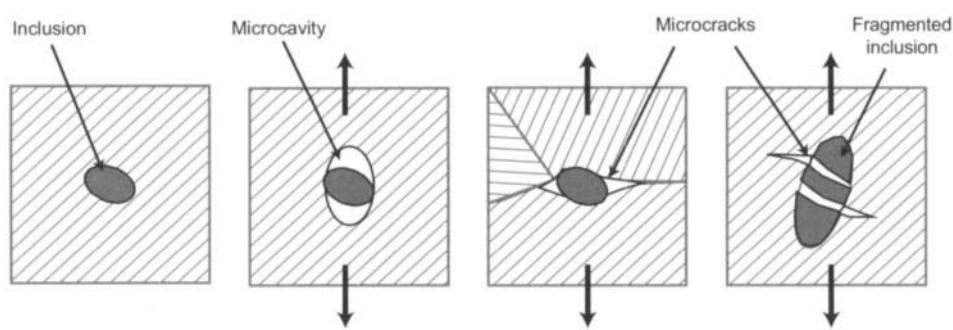


Figure 3.20

Illustrations of an inclusion and damage initiation sites (microcavity or microcrack on grain boundaries or in the grain).

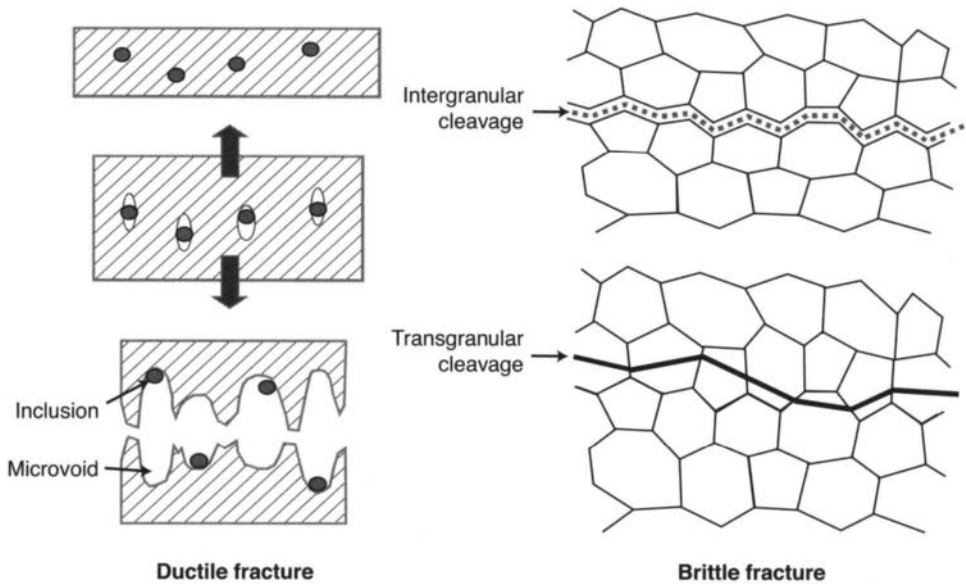
3.1.2.5 Ductile failure and brittle failure

Two types of failure, schematised on Figure 3.21, are generally identified:

- *ductile failure*, which involves high strains (at least locally) and often exhibits facies with *cups* (ductile development of microcavities) and ductile tear and shear zones,
- *brittle failure*, which exhibits sharper, shiny facies (small facets in case of metals) resulting from *cleavage* with transcrystalline (along the grain crystallographic planes) or intergranular (in case of weak boundaries) propagations.

In practice, failures may exhibit brittle zones (trans- and intragranular) and ductile zones simultaneously. Similarly, a distinction must be made between macroscopic behaviour which may be brittle, for example, and “micro” mechanisms which may produce ductile behaviour very locally.

Lastly, we must remember that the notion of failure is highly dependent on the flaws (and their size), whether they are internal or external. If there were no flaws, the materials would be extremely strong. The strengths of carbon, glass, ceramic or polymer fibres with very small diameters (about 10 μm) and containing very few flaws are much greater than those of the usual metals.


Figure 3.21

Diagrams illustrating failures:

- on the left: ductile failure after creation of microcavities leading to cup facies,
- on the right: brittle failures by decohesion or cleavage.

Obviously, the propagation and failure modes are strongly influenced by the material itself (composition, phases, microstructure, etc.), but the environment and the stress conditions are just as important. This is a vast subject and we will only mention the main parameters influencing failure:

- *Material*: high-strength steels are very often brittle (since the elastic limit is high, they can work under high stress but with increased risk of brittle fracture). The notion of brittleness has been quantified for over a century by impact tests (which will be described later) and, for a given material, we can plot the ductile/brittle transition curve, for example the resilience-temperature curve;
- *Temperature*: “all” materials are highly sensitive to this parameter, behaviour becomes brittle as the temperature is lowered. Consequently, there is a “*ductile/brittle transition*” characterised by a *transition temperature* defined using impact tests performed at different temperatures for example. We must be extremely cautious, however, since this transition temperature remains dependent on the test conditions, in particular on the specimen geometry and the impact speed;
- *Stress rate*: increasing the stress rate (application of force or strain) favours brittle failures;
- *Notch and specimen geometry*: the stress is much greater at the bottom of the notch and there is a *stress concentration factor* (K_T function of the geometry). In addition, when applying the mechanical stress, a confined plastic strain zone forms at the bottom of the

notch, increasing the *triaxiality*. The notch geometry therefore has a considerable influence on the “severity” of the flaw. The type of specimen and in particular its thickness also affect the triaxiality and the increase in brittleness. These notions have very important consequences on the methodologies of the “toughness” tests conducted in the field of “fracture mechanics”;

- *Environment*: presence of a corrosive or embrittling environment (e.g. hydrogen in steels) around the material, and in particular in the cracks, may make it more brittle.

3.1.2.6 Description of mechanical stresses and behaviours

The tensile test described in the previous paragraph, used to introduce notions on mechanical behaviour and strain mechanisms in metals, is one of several mechanical tests. These tests can also be used to determine intrinsic and/or important characteristics such as the Young’s modulus, elastic limit, ultimate strength, etc. They demonstrate the limits (often failure) of the materials, but they can also quantify the parameters used in the mechanical constitutive laws (laws used for example to describe the evolution and relations between stresses and strains and which are used in finite element calculation codes).

The following paragraphs outline the various types of stress, test and behaviour.

A. Types of mechanical stress

a. Tension/compression

Tensile (or compressive) stress on a specimen introduces uniform stresses in the material in a cross-section normal to the stress direction (force F) as shown on Figure 3.22.

In the elastic range (small strains), the stress-strain relation is: $\sigma = E \cdot \epsilon$.

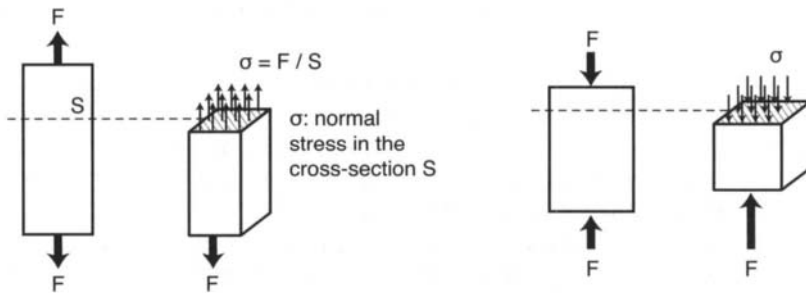
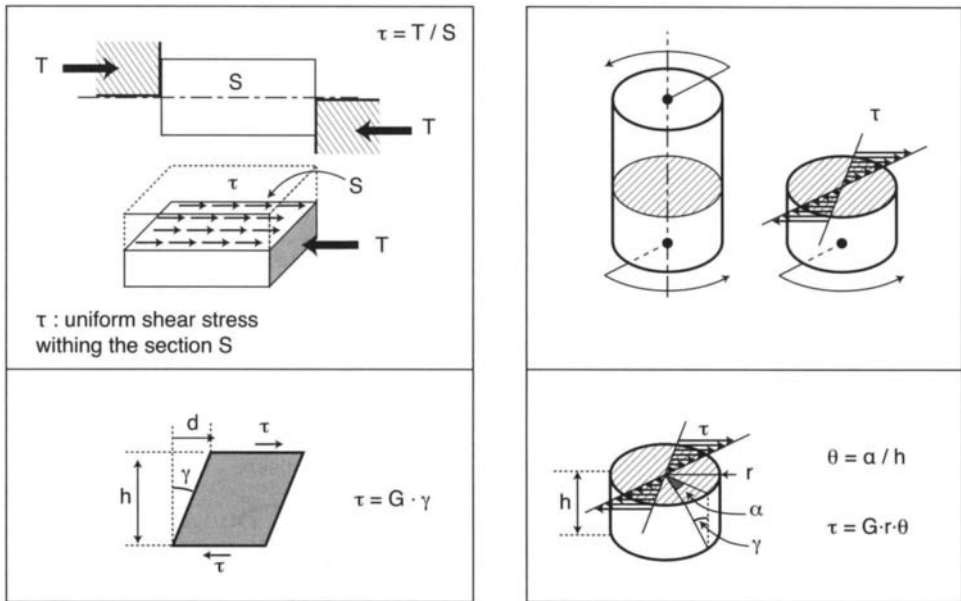


Figure 3.22

Tensile stress (on the left), compressive stress (on the right).

b. Shear/torsion

Figure 3.23 below shows objects subjected to shear stresses. In one case, forces T introduce shear stresses in the material in cross-section S , which is a plane parallel to the direction of forces T (in this case, the shear stress can be expressed simply: $\tau = T/S$). Torsion is another

**Figure 3.23**

Shear stress (simple on the left, torsion on the right).
At the bottom: stress/strain relations (small strains).

frequent configuration. In this case, a cylindrical specimen is subjected to a torque (or torsion moment) at each end, which induces shear stresses in the planes normal to the torsion axis (unlike the previous case, the stress state is not uniform throughout the cross-section).

As with tension, there is a simple relation between stresses and strains provided that the material remains in the *elastic range of small strains*. We can therefore introduce a *shear modulus of elasticity* denoted G .

The element of material subjected to shear stress (Figure 3.23) illustrates the stress/strain relation: $\tau = G \cdot d/h$, (since angle γ is small: $d/h = \tan \gamma = \gamma$).

We note the relation: $\tau = G \cdot \gamma$.

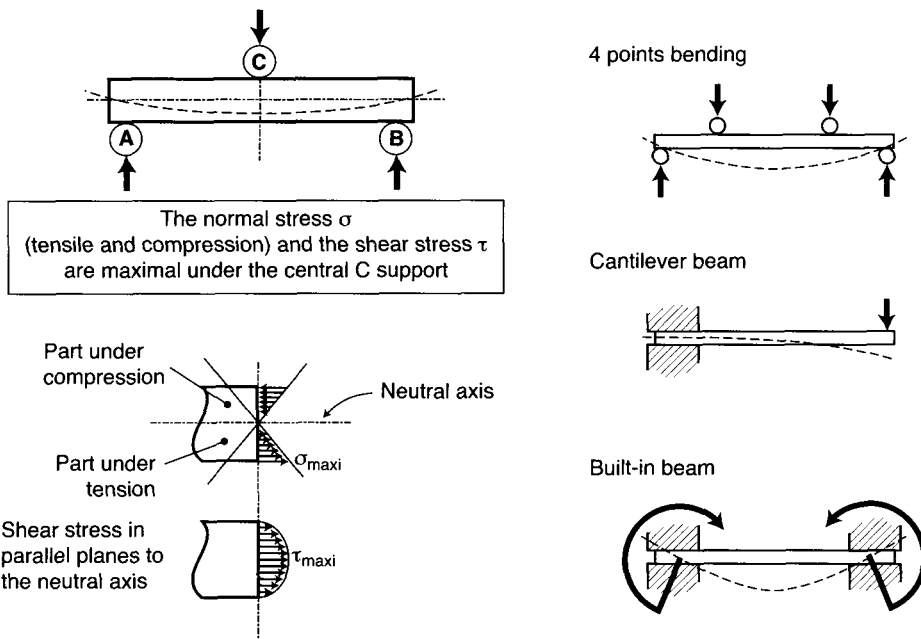
For a cylinder subjected to torsion, the shear stress τ at a distance r from the axis is therefore written: $\tau = G \cdot r \cdot \theta$ (θ is the unit torsion angle, in this case equal to α/h).

For small strains in the purely elastic range, the *elastic constants* discussed here and the Poisson's ratio ν can be related by:

$$E = 2 \cdot G(\nu + 1)$$

c. Bending

The stress state produced by bending is more complex than tension or shear alone, since it induces tensile, compressive and shear stresses in the material. This is illustrated on Figure 3.24 for a specimen subjected to 3-point bending stress. The stresses in the specimen

**Figure 3.24**

Bending stress (3-point on the left and other arrangements on the right).

are not uniform, whether across the thickness or along the length. This type of stress has also been documented in mechanical characterisation standards. It is nevertheless primarily used for rigid materials and/or materials with low failure strain or those more easily manufactured as parallelepipeds (e.g. composite materials). Note that other bending geometries are possible, for example 4-point bending, dual cantilever bending, etc. Stress states in the specimens nevertheless remain complex but with variants. With the *4-point bending test* or the *dual cantilever test* for example, the stress state is unusual since shear is zero between the central supports, the tensile and compressive stresses are constant in all cross-sections normal to the neutral axis and the shape adopted by this central section of the specimen is circular.

B. Some types of mechanical behaviour

The study of laws and behaviour, which involves mechanics, rheology and thermodynamics of continuous media, is a vast, complex field. Our intention here is simply to give a brief reminder of a few terms frequently encountered when describing mechanical behaviour – see Figure 3.25.

a. Elasticity

Purely elastic behaviour is *reversible* and *instantaneous*, there is no time factor. The law describing linear-elastic behaviour (tension or compression) is the simplest and has already been given: $\sigma = E \cdot \epsilon$.

At small strains, metals can be considered as elastic.

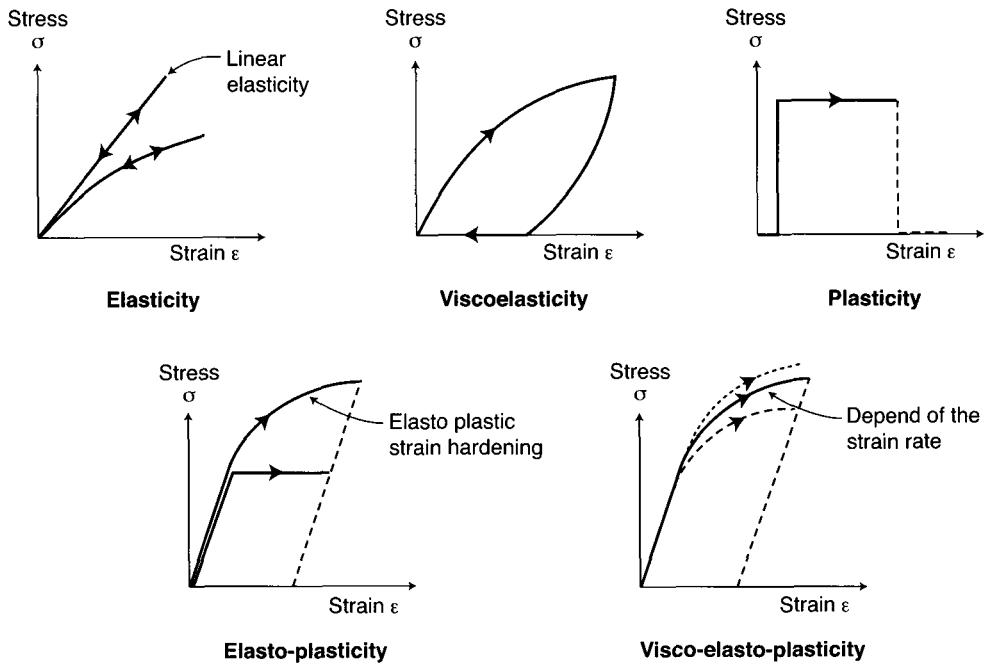


Figure 3.25

Types of mechanical behaviour.

b. Viscoelasticity

Polymers are the most obvious example of materials exhibiting viscoelastic behaviour. Unlike elasticity, the time factor plays an important role. The behaviour is reversible but the responses *always depend on the time and the strain or stress rate*. Viscosity introduces *mechanical damping* which means, for example, that there is a phase difference between a sinusoidal force applied to a viscoelastic solid and its strain response (notion of internal friction).

c. Plasticity

Under the effect of a stress less than a threshold (σ_s), a solid exhibiting *perfectly* plastic behaviour would have zero (or negligible) strain. Upon reaching this stress threshold σ_s , it would deform in a stable manner, like a soil for example which remains in place when the stress is removed.

d. Elastoplasticity

In this case, linear elasticity is followed by purely plastic or *plastic hardening* behaviour. The latter more realistic behaviour may apply to metals and alloys.

e. Elastoviscoplasticity (strain hardening)

By introducing a viscosity component, the responses will become much more complex and strongly depend on the stress time and rates. This type of behaviour model can be applied to metals and alloys for example at high temperatures.

3.1.2.7 Types of mechanical test

We will now provide a brief description of the main types of mechanical test encountered. Numerous tests are used to determine a certain number of parameters in order to characterise the structures and also evaluate their lifetimes. Simple data such as Young's modulus, elastic limit, elongation at break, etc. are used, but much more complex test campaigns can also be conducted, to evaluate fatigue or creep life for example, often in conjunction with temperature "environmental" stresses and/or aggressive fluids.

A. Monotonic/relaxation tests

The mechanical tests most frequently carried out on all materials and described in numerous standards are the so-called *monotonic* tensile tests. They consist in subjecting the specimen to *strain at constant rate* and monitoring the stress response, as illustrated on Figure 3.26. This type of test is frequently conducted in tension and the characteristics (elastic, at break, etc.) that can be deduced were detailed in the first paragraph concerning mechanical behaviour. However, the principle of a monotonic test at constant strain rate applies to other types of stress, for example compression or bending stress.

In a "relaxation" test (Figure 3.27), a strain is also applied and then held constant. Viscoelastic materials then undergo *stress relaxation* (the case schematised on Figure 3.27 exhibits a sharp stress drop rarely found in metals at ambient temperatures).

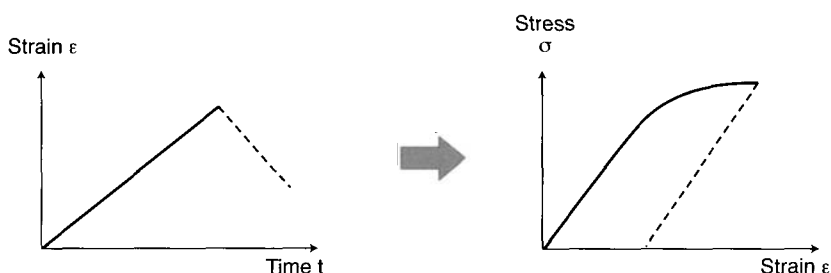


Figure 3.26

Monotonic test: imposed strain and stress response.

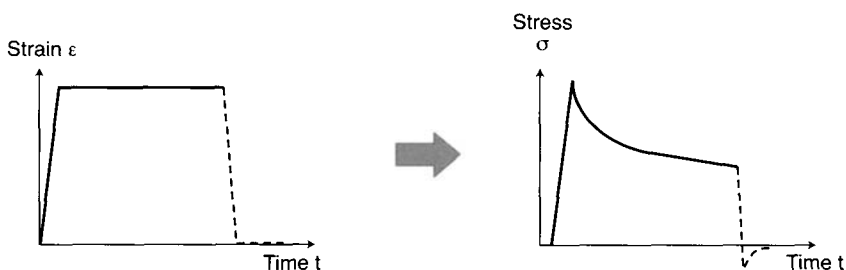


Figure 3.27

Relaxation test: imposed strain.

B. Creep/recovery tests

When conducting creep tests, *the stress or force imposed is maintained constant*. This type of test is important in practice since numerous structures work under imposed forces (or pressures). Figure 3.28 illustrates this test and shows that if this stress is reduced to zero, *recovery* takes place and it takes the material a certain amount of time to return to its initial dimension (viscosity effect); if plastic strain mechanisms have been activated, only partial recovery will occur. The creep curve shows that creep may accelerate up to break (indicated by a star on the curve).

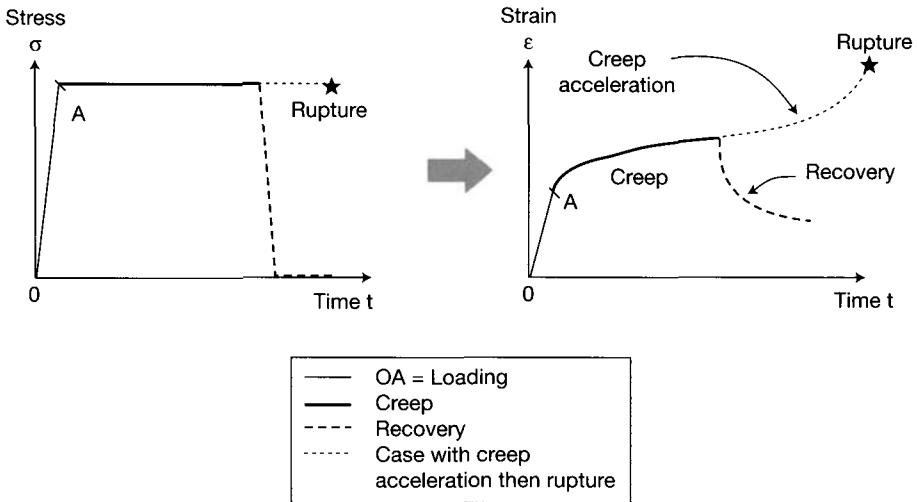


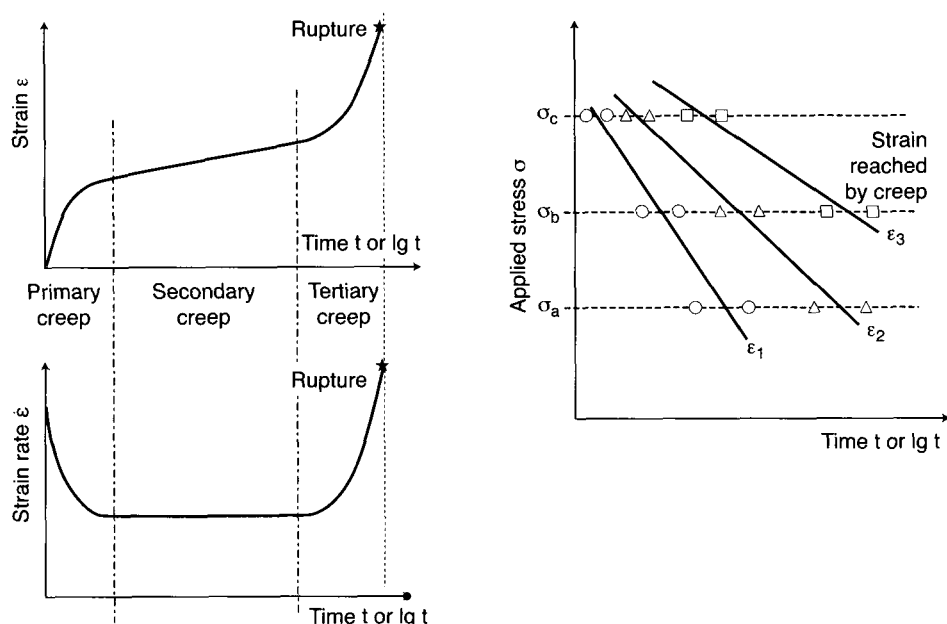
Figure 3.28

Creep test.

In practice, it is difficult to maintain stress rigorously constant. If the stress is imposed by a hanging weight, the force is rigorously constant. During elongation, however, the cross-section of the specimen is reduced slightly (Poisson's ratio) thereby increasing the stress slightly. Strictly speaking, the forced applied would have to be adapted to the geometric evolution of the specimens, which can in fact be achieved using hydraulic test machines slaved to strain measurements taken on the specimens. In case of very high strains, observed for example during severe creep, the specimen may even undergo necking.

Creep tests can be conducted to compare materials, design a structure, determine constitutive laws and evaluate lifetimes by long-term extrapolation [325]. Standards NF EN 10291 [300] and ASTM E319 [287] illustrates these tests. The creep curves can therefore be represented and interpreted in numerous ways. We will only give two examples here, which also provide an opportunity to mention the 3 stages usually involved in creep.

The traditional creep curve [$\epsilon = f(t)$] is often represented as on Figure 3.29 without plotting the loading phase (OA on Figure 3.28); the time scale can be logarithmic. The graph opposite shows the strain rate $\dot{\epsilon}$ which can be plotted against ϵ , t or $\lg t$.

**Figure 3.29**

On the left: test with the three creep stages.

On the right: for a series of creep tests (in this case with 3 stress levels).

Metals exhibit the three creep stages presented here when the temperature is high enough to activate the mechanisms leading to high strains (generally for $T > 0.3$ to $0.5 \cdot T_{\text{melting point}}$):

- *Primary or transient creep*: the strain rate $\dot{\epsilon}$ (or creep rate) decreases with time (work hardening of the material). This is the normal type of creep observed at low temperatures ($T < 0.3 \cdot T_{\text{melting point}}$), the strain rate becomes very low (logarithmic creep);
- *Secondary or steady state creep*: the strain rate $\dot{\epsilon}$ is constant over time. The plastic strain mechanisms involved are mainly related to dislocations (with the creations and motions of dislocations already present during primary creep, we observe grouping of dislocations in cellular substructure in the grains, etc.);
- *Tertiary creep*: the strain rate increases and failure occurs. In particular at high temperature and/or high stress, other mechanisms such as restorations, recrystallisation and diffusion of atoms, slipping at grain boundaries, etc. are involved. As in a monotonic tension test, necking may occur before failure.

Creep type characterisations are widely used for pipelines subjected to high internal fluid pressure, the times required to reach bursting being recorded in tests conducted at different pressures.

Creep is predicted using parametric relations between stress (or strain) at failure, temperature and time. Larson and Miller proposed the following relation:

$$P = \frac{T \cdot C \cdot \log(tr)}{1000} \quad \text{with}$$

P applied stress (N)
 T temperature (K)
 tr time at failure (hours)
 C constant (for steels $18 < C < 28$)

C. Combined stresses (multidirectional)

In practice there are obviously numerous cases where the stress on the element or on the structure is not simple (e.g. only tension or torsion). Stress in cases of bending is complex (tension or compression combined with shear). A few other cases will be mentioned below (see Figure 3.30).

- Tubes with internal (or external) pressure with axial tension (or compression): axial stress can be applied by a traditional mechanical test machine, pressure stress is relatively easy to apply using a hydraulic device. With an internal pressurised tank, end cap effect will introduce (axial) tension in the cylindrical part in addition to (circumferential) tensile stresses due to the internal pressure. This is known as biaxial tension;
- Cylinder or tube under torsion with axial tension (or compression): a device, generally hydraulic, can be added to a traditional machine to impose torque on the system under test. Standard ASTM E2207 is an example [301];
- Plate under biaxial stresses: the test setups may become complex with the use of several hydraulic cylinders, even superimposing normal and shear stresses;
- Specimen under triaxial compression: this type of test is used in particular in rock (or soil) mechanics by applying hydrostatic and therefore triaxial pressure. Problems of tightness must however be solved when the tests are conducted on permeable materials.

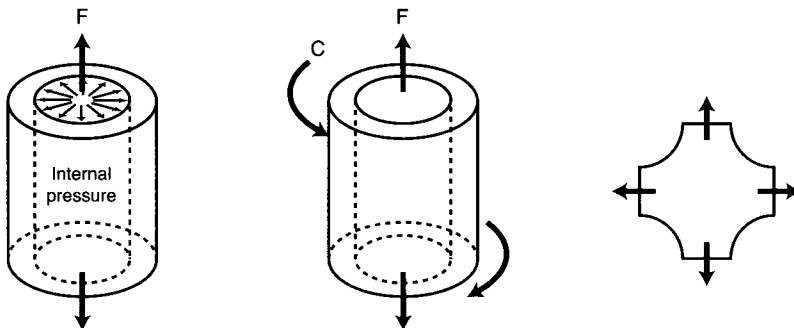


Figure 3.30

Examples of multidirectional loading.

D. Cyclic stresses/Fatigue

Fatigue tests are conducted to reproduce cyclic mechanical stresses as close as possible to those encountered in service by the parts (mechanical loading mode, stress level, stress frequency, etc.). The materials subjected to cyclic stresses that are often well below their elastic limit will nevertheless fail after a certain number of cycles. Damage occurs progressively

inside the material and, locally, one point becomes the *failure initiation zone*. Cracking propagates from this zone through the part up to final failure when the remaining material can no longer withstand the stresses. This type of failure occurs at much lower strains than those observed in the traditional monotonic tension tests, due to progressive cracking which invades a large section of the part.

A part which has failed under fatigue generally exhibits 3 characteristic zones:

- An *initiation zone*, from where the crack starts. It often corresponds to a preexisting flaw which may be located on the surface or inside the part (foundry, machining, welding flaws, or flaws caused by corrosion or various mechanical aggressions, etc.). The initiation zone may also be created at the start of fatigue by accumulation microdamage (as we have seen for example with dislocations);
- A relatively flat and smooth *propagation zone* (in the plane of maximum stress) and which under the microscope reveals a succession of striations called *fatigue striations*;
- A *final failure zone* which often corresponds to sudden tearing.

Fatigue tests can be conducted under imposed *load* or imposed *strain*.

Under high stresses when the metal switches periodically into *plastic strain*, the number of cycles up to failure is low, a situation known as *low cycle fatigue*.

The various stress modes are observed in the fatigue tests: tension, compression, tension/compression, bending, rotary bending, torsion as well as combined modes, in particular tension/torsion or bending/torsion (*static stress* may be superimposed on *cyclic stress*).

Figure 3.31 illustrates stress cycles and the definition of *alternating stresses*. Periodic stress is often sinusoidal but may include linear ramps, especially when using hydraulic test machines.

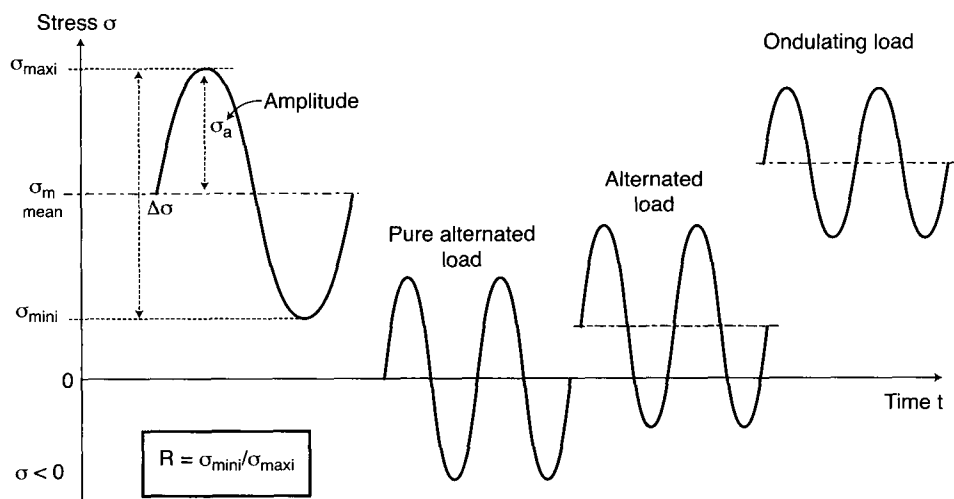


Figure 3.31

Cyclic fatigue (stress-controlled in this case).

The fatigue test parameters are the *minimum/maximum stress ratio* R ($R = \sigma_{\min}/\sigma_{\max}$), the *frequency* and the *maximum stress*.

To analyse the results, the most well-known *endurance diagram* is the *S-N curve* (Stress-Number of cycles) or *Wöhler curve*: it displays the imposed stress levels (e.g. the maximum stress) against the number of cycles to failure N_f (generally a logarithmic scale). A large number of tests must be conducted during the fatigue test campaigns since the results are generally highly dispersed. For a given level of stress, therefore, the N_f may extend over a decade, a situation which is partly due to the experimental conditions but more especially to the phenomena involved in crack initiation and propagation. Figure 3.32 shows an example of this diagram and indicates the three fatigue regions:

- *Low cycle fatigue*: under high stresses generating plastic strains and small numbers of cycles to failure (often from just a few cycles up to 10^4 cycles);
- *High cycle fatigue*: failure still occurs, but the lifetime increases when the stress level decreases;
- *Fatigue limit*, under which fatigue failure no longer occurs, is frequently observed; in this case, the S-N curve extends towards a horizontal asymptote (this region often

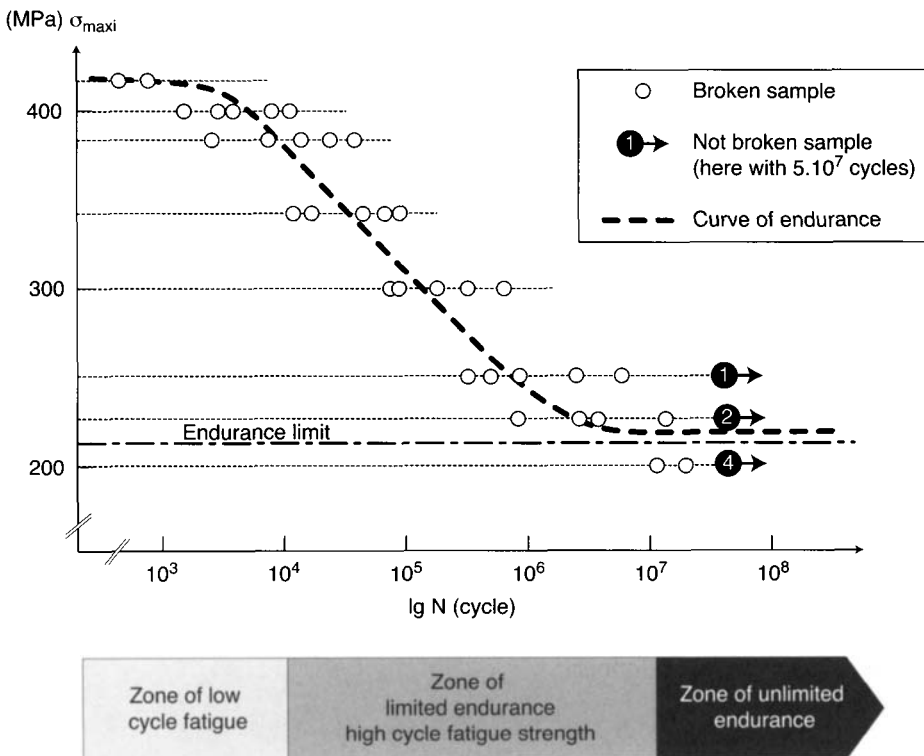


Figure 3.32

Fatigue: example of S-N (or Wöhler) curve.

concerns numbers of cycles to failure $N_r > 10^7$ or 10^8). This asymptote is not always the rule, however, especially when other damage such as corrosion occurs in addition to mechanical fatigue.

Numerous standards and operating procedures, especially statistical, are available to conduct the tests. Failure equiprobability curves (at 90%, 50% and 10% survival) for example can be plotted on the endurance diagram. The reader can refer to various articles and books on fatigue: [323; 324; 326; 334; 341; 346], and standards ISO 1099 [307], ISO 1143 [303] and ASTM E606 [306], ASTM E466 [289].

The fatigue study methodologies also apply to fracture mechanics. *Fatigue cracking tests* may for instance use the toughness specimen geometries (CT and 3PB specimens described on Figure 3.36) and several methods have been developed to monitor crack propagation (optical, ultrasound, electrical measurements, etc.).

Lastly, we may mention the *variable amplitude stress fatigue* tests. The objective here is to assess the behaviour of structures which are subjected to highly variable stresses during service. Several methodologies are available and some test sequences have even been standardised in the aeronautical, automotive and petroleum industries.

E. Hardness

By definition, “*hardness*” is the resistance exhibited by a material to penetration by a harder body. The principle consists in applying a constant force for a given time on an indenter of well-defined geometry and measuring the dimensions of the indentation left by this indenter.

Although the hardness cannot be *directly* related to other properties of materials, we can well imagine that there is a strong likelihood that a very rigid material will be “hard”. This is not always true, however, for example a composite material with polymer matrix may be very rigid in the direction of the fibres, without exhibiting the hardness of steel. Studies establishing correlations between various properties (hardness, Young’s modulus, strength, etc.) and conversion tables can nevertheless be found [304].

Hardness is highly sensitive to the surface state which may quite differ from the state of the material at depths exceeding the penetration depth, a factor which must be taken into account. It is also influenced by the experimental conditions, in particular the load application time, but also the metal microstructure (grain size). The three most widely used tests are described below: *Brinell, Vickers and Rockwell hardnesses* detailed in standards [290-293; 296; 305]. Figure 3.33 illustrates the principles of these three tests. A description of *microhardness* will follow.

a. Brinell hardness

The indenter is a ball of diameter D which is applied under a force F for a time t . The *hardness* H_B is the ratio of the mass applied divided by the area of indentation (spherical cap). It can be calculated using the following formula:

$$H_B = \frac{1}{g} \cdot \frac{2F}{\pi D(D - \sqrt{D^2 - d^2})}$$

The hardness H_B must be given with the values of D (often 5 mm or 10 mm), the force F (the mass F/g can be up to 3 000 kg) and the time t .

b. Vickers hardness

The indenter is a diamond pyramid with square base and a summit angle of 136° . The definition

is similar to that of H_B : $H_V = \frac{1}{g} \cdot \frac{2F \cdot \sin 68^\circ}{d^2}$.

c. Rockwell hardness

There are two indenters (ball or cone with rounded tip), the measurement follows the following sequence:

- application of a first light load ($F_0 = 98 \text{ N}$) which acts as origin,
- application of $F_0 + F_1$,
- force F_1 is released $\rightarrow$ the additional depth of penetration h is used to calculate the Rockwell hardness (relation depending on the geometry and the force applied; there are several Rockwell hardness values: A, B, C, D, E, F, G, K, N and T).

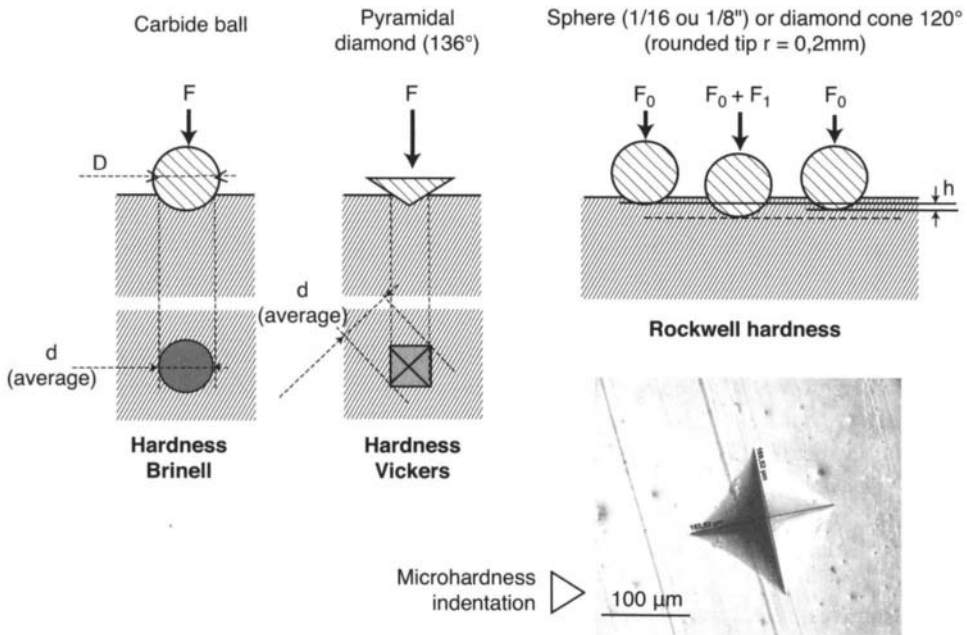


Figure 3.33

Brinell, Vickers and Rockwell hardness tests.

d. Microhardness

A microhardness tester is used to take highly local measurements (about $100 \mu\text{m}^2$), in a specific phase for example. A Vickers type tip is used and the hardness tester is a microscope used to measure the indentation after having applied very small loads ($< 1 \text{ N}$). Figure 3.33 shows an indentation example. This test is conducted mainly in laboratory, unlike the Brinell and Rockwell tests which are frequently implemented in workshops and on sites.

F. Impact strength tests

Scientists have been aware of the notion of the “brittleness” of materials for more than a century and have developed tests capable of demonstrating it. The tests are “dynamic”, in other words they use an impact (at speeds higher than the traditional tension tests for example) in order to produce “sudden” failures. The *Charpy impact* test is the most well-known example used to measure the *impact strength* of a material, expressed for example in J/m² or J/cm² and described in international standards ISO 148 [294], ISO 14556 [298] and ASTM E23 [295]. The Charpy impact test is schematised on Figure 3.34.

This quick test uses specimens of reasonable size (10 × 10 × 55 mm³) with a V-shaped notch (2 mm deep with a 0.25 mm notch radius) or a U-shaped notch (5 mm deep with a 1 mm notch radius). It is generally conducted using a pendulum equipped with a hammer connected to an axis (very low friction) which strikes a specimen (on the face opposite the notch) placed on 2 pads and therefore subjected to bending stress. On steels, the impact speed is generally 5 m/s, the speed being determined by the fall height of the pendulum.

The three embrittling factors (external to the materials) are:

- increase in stress rate,
- temperature decrease,
- increase in notch severity (essentially its “sharpness”).

The energy absorbed by breaking the specimen is calculated using the difference between the initial height (start of hammer fall) and the climb height ([h_1-h_2] on the figure). The energy is divided by the broken area and the impact strength is written (for the Charpy V test): $K_{cv} = Wr/S$ (Wr is the energy at break and S the area). Some improvements or observations increase the quality of these interpretations:

- Although the test is quick and easy, the results are often highly dispersed. Consequently a large number of specimens are required, especially to obtain the *ductile/brittle transition*. In this case, batches of 5 to 10 specimens must be tested at numerous temperatures, for example between – 50 °C and + 200 °C, the transition extending over several tens of degrees;
- *Observation of fracture surfaces* demonstrates that fracture generally starts (at the notch tip) with a ductile tear region followed by a region dominated by brittle fracture by cleavage, lastly terminal ductile tears are observed, sometimes with shear lips on the sides. Quantification of the fraction of brittle facies with respect to the total area also gives a relevant indication of the degree of brittleness;
- Test devices sometimes include an “*instrumented*” hammer with a force sensor. The impact curve (force against time, which may be a few millisecond) can provide a better appreciation of the ductile and brittle natures, if the vibratory phenomena are correctly controlled. The initiation and propagation phases can therefore be quantified. Propagation in case of brittle failure is characterised by low energy absorption. The instruments may also indicate the force at which propagation starts;
- By providing critical force values, the instruments also allow the *use of fracture mechanics methods* in order to assess the “toughness”.

Impact tests other than the Charpy tests are also available, sometimes with weights falling vertically but often with pendulums such as the *IZOD impact* test, which uses the same

specimen as the Charpy V. In this case, however, the specimen is positioned vertically. The lower half of the bar (up to the notch) is clamped and the upper part is struck 22 mm above the notch by the hammer.

Other types of impact test have been designed to be more representative of applications, e.g. impact with a weight falling onto a clamped sample, impact on a specimen under tension or even dropping the object to be tested from a height of several metres (automotive fuel tanks). In addition to impact pendulums and devices with falling weights, hydraulic machines have been developed to conduct well-instrumented mechanical tests at high speeds, but obviously they are much more expensive.

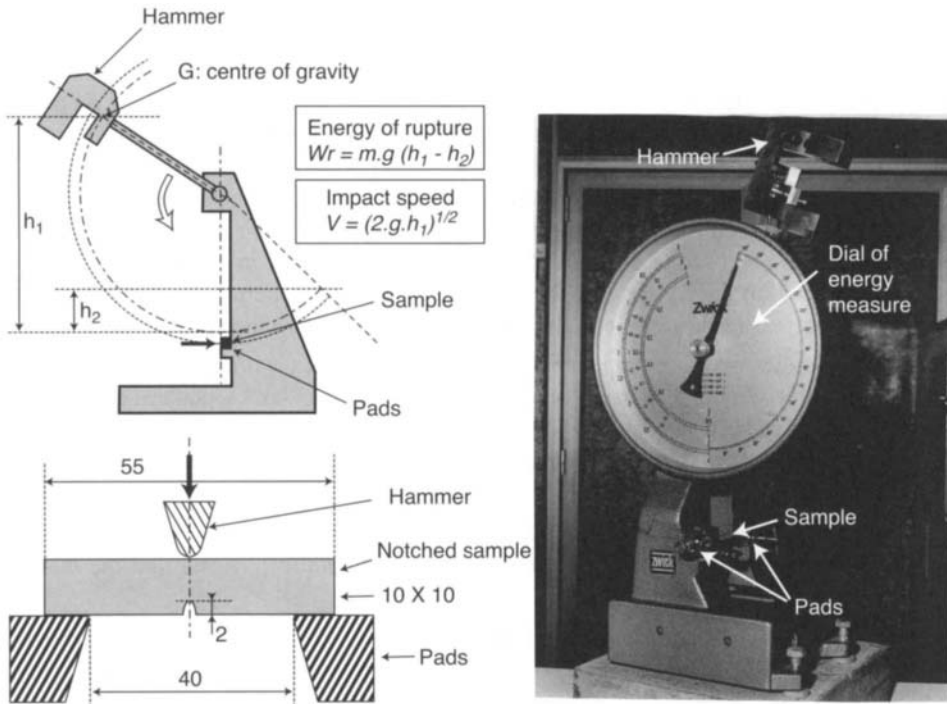


Figure 3.34

Impact pendulum and geometry of the Charpy impact test (on the left: diagram of a Charpy impact pendulum and conventional specimen with V-shaped notch and dimensions in mm – on the right: photograph of a small impact pendulum).

The quantitative resilience values obtained with the various methods and with variable geometries are not comparable. Although there are correlations and comparisons, these values cannot be used to calculate the loads that structures can support or for design purposes. This is obviously the big criticism of resilience. It explains the emergence of *fracture mechanics* towards the middle of the 20th century, which uses flaws (cracks, etc.) as main parameters and which allows characterisation of materials (critical flaws, critical energies, etc.) with *toughness* as new intrinsic property of materials.

G. Notions of fracture mechanics and toughness

Fracture was discussed in the previous paragraphs through its main mechanisms and from the experimental point of view using tension tests and the impact test which characterises impact strength. Parameters such as temperature, stress rate and presence of a notch were already taken into consideration over a century ago.

Very sudden and catastrophic fractures have been observed, however, on large metallic structures (generally at low temperature) such as bridges and the famous American *Liberty Ships* of the Second World War. Built to a standardised, mass produced design to send supplies to Europe, these ships relied extensively on welded sections (instead of rivets), allowing fractures to propagate over long distances (more than 300 cases out of 2 700 ships built), sometimes across the entire hull resulting in some ships splitting in two.

Towards the middle of the 20th century, the birth of “*fracture mechanics*” led to a greater understanding of the notion of *flaw*, one of the main causes of fracture initiation, so permitting quantification that is far more relevant and intrinsic to the material than impact strength, through the use of a new characteristic: *toughness*. While impact strength can be used to compare materials and evaluate their ductile/brittle transition, it cannot be used to calculate critical loads on structures presenting flaws of known size. For given loads, fracture mechanics can also be used to evaluate the critical sizes of flaws, in particular very narrow cracks which develop during fatigue, for example. The nuclear, aerospace and petrochemical industries played a leading role in the development of fracture mechanics.

Numerous studies have been conducted on fracture mechanics and much progress has been made over a period of more than half a century. A large number of books, publications and obviously standards have been published. *We will only provide here a few notions, definitions and experimental examples with a few references to books [331; 343; 345] and standards NF EN ISO 12737 [302] and ASTM E208 [297], ASTM E399 [311], ASTM E813 [309], ASTM E1221 [308].*

The main point to remember is that fracture mechanics provides a means of determining relations between the load on a part, the geometry of the flaws (cracks) and the material through a property known as toughness.

Fracture tests can be performed to determine toughness, but they must apply methodologies extremely rigorously (see standards) in order to obtain valid, relevant results. For more complex parts and structures, the results of toughness tests can be associated with finite element calculations.

Toughness tests are typically divided into 3 categories:

- tests based on linear elasticity fracture mechanics,
- tests based on elastoplasticity fracture mechanics,
- tests based on the local approach of fracture mechanics.

a. Linear elasticity fracture mechanics

The available energy rate or *energy release rate* is denoted G . If G exceeds a critical value, the crack propagates ($G \geq 2\gamma$, γ being a property of the material, surface energy), and relations exist to connect G to the load and to the crack. For example: if F is the applied force

and ∂C the compliance variation when the crack increases by area ∂A : $G = \frac{1}{2} F^2 \frac{\partial C}{\partial A}$.

While the previous approach is based on energy, a parameter called the *stress intensity factor* K has been determined by studying stresses at the tip of the crack. This factor (which is not a stress concentration coefficient) is in fact the key parameter in fracture mechanics since it *simultaneously takes into account the geometries of the part, the crack and the load*. For a given value of K therefore, different parts or structures will have the same stress state at the crack-tip.

Direct relations therefore exist between the stresses and the crack and load geometries. Figure 3.35 illustrates a few examples which are also traditionally used in test geometries. This figure also indicates the 3 crack stress modes traditionally used: *mode I* opening, *mode II* in-plane shear and *mode III* out of plane shear (shear perpendicular to the plane).

As the moment of crack propagation, the stress intensity factor K reaches a critical value denoted K_c , the toughness, an intrinsic characteristic of the material. K_{Ic} , K_{IIc} or K_{IIIc} can be defined depending on the stress mode (I, II or III). Toughness characterises the resistance of a material to propagate cracks.

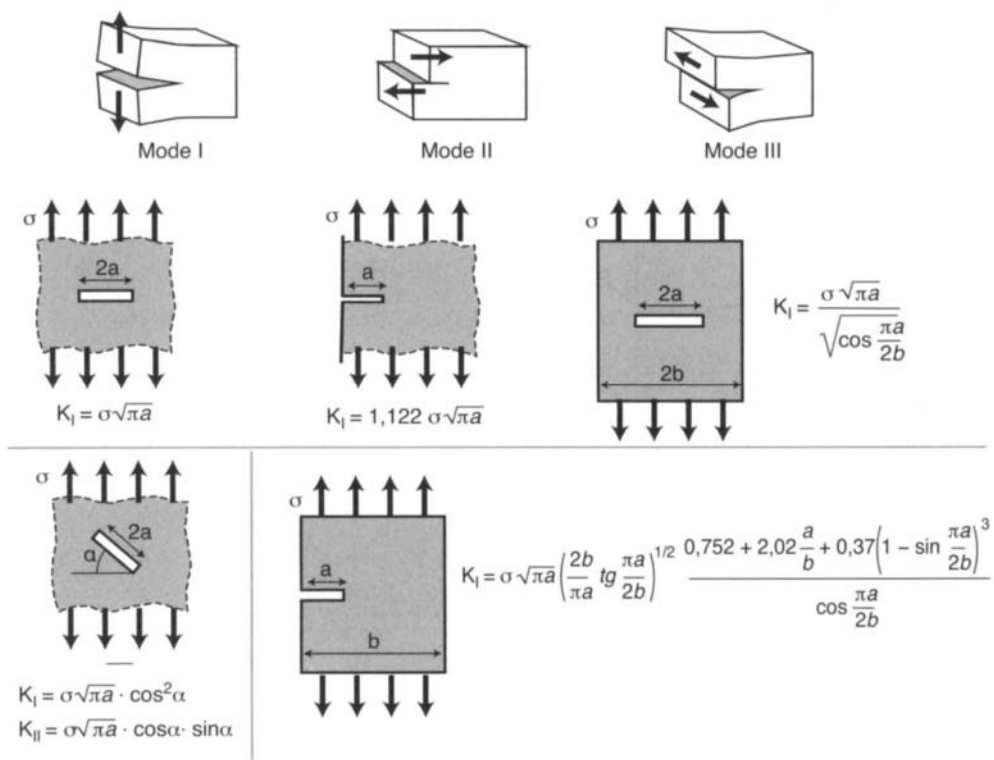


Figure 3.35

Fracture mechanics:

- at the top: fracture modes,
- examples of stress intensity factors K as a function of load, specimen and notch.

Toughness K_{Ic} is usually expressed in $\text{MPa} \cdot \text{m}^{1/2}$. Typical values range between 20 and 200 for steels, 10 and 50 for aluminium alloys and much less for concrete and plastics (between 1 and 10).

It is important to note that environmental conditions may significantly affect toughness. Stress corrosion and hydrogen embrittlement, for example, will lower the toughness of steels sensitive to these types of corrosion.

Figure 3.36 shows two types of very widely used specimen (standard ASTM E399 and in France NF A03-180) with their stress intensity factors K : the CT (compact tension) specimen and a 3PB (three-point bending) specimen (the same geometry can be used in Charpy impact tests). To ensure that the tests are valid, the standard describes the conditions to be respected (in particular the specimen dimensions – especially the thickness B – with respect to the properties of the material and creation of a fine notch for example with fatigue pre-cracking) and describes the analysis methods implemented to determine a critical load P_c (start of crack propagation) which is used to calculate the toughness K_{Ic} .

The principles and methods of fracture mechanics may also be applied to fatigue tests to monitor crack growth (Paris, Forman laws, etc.).

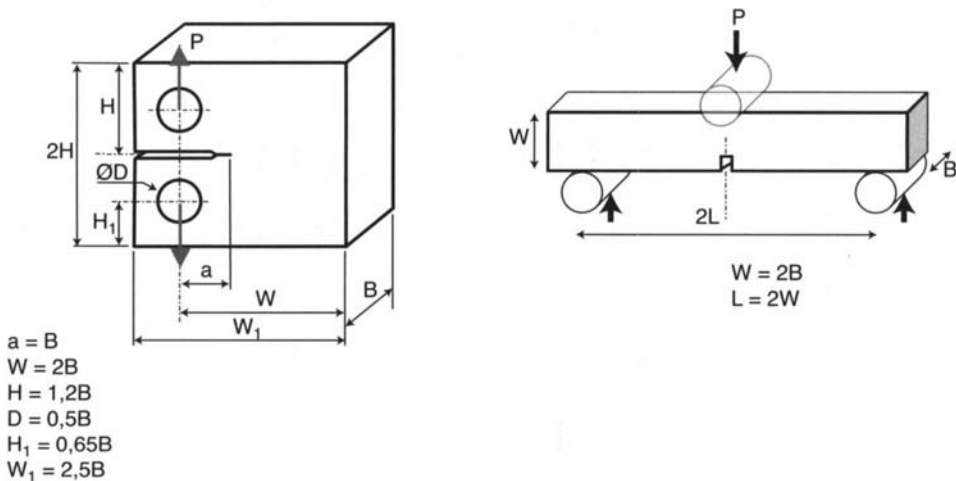


Figure 3.36

Toughness specimens (ASTM E399):

– on the left: CT (compact tension) specimen

$$K_I = \frac{P}{B\sqrt{W}} \left[29.6 \left(\frac{a}{w} \right)^{1/2} - 185.5 \left(\frac{a}{w} \right)^{3/2} + 655.7 \left(\frac{a}{w} \right)^{5/2} - 1017 \left(\frac{a}{w} \right)^{7/2} + 638.9 \left(\frac{a}{w} \right)^{9/2} \right],$$

– on the right: 3PB (3-point bending) specimen

$$K_I = \frac{P}{B\sqrt{W}} \left[11.58 \left(\frac{a}{w} \right)^{1/2} - 18.42 \left(\frac{a}{w} \right)^{3/2} + 87.18 \left(\frac{a}{w} \right)^{5/2} - 150.7 \left(\frac{a}{w} \right)^{7/2} + 154.8 \left(\frac{a}{w} \right)^{9/2} \right].$$

b. Elastoplasticity fracture mechanics

When *linear elasticity fracture mechanics* conditions are no longer met and the material is ductile, *elastoplasticity fracture mechanics* techniques can be applied to propose methods to monitor stable propagation of a crack, then its instability. This characterisation is not intrinsic to the material but valid for a given thickness. We will simply mention the methods here: *R-curve method*, *Dugdale-Barrenblatt model*, *J-integral* and *crack extension force J_{Ic}* (standard ASTM E813).

c. Local approach of fracture mechanics

To conclude our summary of approaches to predict fractures, we will now mention the *local approach*: a criterion is defined locally according to fracture mechanisms (cleavage, cups, etc.) and compared with the stress and strain states in the material, especially near flaws.

Experimentally, notched cylindrical (axisymmetrical) specimens are used (see Figure 3.37) with several notch radii and a very carefully prepared surface to limit failure initiation from surface flaws. In case of cleavage fracture, for example, a large number of tests is required. The results are analysed using a Weibull law (generally applied to study statistical dispersions of brittle fractures) in conjunction with finite element calculations to determine the stress states at time of fracture.

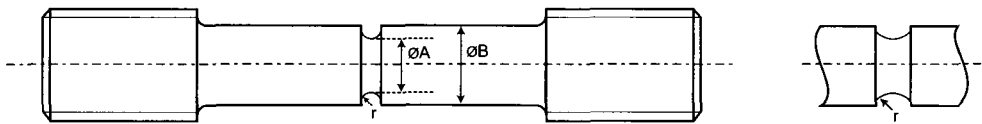


Figure 3.37

Notched axisymmetrical specimen (large notch radius on the right).

3.1.3 Alloys used in the petroleum industry

This paragraph provides information on the main steels and metallic alloys used for equipment in the petroleum industry. Firstly, note that the international standards most frequently used in the petroleum sector to designate alloys are the:

- designation of the American Society of Testing and Materials (ASTM) and the American Society of Mechanical Engineers (ASME) which are close,
- designation of the American Iron and Steel Institute (AISI) and the Society of Automotive Engineers (SAE) which are very similar,
- designation of the Unified Numbering System (UNS),
- designation of the Alloy Casting Institute (ACI),
- designation of the Copper Development Association (CDA),
- designation of the Aluminium Association (AA).

Readers will find further information about these standards in Appendix 1 of this document.

Material specifications are also provided according to their applications by:

- The American Petroleum Institute (API) such as, for example, for oil and gas production, API 5CT (steels for casings, tubings and liners), API 5D (steels for seamless drill pipes), API 5L (steels for pipelines);
- European Standards such as, for example, specification EN10028 (steels for pressure vessels), EN10027 (steels for simple pressure vessels), EN100275 (structural steels).

Obviously, this list is not exhaustive, since metallic materials find numerous applications in the petroleum industry.

3.1.3.1 Ferrous metals (iron content > 50%)

A. Steels

a. Carbon steels

These steels are composed mainly of iron and carbon (maximum 1.5% in theory with less than 0.4% for most carbon steels). Generally, increasing the carbon content of a steel increases the mechanical strength (which is the intended purpose), but decreases the ductility, increases the Ductile-Brittle Transition Temperature (DBTT) and decreases the weldability. Tables 3.3 and 3.4 give the compositions and mechanical properties of a few carbon steels.

Table 3.3 Composition and mechanical properties of a few carbon steels.

ASTM	UNS	Composition (%) ^a	Yield Strength (MPa) ^b	Tensile Strength (MPa) ^b	Elongation (%)
A285A	K01700	0.17 C, 0.90 Mn	165	310-380	30
A53B	K03005	0.30 C, 1.20 Mn	241	415	
A106B	K03006	0.30 C, 0.29-1.06 Mn, 0.10 min Si	241	415	30

^a Single values are maxima, unless indicated otherwise.

^b Values at ambient temperature, the single values are maxima.

b. Killed carbon steels

A distinction is made between rimming steels and killed carbon steels: when they are cast, rimming steels contain excess oxygen which continues to react with carbon, releasing a large volume of carbon monoxide (CO) forming bubbles during solidification shrinkage (blowholes). During rolling, these cavities close and the steel recovers its compactness. In killed steels, the excess oxygen is removed and the resulting structure offers greater resistance to hydrogen embrittlement.

Table 3.4 Composition and mechanical properties of a few API 5L carbon steels (steels for pipelines).

API5L	Composition (%) ^a	Yield Strength (MPa) ^b	Tensile Strength (MPa) ^b
A25 Cl I	0.21 C, 0.30-0.60 Mn, 0.030 P, 0.030 S	172	310
A25 Cl II	0.21 C, 0.30-0.60 Mn, 0.045-0.080 P, 0.030 S	172	310
A	0.22 C, 0.90 Mn, 0.03 P, 0.030 S	207	331
B	0.27 C, 1.15 Mn, 0.03 P, 0.030 S	241	413
X42	0.29 C, 1.25 Mn, 0.03 P, 0.030 S	289	413
X46	0.31 C, 1.35 Mn, 0.03 P, 0.030 S	317	434
X52	0.31 C, 1.35 Mn, 0.03 P, 0.030 S	358	455
X56	0.29 C, 1.25 Mn, 0.03 P, 0.030 S	386	489
X60	0.26 C, 1.35 Mn, 0.03 P, 0.030 S	413	517
X70	0.31 C, 1.35 Mn, 0.03 P, 0.030 S	482	565
X80	0.31 C, 1.35 Mn, 0.03 P, 0.030 S	551	620

^a Single values are maxima, unless indicated otherwise.

^b Values at ambient temperature, the single values are maxima.

c. Low alloy steels

Low alloy steels contain less than 10% of addition elements. Chromium, molybdenum and/or nickel are the main alloy elements of low alloy steels used in the petroleum industry. Table 3.5 provides two examples of compositions and mechanical characteristics illustrating this steel class.

Table 3.5 Composition and mechanical properties of a few low alloy steels.

AISI	UNS	Composition (%) ^a	Yield Strength (MPa) ^b	Tensile Strength (MPa) ^b	Elongation (%)
4130	G41300	0.28-0.33 C, 0.80-1.10 Mn, 0.15-0.30 Si, 0.80-1.10 Cr, 0.15-0.25 Mo	830 ^c	965 ^c	22 ^c
4340	G43400	0.38-0.43 C, 0.60-0.80 Mn, 0.15-0.30 Si, 0.70-0.90 Cr, 0.20-0.30 Mo, 1.65-2.00 Ni	860 ^d	1020 ^d	20 ^d

^a Single values are maxima, unless indicated otherwise.

^b Values at ambient temperature, the single values are maxima.

^c 1 inch diameter bars quenched in water from 860 °C and tempered at 650 °C.

^d 1 inch diameter bars quenched in water from 845 °C and tempered at 650 °C.

• *High Strength Low Alloy steels (HSLA)*

High strength low alloys steels typically contain 0.07% to 0.12% carbon, up to 2% manganese and small additions of niobium, vanadium and titanium (generally less than 0.1%). HSLA steel is preferably manufactured by hot rolling, which increases the mechanical properties by refining the grain size. Addition of 0.1% to 0.2% molybdenum leads to the formation of a fine grain structure of acicular ferrite increasing the hardening effects by precipitation of other addition elements. Some HSLA steels are also called “microalloys”, due to their low content in addition elements compared with the main commercially available alloy steels. Quantities as low as 0.10% of niobium and vanadium may significantly modify the mechanical characteristics of 0.1% C-1.3% C steels. The addition elements are added to modify the microstructure of carbon steels (generally composed of ferrite pearlitic clusters) by forming an almost pure ferrite with a very fine dispersion of metallic carbides. This eliminates the effects of pearlite volume fractions on reduction of hardness, increasing the steel's mechanical strength by precipitation hardening and refining the grain size. Table 3.6 gives the compositions and mechanical properties of a few HSLA steels.

Table 3.6 Compositions and mechanical properties of a few HSLA steels.

ASTM	UNS	Composition (%) ^a	Yield Strength (MPa) ^b	Tensile Strength (MPa) ^b	Elongation (%)
A242 class 1	K11510	0.15 C, 1.00 Mn, 0.2 min Cu, 0.15 P	290-345	435-485	21
A517F	K11576	0.08-0.22 C, 0.55-1.05 Mn, 0.13-0.37 Si, 0.36-0.79 Cr, 0.67-1.03 Ni, 0.36-0.64 Mo, 0.002-0.006 Nb, 0.12-0.53 Cu, 0.02-0.09 V	689	795-930	16

^a Single values are maxima, unless indicated otherwise.

^b Values at ambient temperature, the single values are maxima.

• *Chromium steels up to 9% Cr*

These steels are used mainly for the construction of hydrogen pressure vessels to withstand high temperature hydrogen attack. Chromium carbides are in fact insensitive to high temperature hydrogen attack (see paragraph 1.14). Presence of molybdenum and vanadium in solid solution improves the high temperature creep resistance. 9 Cr-1 Mo steel, in particular, exhibits excellent behaviour with respect to high temperature oxidation (up to about 750 °C).

Table 3.7 gives the compositions and mechanical properties of a few chromium low alloy steels.

Table 3.7 Compositions and mechanical properties of a few low alloy steels.

Steel	ASTM	UNS	Composition (%) ^a	Yield Strength (MPa) ^b	Tensile Strength (MPa) ^b	Elongation (%)
2.25 Cr-1 Mo	A387 (22) class 1	K21590	0.15 C, 0.30-0.60 Mn, 2.00-2.50 Cr, 0.90-1.1 Mo	205	415-585	18
2.25 Cr-1 Mo	A387 (22) class 2	K21590	0.15 C, 0.30-0.60 Mn, 2.00-2.50 Cr, 0.90-1.1 Mo	310	515-690	18
4-6 Cr-0.5 Mo	A335 (P5)	K41545	0.15 C, 0.30-0.60 Mn, 4.00-6.00 Cr, 0.45-0.65 Mo	205	415	
9 Cr-1 Mo	A335 (P9)	K81590	0.15 C, 0.30-0.60 Mn, 8.00-10.00 Cr, 0.90-1.10 Mo, 0.25-1.00 Si	205	415	

^a Single values are maxima, unless indicated otherwise.

^b Values at ambient temperature, the single values are maxima.

• Nickel steels (from 2.5% Ni)

Addition of nickel increases the mechanical strength and in particular improves low-temperature resilience (use for devices operating at low temperatures). They are widely used in LNG units. 3.5% Ni steel can be used down to temperature of – 100 °C and 9% Ni steel down to about – 195 °C. Table 3.8 gives the composition and mechanical tensile characteristics of 9% nickel low alloy steel.

Table 3.8 Compositions and mechanical properties of a few nickel steels.

ASTM	UNS	Composition (%) ^a	Yield Strength (MPa) ^b	Tensile Strength (MPa) ^b	Elongation (%)
A351 (1)	K81340	0.13 C, 0.90 Mn, 0.15-0.30 Si, 8.40-9.60 Ni	515	690-825	20

^a Single values are maxima, unless indicated otherwise.

^b Values at ambient temperature, the single values are maxima.

d. Stainless steels

Stainless steels contain sufficient quantities of alloy elements to generate a thin layer of oxide on the surface which separates the metal and the electrolyte:

- Chromium is the main element which favours the formation of a passive film on the surface. At a content of above 11%, the steel becomes stainless. This corrosion resistance progressively improves with the chromium content;
- Molybdenum increases the action of chromium. Its content varies between 1% and 3%. The average content of 2% significantly improves the resistance to localised corrosion;
- Nickel improves the resistance to acid corrosion, especially crevice corrosion;

- Nitrogen increases the passive layer and also improves the resistance to localised corrosion. For certain grades, its content may reach 0.3%.

Stainless steels are classified according to their microstructure.

• Martensitic stainless steels

These steels have a chromium content between 11% and 17% and contain little or no nickel (Table 3.9). They can be hardened by heat treatment and exhibit high hardness but low ductility and low resilience.

Table 3.9 Compositions and mechanical properties of a few martensitic stainless steels.

AISI	UNS	Composition (%) ^a	Yield Strength (MPa) ^b	Tensile Strength (MPa) ^b	Elongation (%)
403	S40300	0.15 C, 11.5-13.0 Cr	276	515	35
410	S41000	0.15 C, 11.5-13.5 Cr	241	483	30
420	S42000	0.15 C, 12-14 Cr	345	655	20
431	S43100	0.20 C, 15-17 Cr, 1.25-2.5 Ni	655	862	20
440A	S44002	0.6-0.75 C, 16-18 Cr, 0.75 Mo	414	724	20

^a Single values are maxima, unless indicated otherwise.

^b Typical values at ambient temperatures for annealed steel sheets.

• Ferritic stainless steels

These steels have a chromium content between 11% and 28% and contain no nickel. Unlike martensitic steels, they cannot be hardened by heat treatment since no phase transformation occurs at high temperature (Table 3.10).

Table 3.10 Compositions and mechanical properties of a few ferritic stainless steels.

AISI	UNS	Composition (%) ^a	Yield Strength (MPa) ^b	Tensile Strength (MPa) ^b	Elongation (%)
405	S40500	0.08 C, 11.5-14.5 Cr, 1.0 Mn, 1.0 Si, 0.04 P, 0.03 S, 0.1-0.3 Al	276	448	30
409	S40900	0.08 C, 11.5-11.75 Cr, 1.0 Mn, 1.0 Si, 0.045 P, 0.045 S, (6 × C)Ti	241	448	25
429	S42900	0.12 C, 14-16 Cr, 1.0 Mn, 1.0 Si, 0.04 P, 0.03 S	276	483	30
430	S43000	0.12 C, 16-18 Cr, 1.0 Mn, 1.0 Si, 0.04 P, 0.03 S	276	517	30
442	S44200	0.20 C, 18-23 Cr, 1.0 Mn, 1.0 Si, 0.04 P, 0.03 S	310	552	20
446	S44600	0.20 C, 23-27 Cr, 1.5 Mn, 1.0 Si, 0.04 P, 0.03 S, 0.25 N	379	586	25

^a Single values are maxima, unless indicated otherwise.

^b Typical values at ambient temperatures for annealed steel sheets.

• *Austenitic stainless steels*

These steels have a chromium content of between 17% and 19% and contain 8% to 14% nickel giving them an austenitic structure. High carbon grades ($0.05\% < C < 0.1\%$) are used for their high temperature mechanical strength. Series S3XXXX steels (see Table 3.11) can be hardened by cold working. This is the most widely used series of stainless steels.

Table 3.11 Compositions and mechanical properties of a few austenitic stainless steels.

AISI	UNS	Composition (%) ^a	Yield Strength (MPa) ^b	Tensile Strength (MPa) ^b	Elongation (%)
304	S30400	0.08 C, 18-20 Cr, 8-10.5 Ni, 2.0 Mn, 1.0 Si, 0.045 P, 0.030 S	241	586	50
316	S31600	0.08 C, 16-18 Cr, 10-14 Ni, 2.0-3.0 Mo, 2.0 Mn, 1.0 Si, 0.045 P, 0.030 S	248	565	55
316L	S31603	0.03 C, 16-18 Cr, 10-14 Ni, 2.0-3.0 Mo, 2.0 Mn, 1.0 Si, 0.045 P, 0.030 S	234	558	55
317	S31700	0.08 C, 16-18 Cr, 10-14 Ni, 3.0-4.0 Mo, 2.0 Mn, 1.0 Si, 0.045 P, 0.030 S	276	586	50
317L	S31703	0.03 C, 16-18 Cr, 10-14 Ni, 3.0-4.0 Mo, 2.0 Mn, 1.0 Si, 0.045 P, 0.030 S	241	586	55
321	S32100	0.08 C, 17-19 Cr, 9-12 Ni, 2.0 Mn, 1.0 Si, 0.045 P, 0.030 S, (5 × C)Ti	207	586	55
347	S34700	0.08 C, 17-19 Cr, 9-13 Ni, 2.0 Mn, 1.0 Si, 0.045 P, 0.030 S, (10 × C) 5(Nb + Ta)	241	621	50
329	S32900	0.10 C, 25-30 Cr, 3-6 Ni, 1.0-2.0 Mo, 2.0 Mn, 1.0 Si, 0.045 P, 0.030 S	552	724	25

^a Single values are maxima, unless indicated otherwise.

^b Typical values at ambient temperatures for annealed steel sheets.

• *Austeno-ferritic (or duplex) stainless steels*

These steels have a chromium content between 21% and 28% and contain only 4% to 9% nickel (Table 3.12). Presence of molybdenum and nitrogen increases their resistance to localised corrosion. Their structure is composed of 2 phases in equivalent quantities: austenite and ferrite.

Table 3.12 Compositions and mechanical properties of a few austeno-ferritic stainless steels.

UNS	Composition (%) ^a	Yield Strength (MPa) ^b	Tensile Strength (MPa) ^b	Elongation (%)
S32304	0.03 C, 21.5-24.5 Cr, 3.9-5.5 Ni, 0.05-0.60 Mo, 1.0 Mn, 1.0 Si, 0.04 P, 0.03 S, 0.05-0.6 Cu, 0.05-0.20 N	> 400	670	> 30
S38103	0.03 C, 21-23 Cr, 4.5-6.5 Ni, 2.5-3.5 Mo, 1.0 Mn, 1.0 Si, 0.04 P, 0.03 S, 0.08-0.20 N	> 450	800	> 25
S31200	0.03 C, 24-26 Cr, 5.5-6.5 Ni, 1.2-2.0 Mo, 1.0 Mn, 1.0 Si, 0.04 P, 0.03 S, 0.14-0.20 N	> 450	800	> 25
S32550	0.03 C, 24-27 Cr, 4.5-6.5 Ni, 2.0-4.0 Mo, 1.0 Mn, 1.0 Si, 0.04 P, 0.03 S, 1.5-2.5 Cu, 0.10-0.25 N	> 550	800	> 15
S32750	0.03 C, 24-26 Cr, 6.0-8.0 Ni, 3.0-5.0 Mo, 1.0 Mn, 1.0 Si, 0.04 P, 0.03 S, 0.24-0.32 N	> 550	800	> 15

^a Single values are maxima, unless indicated otherwise.^b Typical values at ambient temperatures for annealed steel sheets.**e. Heat-resistant steels**

These steels are designed to offer good mechanical characteristics at high temperatures and good creep resistance. They are used above 600 °C and up to about 1 000 °C. They are rich in nickel, chromium and addition elements Mo, Ti, Nb, Al, Si (Table 3.13):

Table 3.13 Compositions and mechanical properties of a few heat-resistant stainless steels.

ACI	ASI	UNS	Composition (%) ^a	Tensile Strength (MPa) ^b	Elongation (%)
HC	446	J92695	0.5 C, 26-30 Cr, 4 Ni, 1.0 Mn, 2.0 Si	160	20
HD	327	J93005	0.5 C, 26-30 Cr, 4-7 Ni, 1.5 Mn, 2.0 Si	160	18
HH	309	J93503	0.2-0.5 C, 24-28 Cr, 11-14 Ni, 2.0 Mn, 2.0 Si, 0.2 N	128	30
HK	310	J94224	0.2-0.6 C, 24-28 Cr, 18-22 Ni, 2.0 Mn, 2.0 Si	160	16
HN		J94213	0.2-0.5 C, 19-23 Cr, 23-27 Ni, 2.0 Mn, 2.5 Si	138	37
HP		J95705	0.35-0.75 C, 24-28 Cr, 18-22 Ni, 2.0 Mn, 2.5 Si	180	27
HT	330	J94605	0.35-0.75 C, 13-17 Cr, 33-37 Ni, 2.0 Mn, 2.5 Si	130	26
HU		J95405	0.35-0.75 C, 17-21 Cr, 37-41 Ni, 2.0 Mn, 2.5 Si	140	20

^a Single values are maxima, unless indicated otherwise.^b Typical mechanical properties at 875 °C.

Some types of equipment are manufactured by moulding or centrifuging (especially oven tubes, manifolds, quenching exchangers).

Annexes

ANNEXE 1

International standards on designation of metal materials

This appendix provides information on the international standards most often used in the petroleum industry on the designation of alloys:

A1.1 DESIGNATION OF THE AMERICAN SOCIETY OF TESTING AND MATERIALS (ASTM) AND THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS (ASME) WHICH ARE VERY SIMILAR

The first part of the designation is a letter:

- A for ferrous metals,
- B for non ferrous metals,
- C for ceramics and concretes,
- D for other materials.

A letter S in front of this letter indicates the conformity with the ASME code.

The second numerical part characterises the family to which the material belongs but also the manufacturing mode related to its use. The same material may therefore be designated under different numbers, each being specific to the manufacturing and/or use conditions.

The grade or type of material (that of the AISI nomenclature) is also indicated.

A1.2 DESIGNATIONS OF THE AMERICAN IRON AND STEEL INSTITUTE (AISI) AND THE SOCIETY OF AUTOMOTIVE ENGINEERS (SAE) WHICH ARE VERY SIMILAR

A1.2.1 Carbon and low alloy steels

Carbon steels and low alloy steels are designated by a four digit number, where the first two digits indicate the alloying elements and the last two digits indicate the amount of carbon, in hundredths of a percent by weight:

Carbon steels	
10xx	Plain carbon (Mn 1.00% max)
11xx	Resulfurized
12xx	Resulfurized and rephosphorized
15xx	Plain carbon (Mn 1.00% to 1.65%)
Manganese steels	
13xx	Mn 1.75%
Nickel steels	
23xx	Ni 3.50%
25xx	Ni 5.00%
Nickel-chromium steels	
31xx	Ni 1.25%, Cr 0.65% or 0.80%
32xx	Ni 1.25%, Cr 1.07%
33xx	Ni 3.50%, Cr 1.50% or 1.57%
34xx	Ni 3.00%, Cr 0.77%
Molybdenum steels	
40xx	Mo 0.20% or 0.25%
44xx	Mo 0.40% or 0.52%
Chromium-molybdenum (Chromoly) steels	
41xx	Cr 0.50% or 0.80% or 0.95%, Mo 0.12% or 0.20% or 0.25% or 0.30%
Nickel-chromium-molybdenum steels	
43xx	Ni 1.82%, Cr 0.50% or 0.80%, Mo 0.25%
43BVxx	Ni 1.82%, Cr 0.50%, Mo 0.12% or 0.35%, V 0.03% min
47xx	Ni 1.05%, Cr 0.45%, Mo 0.20% or 0.35%
81xx	Ni 0.30%, Cr 0.40%, Mo 0.12%
86xx	Ni 0.55%, Cr 0.50%, Mo 0.20%
87xx	Ni 0.55%, Cr 0.50%, Mo 0.25%
88xx	Ni 0.55%, Cr 0.50%, Mo 0.35%

93xx	Ni 3.25%, Cr 1.20%, Mo 0.12%
94xx	Ni 0.45%, Cr 0.40%, Mo 0.12%
97xx	Ni 0.55%, Cr 0.20%, Mo 0.20%
98xx	Ni 1.00%, Cr 0.80%, Mo 0.25%
Nickel-molybdenum steels	
46xx	Ni 0.85% or 1.82%, Mo 0.20% or 0.25%
48xx	Ni 3.50%, Mo 0.25%
Chromium steels	
50xx	Cr 0.27% or 0.40% or 0.50% or 0.65%
51xx	Cr 0.80% or 0.87% or 0.92% or 1.00% or 1.05%
50xxx	Cr 0.50%, C 1.00% min
51xxx	Cr 1.02%, C 1.00% min
52xxx	Cr 1.45%, C 1.00% min
Chromium-vanadium steels	
61xx	Cr 0.60% or 0.80% or 0.95%, V 0.10% or 0.15% min
Tungsten-chromium steels	
72xx	W 1.75%, Cr 0.75%
Silicon-manganese steels	
92xx	Si 1.40% or 2.00%, Mn 0.65% or 0.82% or 0.85%, Cr 0.00% or 0.65%
High-strength low-alloy steels	
9xx	Various SAE grades
xxBxx	Boron steels
xxLxx	Leaded steels

A1.2.2 Stainless steels

- 200 Series: austenitic chromium-nickel-manganese alloys,
- 300 Series: austenitic chromium-nickel alloys,
- 400 Series: ferritic and martensitic chromium alloys,
- 500 Series: heat resisting chromium alloys,
- 600 Series: martensitic precipitation hardening alloys.

A1.3 DESIGNATION OF THE UNIFIED NUMBERING SYSTEM (UNS)

The *Unified Numbering System* (UNS) is a widely accepted alloy designation system. It consists of a prefix letter and five digits designating a material composition. A prefix of S indicates stainless steel alloys, C for copper, brass, or bronze alloys, T for tool steels, etc.

UNS series	Metal type(s)
A00001 to A99999	Aluminum and aluminum alloys
C00001 to C99999	Copper and copper alloys
D00001 to D99999	Specified mechanical property steels
E00001 to E99999	Rare earth and rare earth-like metals and alloys
F00001 to F99999	Cast irons
G00001 to G99999	AISI and SAE carbon and alloy steels (except tool steels)
H00001 to H99999	AISI and SAE H-steels
J00001 to J99999	Cast steels (except tool steels)
K00001 to K99999	Miscellaneous steels and ferrous alloys
L00001 to L99999	Low-melting metals and alloys
M00001 to M99999	Miscellaneous nonferrous metals and alloys
N00001 to N99999	Nickel and nickel alloys
P00001 to P99999	Precious metals and alloys
R00001 to R99999	Reactive and refractory metals and alloys
S00001 to S99999	Heat and corrosion resistant (stainless) steels
T00001 to T99999	Tool steels, wrought and cast
W00001 to W99999	Welding filler metals
Z00001 to Z99999	Zinc and zinc alloys

Introduction

Controlling the corrosion of equipment used in industrial processes and especially in the petroleum industry is a major importance in guaranteeing their continued development under optimum conditions in terms of reliability and safety. To meet society's demand for fuel, the petroleum industry must control all hydrocarbon production, transportation, refining, and storage processes. The reliability of the equipment used during these steps is highly critical. The choice of materials, generally metallic, is based on knowledge acquired by specialists over the past decades and on studies dedicated to satisfying the new objectives of the petroleum industry and the new petroleum environments. For example, the development of oil fields storing oil and gas at increasingly high temperatures, with high contents in acid gases such as CO_2 and H_2S , requires an excellent knowledge of the corrosion resistance of equipment used for drilling, production and transportation of petroleum effluents. Similarly, the traditional refining industry must adapt in order to process crude oils that are becoming increasingly corrosive due to the presence of naphthenic acids and high concentrations of sulfur containing products in order to convert them into low-sulfur fuels and thereby limit their impact on the environment during combustion. Manufacture of synthetic fuels from natural gas, coal or biomass via synthesis gas, for example, requires in-depth knowledge of the corrosion resistance of the metallic materials used to make the equipment of these new processes. The refineries must also limit their energy requirements and reduce their external water demand for the heat exchanger circuits, which means that the flows must be recycled. As a result, the water composition will contain more corrosive elements and the water circuits will be more sensitive to corrosion.

The aim of the petroleum industry is to produce large quantities of fuels under economically viable conditions. By analysing the experience acquired on equipment behaviour and by creating monitoring and inspection programs, the corrosion costs can be included with the operating costs. However, any unplanned operating shutdown caused by corrosion generates high additional costs, whether direct (repair or replacement of damaged equipment) or indirect (immobilisation of the production tool).

The total cost worldwide of all types of corrosion and its prevention is estimated at between 2% and 4% of the GNP. The petroleum production and refining industries represent respectively 1% and 2.7% of this total cost [4]. For the United States, this corresponds to a direct cost of 1.4 billion dollars per year for the upstream petroleum sector and 3.7 billion dollars per year for the downstream sector [4]. The total cost (direct and indirect impacts) of corrosion and its prevention can be estimated at about 10 billion dollars per year for the American petroleum industry and at about 35 billion dollars per year for the worldwide petroleum industry.

For the petroleum production industry, 43% of the corrosion cost concerns surface pipelines and development costs, 34% casings and 23% the investments related to corrosion. For surface petroleum production, the cost of corrosion is estimated at 0.2 dollars per barrel of oil produced and at 0.09 dollars per barrel of water produced [2]: as shown on Figure 0.1, a large proportion concerns the cost of anticorrosion chemical treatments, then inspection, monitoring and repair costs.

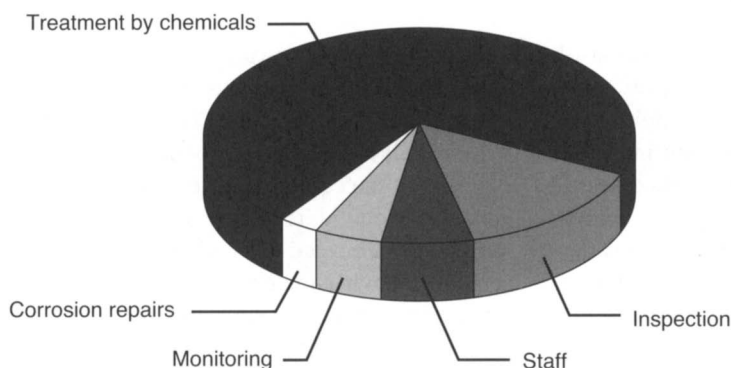
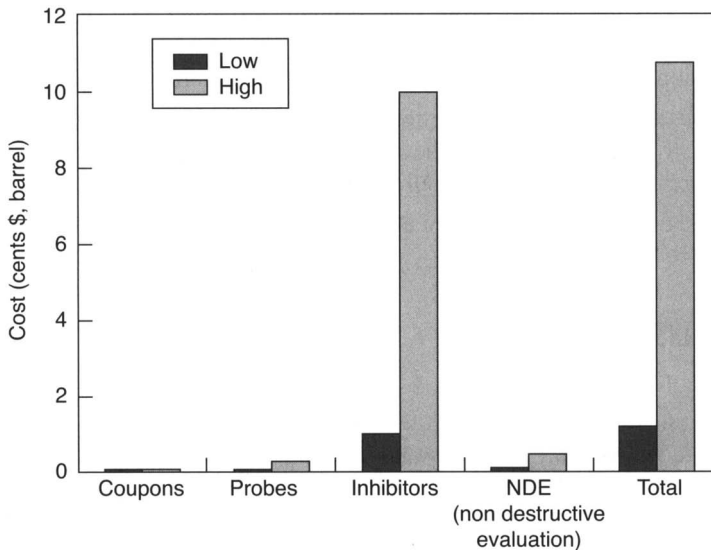


Figure 0.1

Distribution of corrosion costs (source: corrosioncost.com).

In the refining industry, 46% of the cost concerns maintenance, 38% the reactors and equipment and 16% the cost due to clogging. The cost of corrosion control is estimated at 0.31 dollars per barrel for the complete chain of refining processes. As shown on Figure 0.2, for a distillation unit, the cost of corrosion control, between 0.015 and 0.11 dollars per barrel, includes the corrosion coupons, sensors, inhibitors and non destructive testing.

The above figures have been taken from financial reports based on equipment and processes operating under standard conditions. They do not include any unscheduled events. The few major accidents in the petroleum industry caused by corrosion sadly illustrate these exceptional costs and their impact on the environment and the human safety. In 1984, an absorption column of a plant for treatment of acid gas by MEA-based chemical solvents split and was blown more than a kilometre away. The accident left 17 dead and 17 more injured, and caused more than \$100 million worth of damage. Investigators found that the accident was due to stress corrosion of hard brittle steel where repair welds had been made

**Figure 0.2**

Distribution of corrosion control costs for a distillation unit
(source: corrosioncost.com).

ten years earlier [5]. In 2006, leaks caused by bacterial corrosion stopped oil production from Alaska for several days, creating tension on the oil market [1; 3].

These examples show that corrosion control is a key issue for the technical and financial performance of the petroleum industry. The various actors in the industry as well as anyone else interested should therefore be able to obtain basic information on the impacts of environments specific to the petroleum industry, the corrosion resistance of metallic equipment and the main methods of preventing corrosion.

This book therefore aims to provide basic information to non-specialists in corrosion and/or in the petroleum industry to understand the main phenomena involved in the corrosion and degradation of metallic materials in this industry. The information contained in this document may also be useful for processes in other industries such as chemistry or water treatment.

The book is composed of 3 main sections which may be consulted independently, depending on the reader's requirements and knowledge.

Section 1 describes depending on the chemical environment (and therefore the equipment and/or process) the main phenomena encountered in the petroleum industry and the solutions implemented to prevent them. Mechanisms leading to corrosion in these specific environments are described. If necessary, the reader may refer to the specific chapters in Section 3 provided for reference, to obtain details concerning the corresponding basic corrosion mechanisms. Similarly, for the prevention methods, cross-references are given to chapters in Section 2 describing the techniques.

Section 2 tackles the various protection techniques (design, choice of metallic alloys, application of coatings, use of corrosion inhibitors or bactericide additives, cathodic protection) and corrosion monitoring techniques used in the petroleum industry.

Section 3 presents the basic information on the main steels and alloys used in the petroleum industry (structure, properties), the main corrosion modes and other damage modes (high temperature ageing) affecting metallic materials.

An index and a glossary are provided at the end of the book to guide the reader.

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INDEX

Index Terms

Links

A

Acid

– carbonic	3	
– hydrochloric	23	26
– hydrofluoric	30	
– naphthenic	52	
– polythionic	55	
– sulfuric	27	

Acid gas treatment 41

Acoustic emission 114 130

Activation energy 204

Activity (chemical) 200

Additive (see inhibitor)

Alcohol

– ethanol	40	
– methanol	39	198

Alkaline

– carbonate	36	
– caustic	34	
– near-neutral	38	

Alkylation 28 32 68

Alloy

– aluminium base	197	
– cobalt base	197	
– copper base	195	
– nickel base	196	
– titanium base	198	

<u>Index Terms</u>	<u>Links</u>			
Amine units	41			
Ammoniac	25	29		36
	103	195		
Austenite	154			
B				
Bacteria				
– acidinogenic	237			
– oxidising	236			
– sulfate-reducing (SRB)	16			
– sulfidogenic	235			
Bactericide	17			
Bending	171			
Biofilm	234			
Borescope	126			
Brass	195			
Bronze	196			
Butler Volmer equation	211			
C				
Carbon (high temperature carbon attack)				
– carburisation	71			
– coking	68	104		
– metal dusting	69	71		104
	218	252		
Carbon dioxide CO ₂				
– corrosion	3			
– treatment	41			
Cast iron	154	195		248
Catalytic reforming	23	59		68
	92	103		251

<u>Index Terms</u>	<u>Links</u>			
Cathodic protection	19	96		
Cement (anticorrosion)	95			
Centrifuging	194			
Chemical analysis of solutions	110			
Chlorides	20	23		
Chlorine	17	198		218
Coatings				
– cladding	94			
– composite liner	92			
– organic and paints	88			
– weld overlay	94			
Coker	36	55		65
	68	103		
Coking (see carbon high temperature attack)				
Concentration cell	226			
Control - non destructive	125			
Corrosion				
– bacterial	16	233		
– cavitation	233			
– chemical	202			
– crevice	20	85		229
– electrochemical	202	225		
– galvanic	86	225		
– high temperature	217			
– intergranular	55	230		
– pitting	20	228		
– stress cracking	8	20		231
– transgranular	20	34		28
	231			
– uniform	224			
Corrosion rate	224			
Cost of corrosion	XV			

<u>Index Terms</u>	<u>Links</u>		
Coupons (corrosion)	106		
Cracking			
– intergranular	57		
– transgranular	20	28	
Creep	175		
Cyanide	36		
D			
Decarburisation (see high temperature hydrogen attack)			
Deformation			
– elastic	162		
– plastic	162		
Depassivation	21	232	
Disbonding	61		
Dislocations	14	148	152
	166	231	
Distillation			
– atmospheric	13	23	52
	103	251	
– vacuum	23	65	251
E			
Eddy current	127		
Elasticity	172		
Elastoplasticity	173		
Electrical charge transfer	211		
Electrical conductivity	108	117	217
Electrolyte	203	252	
Ellingham diagram	201	218	223

<u>Index Terms</u>	<u>Links</u>		
Embrittlement			
– at 475°C of stainless steels	255		
– creep	239		
– hydrogen	8		
– temper	238		
Energy level	203		
Epoxy	89		
Equilibrium diagram (alloys)	152		
Erosion corrosion	86	233	
Exchanger	7	13	23
	30	43	46
	52	74	85
	196	198	
F			
Faraday law	203		
Fatigue			
Fatigue corrosion	232		
Fatigue mechanical	177		
Ferrite	154		
Fluid catalytic craking (FCC)	34	55	65
	103		
Free enthalpy	199		
Furnace	28	52	55
	62	68	72
G			
Galvanic serie	226		

<u>Index Terms</u>	<u>Links</u>		
H			
Hardness	180		
– Brinell	180		
– Rockwell	181		
– Vickers	181		
Harmonic analysis	119		
Heat affected zone (HAZ)	159		
Helmotz double layer	203		
HIC	10	30	43
	252		
Hydrocracking	58	103	
Hydrodynamic	4	8	21
	29	32	54
	85		
Hydrogen attack at high temperature (HTHA)			
– decarburisation	88		
– hydritation	61		
Hydrogen sulfide (H ₂ S)			
– corrosion	8		
– embrittlment	8		
– treatment	41		
Hydrolysis of chlorides	23		
Hydrotreatment	23	26	55
	58	85	94
	240	252	
I			
Impact strength	182		
Impedance - electrochemical	120		
Inhibitor	98		
Intermetallic sigma phase	241		

<u>Index Terms</u>	<u>Links</u>		
Iron carbon diagram	154		
L			
Liquid metal			
– cadmium	15		
– lead	15		
– mercury	13		
– zinc	15		
Liquid penetrant inspection	126		
M			
Magnetoscopy	127		
Martensite	156	252	
Mass transfer	216		
Mechanical damage	167		
Mechanical stress	170		
Mechanical tests tensile	174		
Merox treatment	34	252	
Metal dusting	69	71	104
	218	252	
MFL (Magnetic flux leakage)	133		
Microstructure of metallic alloys	148		
Molten salts	73		
N			
Necking	163		
Nernst equation	205		

Index Terms

Links

O

Offshore	14	16	89
	96	109	124
	127	134	198
Optical sensor	112		
Overvoltage	213		
Oxidation			
– electrochemical	202		
– high temperature	62	217	

P

Paint	88		
Passivity	209	230	253
Phosphatation	95		
Pigging	131		
Pilling and Bedworth coefficient	220		
Pipeline	3	8	16
	20	38	88
	96	133	
Plasticity	173		
Poisson coefficient	171		
Polarisation - electrochemical polarisation	117	214	
Polarisation resistance	118	216	
Polyamide	89		
Potential			
– chemical	199		
– corrosion	122	214	
– reversible	204		
– standard electrode	205		
Pourbaix diagram	206	224	228

Index Terms

Links

Prediction model

- Couper and Gordman (high temperature sulfidation) 66
- McConomy (high temperature sulfidation) 65
- Nelson (high temperature hydrogen attack) 59

Probe - corrosion

- bacterial 124
- electrical resistance 108
- galvanic 117
- hydrogen 100
- multi array 123

Pump	3	9	50
	195		

R

Radiography	128		
Reduction - electrochemical	202		
Reference electrode	205	212	
Riser	198	253	
Risk based inspection (RBI)	137		

S

Sacrificial anode	96		
Sensitisation	56	230	239
SOHIC	10		
SSC	10		
Steamcracker	68		
Steel	188		
– austenitic stainless steel	193		
– austeno-ferritic (duplex) stainless steel	193		
– carbon steel	188		

Index Terms

Links

Steel (*Cont.*)

– ferritic stainless steel	192		
– heat resistant (refractory) steel	194		
– killed carbon steel	188		
– low alloy steel	189		
– martensitic stainless steel	192		
– nickel steel	191		
Sulfidation (high temperature)	65	218	
Surface treatment	95		

T

Tafel coefficient	213		
Tensile test	161		
Thermal treatment	168		
– annealing	158		
– austenitisation	156		
– normalizing	252		
– post welding	158		
– quench	156		
– stabilisation of stainless steels	57	84	240
– stress relieving	33	35	86
– tempering	158		
Thermography	129		
TOFD (Time of flight diffraction)	129		
Torsion (mechanical)	170		
Toughness	184		

U

Ultrasound	128	132	134
------------	-----	-----	-----

Index Terms

Links

V

Visbreaking	65
Viscoelasticity	173

W

Wagner mechanism	221
------------------	-----

Y

Yield strength	162
----------------	-----