

SUPERSEDED

**GUIDE
FOR
INSPECTION OF REFINERY EQUIPMENT**

**CHAPTER II
CONDITIONS CAUSING DETERIORATION OR FAILURES**

**SECOND EDITION
1973**

STACK



AMERICAN PETROLEUM INSTITUTE

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PREFACE

This chapter is one of a series which make up the manual, *Guide for Inspection of Refinery Equipment*. It is based on the accumulated knowledge and experience of engineers of the petroleum industry. All users are invited to submit suggested revisions to the director of the Division of Refining, American Petroleum Institute, 1801 K Street, N.W., Washington, D. C. 20006

The information contained in this publication has been arranged in its present form as a means of facilitating continuity of presentation and convenience of reference. It does not constitute, and should not be construed to be, a code of rules, regulations, or minimum safe practices. It is not intended that the practices described in this publication supplant practices that have proven satisfactory. Nor is it intended that this publication discourage innovation and originality in the inspection of refineries. Users of the publication are reminded that no book or manual is a substitute for the judgment of a responsible engineer.

The *Guide for Inspection of Refinery Equipment* is subdivided as follows:

Chapter	I	Introduction
Chapter	II	Conditions Causing Deterioration or Failures
Chapter	III	General Preliminary and Preparatory Work
Chapter	IV	Inspection Tools
Chapter	V	Preparation of Equipment for Safe Entry and Work
Chapter	VI	Unfired Pressure Vessels
Chapter	VII	Heat Exchangers, Condensers, and Cooler Boxes
Chapter	VIII	Direct-Fired Boilers and Auxiliary Equipment
Chapter	IX	Fired Heaters and Stacks
Chapter	X	Pumps, Compressors, and Blowers, and Their Drivers
Chapter	XI	Pipe, Valves, and Fittings
Chapter	XII	Foundations, Structures, and Buildings
Chapter	XIII	Atmospheric and Low-Pressure Storage Tanks
Chapter	XIV	Electrical Systems
Chapter	XV	Instruments and Control Equipment
Chapter	XVI	Pressure-Relieving Devices
Chapter	XVII	Auxiliary and Miscellaneous Equipment
Chapter	XVIII	Protection of Idle Equipment
Chapter	XIX	Inspection for Accident Prevention
Chapter	XX	Inspection for Fire Prevention
Appendix		Inspection of Welding

TABLE OF CONTENTS

	PAGE
201 GENERAL	7
201.01 Relationship of the Inspection Problem to Causes of Deterioration ..	7
201.02 Summary of Causes of Deterioration	7
202 CORROSION	8
202.01 Introduction	8
202.02 Corrosive Components of Crude Oil	22
202.03 Corrosive Materials Added to the Process	8
202.04 Environmental Corrosion	27
202.05 Corrosion at High Temperatures	31
202.06 Important Corrosion Phenomena	34
202.07 Corrosion Occurrences with Attempts at Corrosion Control	40
203 EROSION	40
203.01 Introduction	40
203.02 Discussion	40
204 EFFECTS OF HIGH TEMPERATURES	43
204.01 High-Temperature Strength	43
204.02 Metallurgical Structural Changes	45
204.03 Metallurgical Chemical Changes	50
205 SUBNORMAL AND AMBIENT TEMPERATURE EFFECTS	52
205.01 Brittle Fracture	52
206 EXCESSIVE PRESSURES	53
206.01 Introduction	53
206.02 Causes of Excessive Pressures	53
206.03 Effects of Excessive Pressures	53
207 OVERLOADING	54
207.01 Introduction	54
207.02 Evidences of Overloading	56
208 EARTHQUAKES AND EARTH SETTLEMENTS	56
209 MECHANICAL AND WIND DAMAGE	56
209.01 Introduction	56
209.02 Examples of Mechanical and Wind Damage	56
209.03 Causes of Mechanical and Wind Damage	58
210 FAULTY MATERIAL AND EQUIPMENT	60
210.01 Introduction	60
210.02 Situations Leading to Improper Selection of Material and Equipment ..	61
210.03 Evidences of Faulty Material and Equipment	63
APPENDIX I—COMMON REFINERY METALS AND ALLOYS	64
A. Ferrous Alloys	64
B. Nonferrous Metals and Alloys	65
REFERENCES	65
BIBLIOGRAPHY	67
INDEX	69

GUIDE FOR INSPECTION OF REFINERY EQUIPMENT

CHAPTER II

CONDITIONS CAUSING DETERIORATION OR FAILURES

201 GENERAL

201.01 Relationship of the Inspection Problem to Causes of Deterioration

Practically all refinery equipment suffers deterioration as a result of the conditions to which it is subjected. Under normal operating conditions this deterioration is usually, but not always, gradual. It generally occurs as metal loss, and occasionally as structural or chemical changes in the metal which result in weakening with no loss of metal. When equipment is subjected to abnormal conditions, deterioration may be much more rapid. Abnormal conditions may result from operational upsets caused by such things as instrument failure, or water in normally dry feedstock; or they may be the result of occurrences such as fires, earthquakes, or high winds.

New equipment and materials purchased for refinery use are generally bought according to specifications. These specifications take into account the expected conditions at which the equipment will operate and are usually based on recognized codes and standards. New equipment is also built by refinery or contractor forces. The design and fabrication of such equipment are, as a rule, also based on accepted codes and standards.

Inasmuch as the primary function of any inspection organization is to assure that equipment is safe to operate, it is of utmost importance that conditions causing deterioration and failure be recognized and understood. New materials and equipment purchased or fabricated in the refinery must be inspected to determine whether or not they meet the standards specified and, if they do not, whether they should be rejected or accepted. Operating equipment must also be inspected periodically to establish metal loss rates, because such rates determine the frequency of inspection and the predicted life of the equipment. When deterioration is not accompanied by loss of metal, it often shows up as cracking or as difficulties in making welding repairs. In such cases, metallurgical examination may be required to determine the exact cause.

Chapter II covers the more common causes of deterioration of refinery equipment. An understanding of these causes will not only permit the inspector to carry out his primary function better, but will make it possible for him to make sound recommendations for repair methods and materials.

Readers of this Guide can supplement its contents by referring to other sources of corrosion information. There have been numerous publications on corrosion published by the American Petroleum Institute, and various corrosion journals, abstracts, and data surveys published by the National Association of Corrosion Engineers. The reader should also refer to the bibliography for a limited list of the wide variety of materials published on corrosion.

201.02 Summary of Causes of Deterioration

Many of the contaminants in oil and chemicals handled in process units react with metals in such a way as to cause corrosion. Some materials fed or formed in process operations can cause erosion. In some operations, both erosion and corrosion occur. When this happens, the losses in metal thickness are often greatly in excess of losses that would be estimated from the separate effects of corrosion and erosion. In general, metal losses take place over a period of time. Accurate records of such losses are very important because it is from such records that proper inspection intervals and expected life of equipment are determined. However, metal losses are not always constant, but are a function of such variables as salt and sulfur content of crude oils, chemicals used in refining, and operating temperatures and pressures. It is essential, therefore, that the inspector be generally aware of the day-to-day operation of equipment and that he reestablish metal loss rates at frequent intervals.

Stress reversals in parts of equipment are quite common, particularly in reciprocating parts. If stresses are high enough and reversals frequent enough, failure of parts occurs by fatigue. The possibility of such failures in machinery parts, for example, in pumps and compressors, is taken into consideration in the design of such equipment. Less frequent, but usually more serious, are fatigue failures in piping and pressure vessels that result from cyclic temperature and pressure changes. Fatigue failures in machinery start as cracks at the surface of the metal and progress with each stress reversal, at first slowly and then more rapidly. In the final stages, crack propagation can be exceedingly rapid. Periodic inspection of reciprocating parts will frequently establish the presence of fatigue cracks before complete failure occurs. Similarly, inspection of

pipng and vessels that operate under cycling conditions will often permit repairs or replacement before failure. Locations where metals having different thermal coefficients of expansion are joined by welding are often susceptible to thermal fatigue, and cracks sometimes start when equipment is shut down and cooled off.

Where equipment is subjected to temperatures above those for which it is designed, distortion often occurs; and because metals become weaker at higher temperatures, such distortion may result in failure, particularly at points of stress concentration. If temperatures become excessive, structural and chemical changes in the metals may also take place and may permanently weaken equipment. Such changes can occur as a result of fires, and any equipment that has been exposed to fire may be considerably weakened. Excessive metal temperature, due to fire exposure or even a severe process upset, can result in the failure of a vessel at or below its design pressure.

At subfreezing temperatures, water and some chemicals handled in refinery equipment may freeze and cause bursting of piping and vessels. In northern refineries, where freezing conditions often occur, equipment prone to freezing is kept warm by heating using steam, hot oil, or electrical means. Equipment that is not operated continuously, such as fire water lines and water drawoff lines on process equipment, is particularly susceptible to damage in freezing weather.

Carbon steels are susceptible to brittle failure at ambient temperatures or below. A number of tank failures have been attributed to the brittle condition of the steel at low temperatures, combined with high loads that have been imposed by thermal stresses set up by rapid temperature changes.

Excessive pressure seldom contributes to failure of equipment under normal conditions because protection is provided by safety valves or by the equipment being designed for the maximum pumping pressure to which it may be subjected, or both. Failure under such conditions can, of course, occur if excessive metal loss has taken place or cracks or notches create undetected weaknesses.

Overloading of equipment is an infrequent inspection problem because designs are generally adequate to carry the expected loads. Before applying hydrostatic tests to equipment or adding any other additional load, it should be ascertained that the vessels involved, the supporting structure, and the foundation are designed for such loads.

Earthquakes, earth settlement, and wind loading are normally considered in the design of refinery equipment and seldom contribute to deterioration or failure. Where equipment has been subjected to abnormal conditions, however, it may be severely damaged, particularly the foundations and supporting structure. Mechanical damage that may result from equipment being dropped or from its being struck by vehicles, and the like, generally occurs, fortunately, during shutdown periods.

Major pieces of equipment, such as towers, drums, pumps, and exchangers, are generally always inspected and tested either at the manufacturers' shops or before being put into operation in a refinery, and the inspector knows definitely whether or not such equipment is acceptable. The manufacture of smaller items, such as valves and pipe fittings, is generally not as closely controlled. This smaller equipment is a source of real problems. The wrong material, or even the wrong gaskets used in assembly, may lead to failure.

202 CORROSION

202.01 Introduction

Corrosion has always been a major problem in the refining industry. As the industry has grown and adopted modern processes, some of which employ corrosive chemicals, corrosion problems have become more numerous and complex. Many investigators have endeavored to place a cost on corrosion in the refining industry. The results of an exhaustive survey in this field were presented during the 19th Midyear Meeting of the American Petroleum Institute's Division of Refining (1954) by the Subcommittee on Corrosion. This committee estimated that the cost of corrosion in refinery operations is approximately \$0.1125 per barrel of crude oil processed. In the 1970's this cost could be several times higher because of rising expenditures for labor and materials.

The inspector can do much to help control the cost of corrosion by detecting deterioration before it results in lost production or extensive damage to equipment. A full understanding of the problem is of primary importance to the inspector. It is the purpose of this section of Chapter II to discuss corrosive elements encountered in refining processes and how these result in deterioration of equipment. Corrosion problems in refining operations can be divided into three major groups, as follows:

1. Corrosion from components present in the crude oil.
2. Corrosion from chemicals used in refinery processes.
3. Environmental corrosion.

202.02 Corrosive Components of Crude Oil

202.021 GENERAL: The corrosion problems attributed to constituents present in the crude oil are generally believed to be caused by one or more of the following compounds:

Hydrogen chloride and organic and inorganic chlorides
Hydrogen sulfide, mercaptans, and organic sulfur compounds
Carbon dioxide
Dissolved oxygen and water
Organic acids
Nitrogen compounds

The aforementioned corrosive components in crude oil first become apparent in the primary processing unit of the refinery, the crude pipe still, or the distillation towers. In general, as the crude oil flows from tankage through the crude distillation unit, one or more of these chemical components can cause various types of corrosion problems. Temperature levels change, the components separate or form new ones, and the environment for corrosion changes in each section of the distillation unit. For example, the equipment section affected and the corrosive compounds that will most likely cause trouble are shown as follows:

- Tankage—Hydrogen sulfide, dissolved oxygen and water.
- Preheat Exchanger—Hydrogen chloride and hydrogen sulfide.
- Preheat Furnace—Hydrogen sulfide and sulfur compounds.
- Crude Tower Flash Zone—Hydrogen sulfide, sulfur compounds, and organic acids.
- Middle Zone—Hydrogen sulfide.
- Top Zone—Hydrogen chloride and water.
- Tower Overhead System—Hydrogen chloride, hydrogen sulfide, and water.
- Vacuum Furnace—Hydrogen sulfide, sulfur compounds, and organic acids.
- Tower—Hydrogen sulfide and organic acids.
- Overhead—Hydrogen chloride and water.
- Bottoms Exchange—Hydrogen sulfide and sulfur compounds.

In addition, neutralized salts such as ammonium chlorides and sulfides can cause trouble throughout most of the equipment sections, particularly when moist with condensed water.

As the oil products of distillation leave the crude unit, many of the corrosive components contained in the products pass on to further processing in downstream units such as catalytic cracking, visbreaking, coking, desulfurizing, and reforming.

Control of corrosion by these components of the crude oil or their products is by use of chemical treatment, inhibitors, alloy metals or nonmetallic materials, or by use of other corrosion mitigation methods. The methods of control used in the crude distillation unit are also used in many of the downstream process units. The following paragraphs describe in detail the controls for each of the problem-causing compounds.

202.022 HYDROGEN CHLORIDE AND ORGANIC AND INORGANIC CHLORIDES: Because brine is produced along with the crude oil, and the separation of crude from brine is not perfect, all crudes contain salt. Although it is the general practice in crude assays to analyze the crude oil for chlorides (mainly inorganic)

and report total chlorides as sodium chloride (common salt) in pounds per thousand barrels of crude oil, the brine is generally believed to be roughly of the same analysis as sea water.^{1*} A typical analysis of sea water is given in the following tabulation, and the brine in crude oil roughly corresponds to this analysis.

Salt	Percent by Weight of Total Salt
Sodium chloride	68.1
Magnesium chloride	14.4
Sodium sulfate	11.4
Calcium chloride	3.2
Potassium chloride	1.9
Sodium bicarbonate	0.6
Potassium bromide	0.3
Other salts	0.1
Total	100.0

Magnesium and calcium chlorides, when dissolved in water and heated, form hydrochloric acid that is very corrosive.² This reaction, called hydrolysis, takes place at reasonably low temperatures (300 F to 400 F). Sodium and potassium chlorides do not hydrolyze and consequently do not cause serious corrosion in crude distillation units.

Hydrogen chloride, which is dry hydrochloric acid, is normally not corrosive in process streams. Corrosion by hydrogen chloride only becomes serious where water is available to form hydrochloric acid. (Corrosion that occurs where liquid water is present is generally called low-temperature corrosion.) Some corrosion by hydrogen chloride may occur in the preheating exchangers of crude oil distillation units. Fig. 1 shows an unusually

* See References on p. 65.

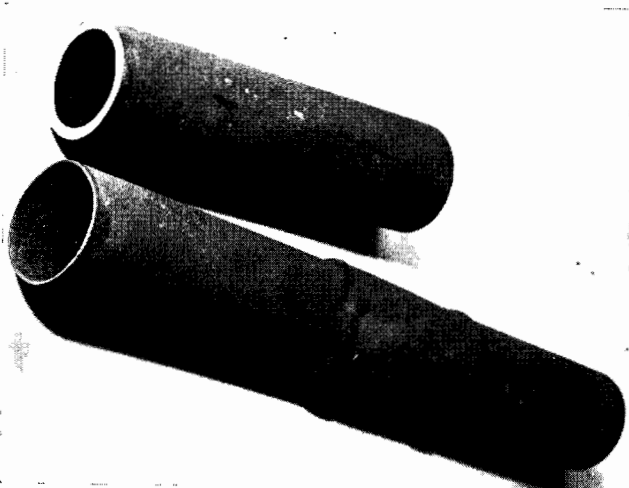


FIG. 1—Corroded Carbon-Steel Tube From Pipe Still Crude-Oil Preheat Exchanger.

severe case of preheat-exchanger corrosion. Corrosion of carbon steel in the preheating exchanges may vary from negligible to approximately 0.120 in. per year. The rate varies with crude oil type and the presence of other corrodents; it increases with increased temperature, salt, and liquid-water content. Most corrosion in preheat exchangers is caused by high-temperature hydrogen sulfide attack.

In general, the principal evolution of hydrogen chloride will occur in the furnaces. At these locations, however, liquid water does not exist, and corrosion by hydrochloric acid does not occur. The dry hydrogen chloride gas is carried through the processing equipment, and little or no corrosion occurs until temperatures are lowered to near the dew point of water.

In most primary distillation processes, steam stripping is employed to assist distillation. This steam, when condensed in the presence of hydrogen chloride gas, produces hydrochloric acid. In many of these processes the tower top temperature is above the dew point of water, but metal temperatures of the shell, piping, or thermocouples may be below the dew point. Where exchangers exist in the distillation overhead systems,

water condensation can occur in the exchangers, and variable rates of corrosion are generally found at this point. Most of the water condensation occurs in the overhead condensers, and corrosion is severe in the condensers, in the piping, and in the distillate drum where the water is separated from the distillate.

The corrosion rates in the overhead equipment vary considerably, depending on the type of crude oil processed, salt content, sulfur content, hydrogen sulfide evolution, and on the pH of the overhead stream.* Corrosion rates as high as 5 in. per year have been measured on steel coupons inserted without chemical control in a pipe still overhead system. This is indicative of the high corrosion rates that can be encountered under certain conditions. Fig. 2 and 3 illustrate the severe corrosion that can occur in overhead equipment. If the amount of hydrogen chloride in the overhead stream is high, pH control by ammonia addition is required to neutralize hydrochloric acid (HCl) before

* The pH is a relative measure of the acidity or alkalinity of materials. All pH values below 7 indicate increasing acidity with decreasing numbers, pH of 7 is neutral, and pH values above 7 indicate increasing alkalinity with increasing numbers up to 14.



FIG. 2—Corrosion of an Admiralty Pipe Still Overhead Condenser Bundle.
Most severe corrosion occurred just under the condenser inlet nozzle.



FIG. 3—Tubes Removed From the Condenser Bundle Shown in Fig. 2.
These severely corroded admiralty tubes were located just under the condenser inlet.

a water dew point is reached. If such control is inadequate, an organic corrosion inhibitor should also be added. At all times, pH control in the 5 to 8 range should be maintained. Generally the pH should be 6.5 maximum to minimize ammonium chloride (NH_4Cl) fouling with resultant corrosion underneath deposits. With appropriate pH control, the corrosion rate should be very low, except that at the first point of condensation the temperature and pressure may be such that hydrochloric acid and ammonia (NH_3) can dissociate and corrosion may occur. Monel is generally resistant to corrosion by weak hydrochloric acid, and is commonly used in the top section of crude towers and for condensers and distillate-drum liners in pipe still overhead systems. Typical corrosion rates for monel in this service vary up to 0.002 in. per year. Corrosion rates on admiralty or 70 copper-30 nickel are inter-

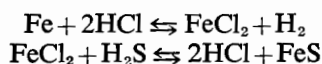
mediate between carbon steel (high rate) and monel (low rate) and usually vary up to 0.5 in. per year.

In the distillate drum, most of the hydrochloric acid or neutralized salts will be removed in the water drawoff. This separation, however, is not complete; acidic water may be entrained in the distillation-tower reflux and may cause corrosion in the reflux pumps and piping. Corrosion in these locations is considerably reduced below that which occurs ahead of the distillate drum because the corrodent is carried only to the degree of moisture solubility and entrainment. However, because the reflux is not immediately heated to tower vapor temperatures, the water entering with the reflux may remain as a liquid on the top several trays of the tower where it can absorb more hydrogen chloride gas and increase in corrosiveness. As a result, the top trays and those portions of the tower

immersed or washed with liquid suffer corrosion. Those places where liquid flows over downcomers or leaks from weepholes and contacts the tower shell are particularly susceptible. Little, if any, corrosion takes place in the vapor spaces of towers unless the temperature is below the dew point, except in more or less stagnant areas, such as safety-valve nozzles, where the temperature may drop low enough for condensation of water vapor to occur.

The hydrochloric acid produced in the crude oil distillation process may cause severe corrosion in itself. This corrosion is more serious in refining sour crudes.*

- In the presence of hydrogen sulfide, the corrosion of iron by hydrochloric acid becomes a cyclic reaction, as illustrated in the following formulas, and corrosion can be expected to reach serious proportions.



A study of these chemical reactions shows that the hydrochloric acid (HCl), which causes the primary corrosion of the iron (Fe) to produce iron chloride (FeCl₂), is regenerated—so that it can continuously repeat the cycle—by the action of hydrogen sulfide (H₂S) on the iron chloride, to produce iron sulfide (FeS) with the reappearance of hydrochloric acid. The double arrows indicate that the chemical reaction may proceed in either direction depending on specific conditions.

One method for reducing corrosion by salts and hydrochloric acid, which is generated by the hydrolysis of salts, is the elimination of the brine from the crude oil. Most of the producing fields endeavor to do this by settling. This, of course, accomplishes the removal of both water and salt, which are the corrodents. In some cases, adsorption systems are employed to dry the crude oil further. In general, these are the only steps taken to reduce corrosive constituents prior to the time the crude oil enters the refinery.

Even in the cases where judicious control of brine in crude oil is exercised in the producing fields, it is found that considerable salt is generally contained in the crude as it is received in the refinery. The salt content is generally higher in the winter because oil-field brine settlers are less effective at low temperatures.

Most modern refineries operate desalting equipment to reduce the salt content of the crude-oil feed to distillation units. While this equipment will reduce the salt content to as little as 1 to 10 lb per thousand barrels, corrosion by hydrochloric acid may still be serious. A crude oil distillation unit that feeds 60,000 bbl of

crude oil per day, desalted to 10 lb per thousand barrels, can produce a total of 90 lb of hydrogen chloride daily by hydrolysis of magnesium and calcium chloride. If this is totally united with iron, 70 lb of iron will be consumed daily. This represents a yearly loss of about 13 tons of metal, and as this corrosion largely occurs in the overhead equipment, rates of loss of this magnitude are serious. Although this reaction would not go to completion, these figures serve to indicate that even though corrosion is reduced by desalting, it is by no means eliminated.

Chemicals are frequently used to control corrosion by hydrochloric acid produced in crude oil distillation units. The chemicals used are alkaline agents such as sodium hydroxide, sodium carbonate, calcium hydroxide, anhydrous ammonia, or aqueous ammonia. In general, there are two principal methods of injecting chemicals into the process streams. The most widely used is the injection of ammonia into the overhead stream at some point ahead of condensation. The second method uses injection of sodium hydroxide or sodium carbonate into the crude-oil feed as it is introduced to the process unit. A combination of these two methods may also be used.

The addition of alkaline solutions, such as caustic soda, to the crude-oil feed should be made with caution because in almost all cases these streams will be heated. If sufficient quantities are injected, conditions conducive to stress corrosion cracking (see Par. 202.064) may occur in the process. Also, it should be cautioned that caustic concentrates in the residual product and can lead to corrosion problems in downstream units that process the residuals, for example, cokers and vis-breakers.

Anhydrous ammonia or aqueous ammonia are commonly employed as neutralizers in distillation overhead streams. These chemicals are generally injected into the distillation-tower overhead line some distance ahead of the point of initial condensation. Anhydrous ammonia is normally vaporized and added as a gas, and aqueous ammonia is added as a liquid. In either case, intimate contacting can be effected. It has been found that corrosion of iron by hydrochloric acid generally becomes almost negligible when the pH of the water condensate is above 5. In the case of copper alloys, pH values on the water condensate must be kept below pH 8 to avoid stress corrosion or corrosion-fatigue failures in admiralty exchanger and condenser tubes. In the absence of oxygen, no damage to copper alloys results at pH values of 7 to 8. If the alkalinity is allowed to exceed pH 9, direct chemical corrosion of copper alloys can occur, particularly at the dew point, even though the totally condensed stream (where normally sampled for pH) is at a lower pH.

When ammonia is used on overhead systems to neutralize hydrochloric acid, deposits of ammonium chloride can form when sufficient water is not present to wash these deposits from the equipment. Serious

* The term "sour crudes," as used in this chapter, refers to those crude oils which contain dissolved hydrogen sulfide or evolve it upon processing.³ "Sweet crudes" contain no dissolved hydrogen sulfide and relatively small amounts of mercaptans and other reactive sulfur compounds.³ Generally, "sweet crudes" have a sulfur content less than 0.5 percent weight, and "sour crudes" have a sulfur content above 1.0 percent weight.

corrosion and stress corrosion cracking of some copper alloys can occur under these deposits. Such deposits can be prevented by injection of fresh water or recirculation of condensed water to dissolve and wash forward the ammonia salts.

Hydrogen chloride can also be produced in hydrogenation processes from organic chlorides in the feed, and can cause corrosion in units downstream of the crude distillation unit unless neutralized.

202.023 HYDROGEN SULFIDE, MERCAPTANS, AND ORGANIC SULFUR COMPOUNDS

a. General Discussion: It is generally felt that hydrogen sulfide is the most active of the sulfur compounds in causing corrosion in refinery equipment.⁴ Hydrogen sulfide is sometimes present in the crude oil as such, and additional hydrogen sulfide may be formed by the decomposition of organic sulfur compounds at the process temperatures. Corrosion increase will be somewhat on the order of the increase in total sulfur content,⁵ as shown in Fig. 4. Some points show a wide divergence from the curve. This divergence may be attributed to differences in the type of sulfur compounds present. Some are more resistant to thermal decomposition than others, and some may be noncorrosive. Rates of corrosion from sulfur compounds may also vary because of the effect of other corrodents present.

b. Sulfur Corrosion at Low and Intermediate Tem-

peratures: Hydrogen sulfide causes corrosion of refinery equipment even at atmospheric temperatures, and considerable corrosion is found in storage tanks containing some types of high-sulfur crude oils. (Refer to Par. 205.01.) Corrosion of this type occurs in cone-roof storage tanks in the presence of moisture and oxygen⁶ and has been known to penetrate $\frac{3}{16}$ -in.-thick tank roofs and upper shell rings in 2 to 3 years. Sufficient oxygen is always available for the corrosion to proceed, and moisture condenses on the roof and shell. In view of the fact that moisture is needed for this corrosion to take place, corrosion of this type is generally more severe on the shady side of the tank in warm climates. In cooler climates, temperature conditions may be such that condensation occurs around the entire tank, and the corrosion rate will be highest on the hottest (sunny) side. Hydrogen sulfide also causes corrosion by the formation of iron sulfide scale in the overhead systems of distillation equipment where water is present. If hydrogen chloride is also present, it dissolves this scale, generating more hydrogen sulfide and exposing fresh metal surfaces to attack. This reaction may also operate in the opposite direction, as explained previously. In general, corrosion of overhead systems of crude-oil pipe stills by hydrogen sulfide is much less serious than corrosion by hydrogen chloride.

Other manifestations of corrosion caused by hydro-

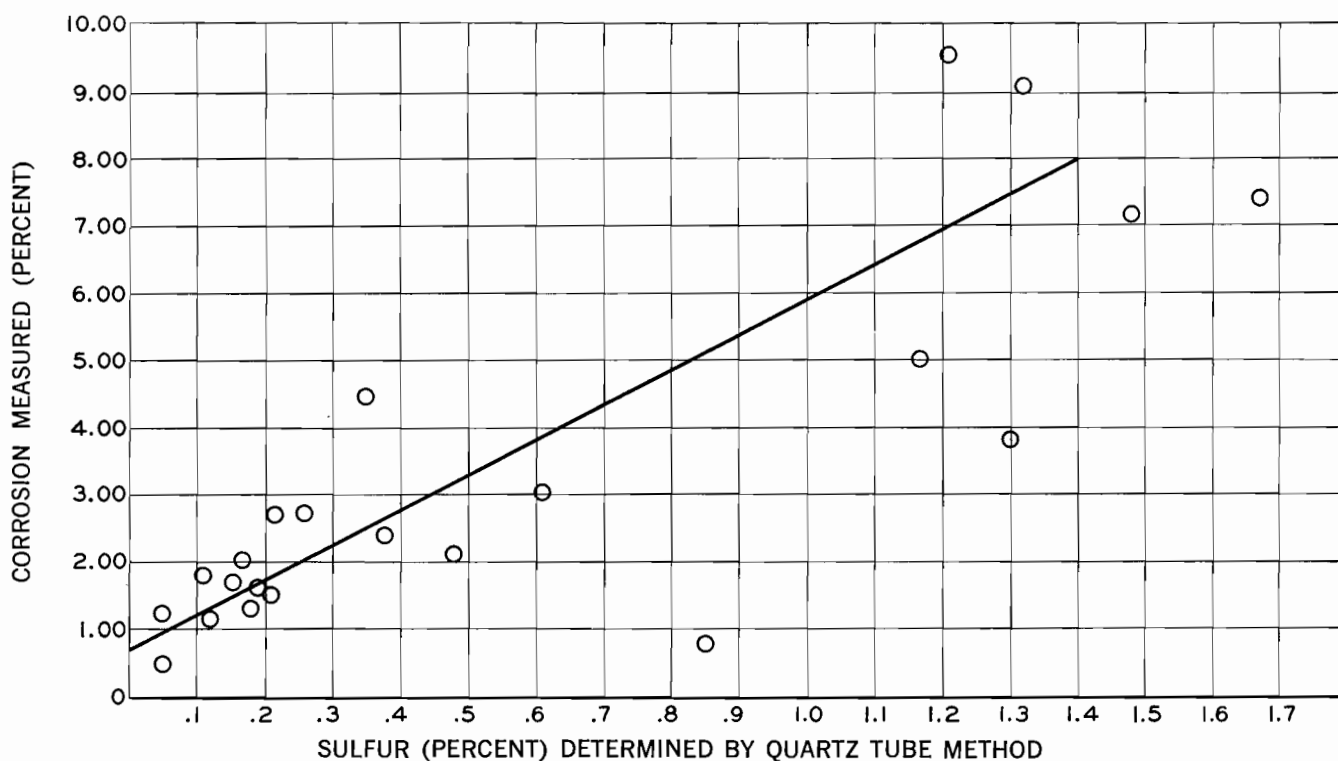
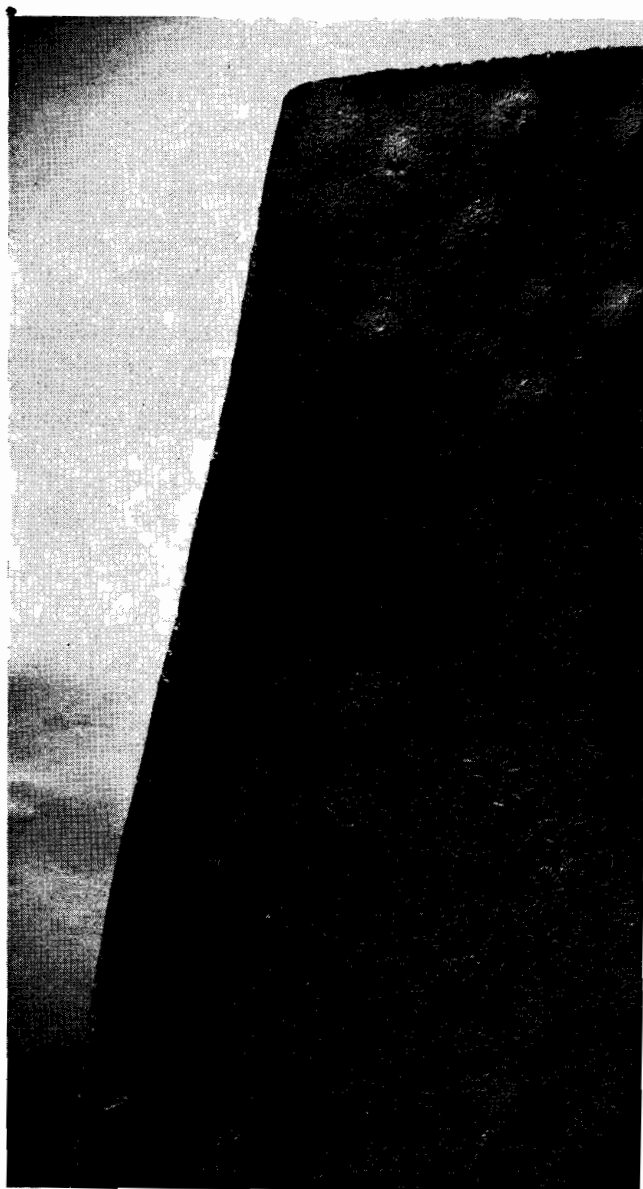


FIG. 4—Corrosion Measured as a Function of Total Sulfur Content of Various Crude Oils.

gen sulfide are hydrogen blistering and hydrogen embrittlement. These attacks have been serious in the gas-compression and fractionating equipment of catalytic cracking units and equipment handling some crude oils, some crude-oil fractions, and some natural gasolines. They have also occurred in equipment handling phenol, sulfuric acid, and mixtures of hydrocarbons and hydrofluoric acid. This hydrogen attack occurs both in alkaline solutions (in the presence of cyanides) and in acid or sour (see reference 61) solutions when steel is corroded slowly by weak acids. Some of the atomic hydrogen (H_1) formed as a product of the corrosion re-

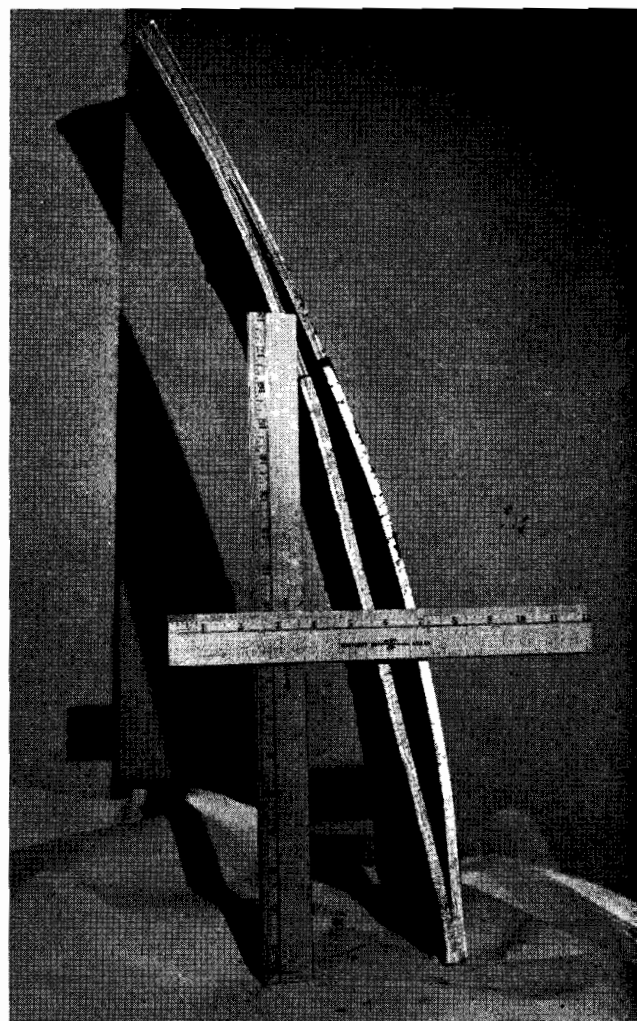
action enters the metal. If voids such as laminations or nonmetallic inclusions (slag, etc.) are present in the steel, hydrogen collects in them and forms molecular hydrogen. Molecular hydrogen (H_2) cannot pass through the steel; therefore, it remains in the void. As more molecular hydrogen forms, pressure builds up and eventually causes the steel to blister or rupture. Fig. 5 through 9 illustrate hydrogen blisters. Clean steel without inclusions can embrittle and crack at welds⁶¹ and stress raisers without blisters being present.

c. *High-Temperature Sulfidic Corrosion:* Temperature plays an important part in corrosion by hydrogen sulfide.⁷ In the absence of water, corrosion is not serious at low temperatures, and a metal temperature above 450 F is necessary for high-temperature sulfidic corrosion to occur at an accelerated rate. In refineries that process sweet crude oils, only slight corrosion of



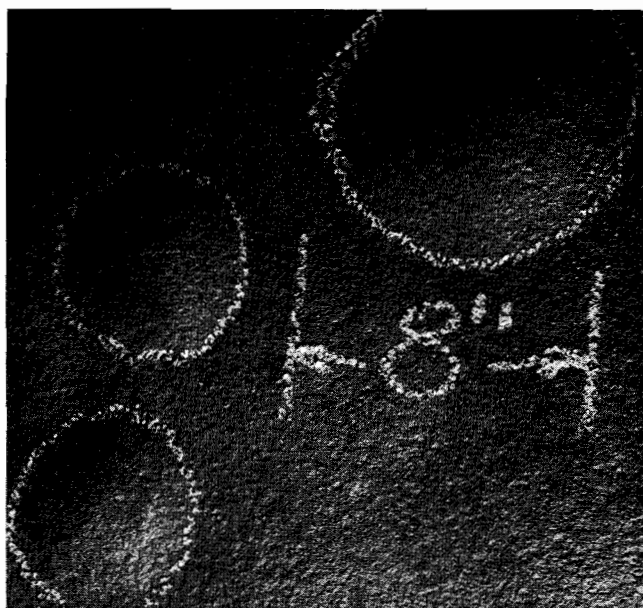
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FIG. 5—Appearance of Hydrogen Blisters on Exterior of a Vessel Shell.



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FIG. 6—Cross-section of a Large Hydrogen Blister in a Pressure Vessel Shell.



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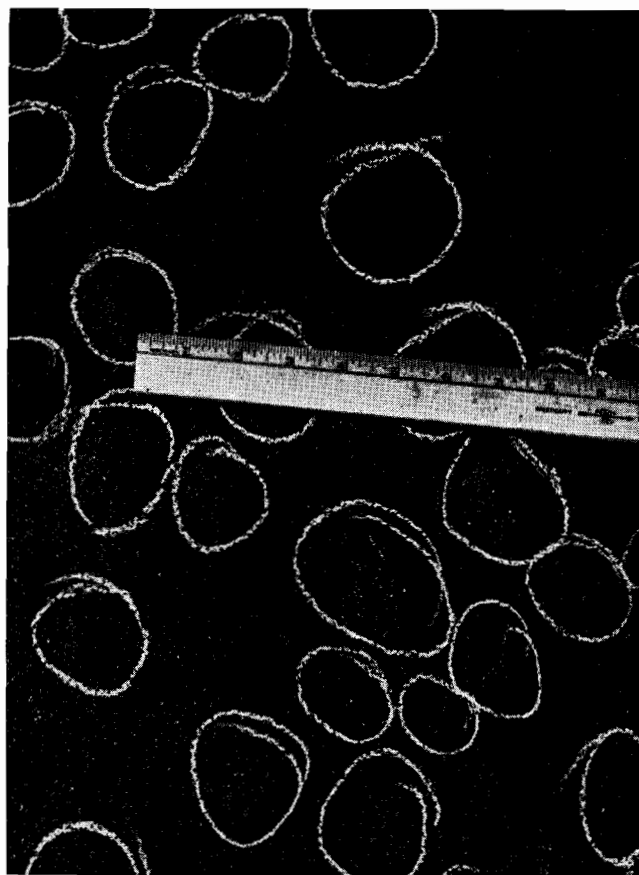
FIG. 7—Hydrogen Blisters in a Pressure Vessel Shell.

Note that the largest blister is approximately 8 in. in diameter.

carbon steel may be expected, with corrosion rates of approximately 0.01 in. per year. Carbon steel furnace tubes normally give service lives of more than five years in sweet crude service and very little corrosion is experienced in the shells of distillation towers, although, even with low rates, thin internal equipment subject to corrosion from two sides may deteriorate rapidly. Internals made of 12 percent chromium steel are very resistant to attack.

In refineries that process sour crude oils, severe corrosion may occur in crude oil distillation units in those locations where the metal temperatures exceed 450 F. At this temperature and above, decomposition of sulfur compounds to hydrogen sulfide occurs, and rates as high as 0.5 in. per year have occurred in carbon steel furnace tubes handling high-sulfur crudes. Severe sulfidic corrosion of carbon steel radiant section tubes is shown in Fig. 10 and 11. Furnace tubes of 5 percent chromium material give up 3 to 10 times the life of carbon steel under these conditions. In vacuum furnaces, where corrosion is more severe, 9 percent chromium tubes hold up well. Severe sulfidic corrosion may be found in the lower portion of fractionating towers.

In thermal cracking and other operations, oil can be heated to temperatures on the order of 900 F. Corrosion may be expected in equipment where the metal temperature is between 450 F and approximately 900 F; above 900 F, indications are that corrosion is reduced, possibly because of coke forming a protective



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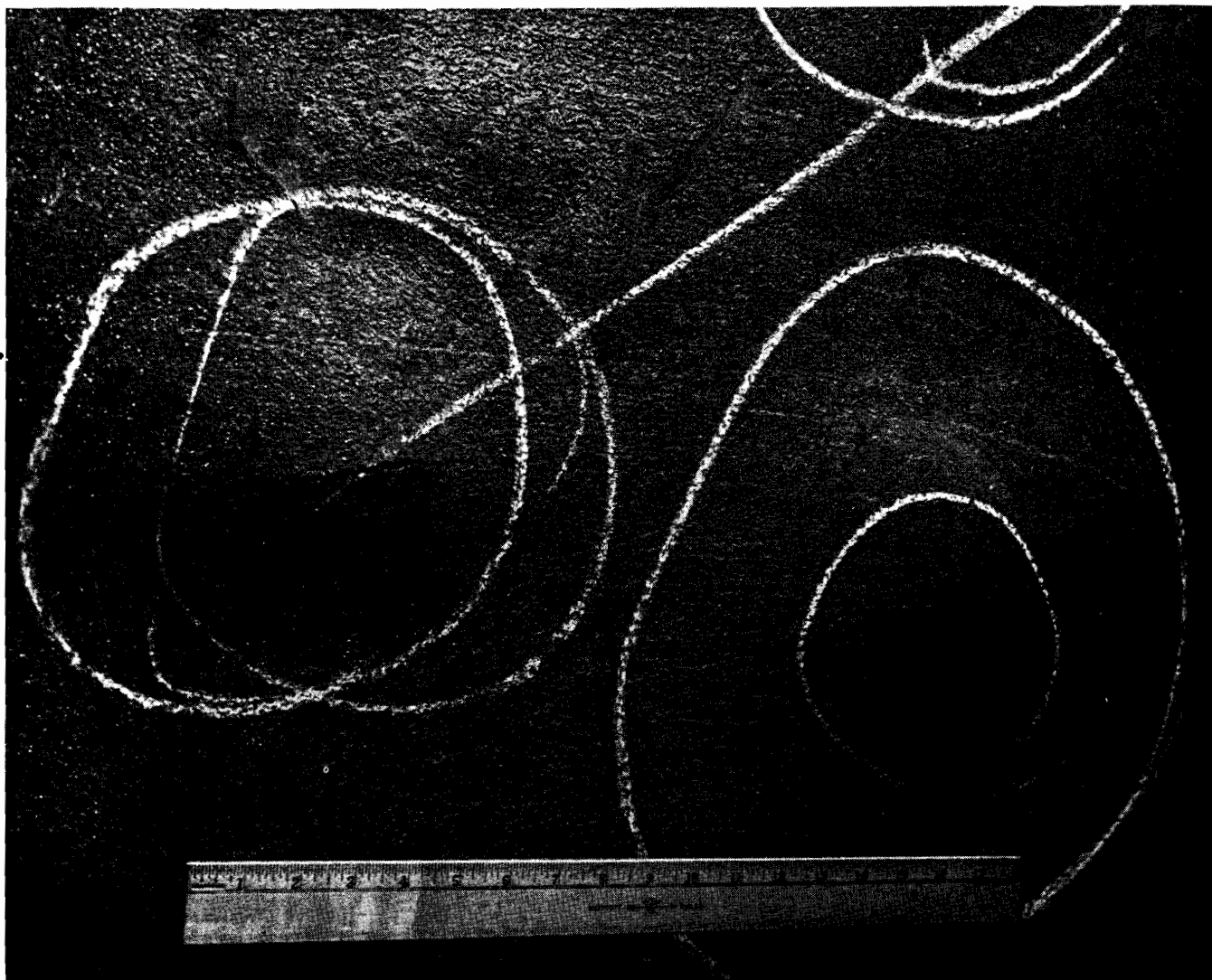
FIG. 8—Extensive Hydrogen Blistering.

Note that the blisters have ruptured.

coating on the metal. The furnace, soaking drums, separators, high-temperature exchangers, the lower portion of the fractionating towers, and attendant piping are usually susceptible. Corrosion in the tower internal equipment follows the same pattern, decreasing upward through the tower as temperatures decrease to 450 F and below.

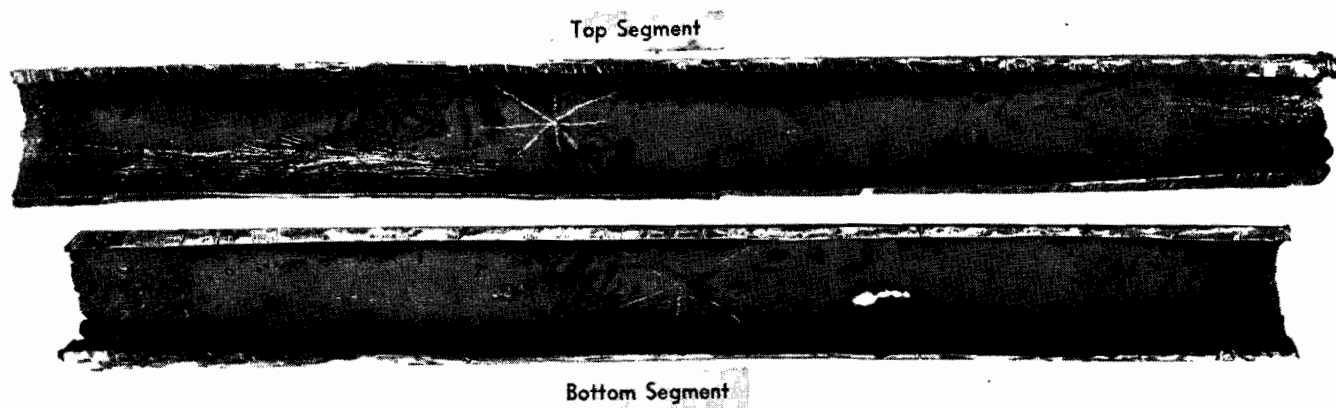
Corrosion rates vary widely, depending on the crude oil refined and the processing temperatures. In thermal cracking units that process sweet crude oils, corrosion rates of 0.120 to 0.180 in. per year are normal for carbon-steel furnace tubes. In general, coke formations in soaking drums protect the walls from corrosion; without coking, the corrosion rate is high—approximately 0.20 in. per year. The corrosion rates for separators and lower portions of fractionators may be as high as 0.07 in. per year.

Conditions in catalytic cracking operations are somewhat similar to those encountered in thermal cracking units. Corrosion of catalytic cracking-unit reactors that operate above 900 F has not been serious, although localized corrosion can occur at spots where there is



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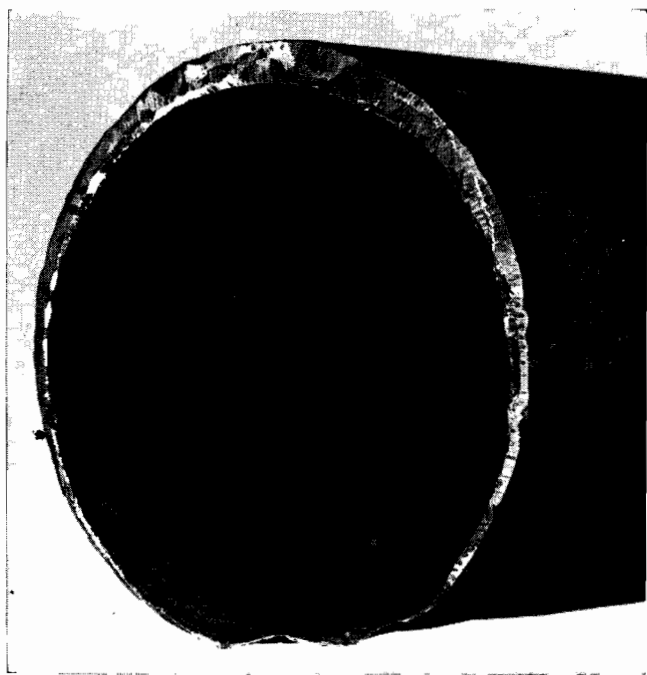
FIG. 9—Close-up View of the Blisters Shown in Fig. 8.



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FIG. 10—Specimen of a Corroded Crude-Oil Pipe Still Radiant Section Tube That Eventually Failed.

Feedstock was a high-sulfur New Mexico crude oil.



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FIG. 11—Cross-Section of a Radiant Tube in Corrosive Crude-Oil Service.

Note the high degree of eccentric corrosion. The thin side of the tube was next to the fire.

local cooling such as at nozzles, platform supports, and the like. Corrosion takes place, however, when temperatures are reduced below 900 F, and in many cases where both liquid and vapor phases exist. It continues until the lower limit of 450 F is reached. Corrosion rates at the fractionator flash zones of approximately 0.10 in. per year may occur. Turbulence and erosion from an entrained catalyst accelerate the metal loss at this location. The rate is markedly reduced just above the flash zone where there is no catalyst present. As in the case of thermal cracking-unit fractionators, severe corrosion does not occur in the upper portion of these towers.

The corrosion by hydrogen sulfide in coking processes may be expected to follow the pattern discussed for thermal cracking processes. The exact type and sulfur content of the feed have an important bearing on the magnitude of corrosion. Little corrosion should occur with metal temperatures below 450 F. Above 450 F, corrosion will increase as the temperature increases. At approximately 900 F, corrosion will decrease sharply. Such equipment as furnace tubes, towers, tower internals, vessels, exchangers, and pumps are affected. Corrosion rates are abnormally higher at points of high velocity and turbulence. The straight chromium steels (no nickel), 12 percent chromium and those with $\frac{1}{2}$ to 1 percent molybdenum, such as 5,

7, and 9 percent chromium, have good resistance to this corrosion; the austenitic stainless steels, such as 18 chromium-8 nickel steel, have excellent corrosion resistance.⁷

In gas-handling and stabilization units, one of the functions is generally the removal of hydrogen sulfide. In general, the operating temperatures are low and high-temperature hydrogen sulfide corrosion is not severe except in equipment such as reboilers, either of the fired-heater type or the shell and tube type, where the temperature may exceed 450 F. In reboilers of the fired-heater type a corrosion rate of 0.09 in. per year has been measured. Of particular interest may be the fact that convection section tubes normally operate at temperatures at which little corrosion occurs; but the temperatures at tube supports are higher, and severe localized corrosion may occur in the tubes at the points where they pass through the tube supports. The tube metal immediately below tube fins or studs may also be hot enough to cause severe local corrosion to occur.

d. High-Temperature Hydrogen Sulfide Corrosion in the Presence of Hydrogen: This attack by hydrogen sulfide is separated in discussion from the previous section on high-temperature hydrogen sulfide corrosion because of the severity and mechanism of its attack. Industry found that correlations for corrosion based on sulfur content in sour stocks (Fig. 4) did not hold when hydrogen in significant quantities was present such as in hydrosulfurizers and catalytic reformers. As noted in Par. 202.023a, the corrosion based on sulfur content may vary, dependent on decomposition, into hydrogen sulfide. Under catalytic conditions (as in these processes), almost all detectable sulfur is converted to hydrogen sulfide and correlations are based on either partial pressure or hydrogen sulfide concentration (mol, volume percent) in the process stream.

The literature contains a number of these correlations that show *iso*-corrosion lines based on concentration of hydrogen sulfide in hydrogen versus temperature.⁸⁻¹⁰ Since the reaction for corrosion of iron is reversible, a curve is shown under which iron sulfide in hydrogen is reduced to iron and hydrogen sulfide and corrosion does not occur.

As can be noted, the operating temperatures in catalytic processes make their equipment susceptible to the highest corrosion rates if the hydrogen sulfide content is allowed to be more than a minor amount. Curves are shown for both stainless steels and carbon or chromium steels. The stainless steel curves were developed for naphtha reforming conditions and generally apply at higher temperatures. However, when temperatures are lower in hydrosulfurizers, chromium steels, such as 5, 7, or 9, in some cases are no longer corroded as much or more than carbon steel (see Par. 204.035 for hydrogen attack on steels which would determine the minimum alloy content for a given pressure and temperature of hydrogen). The low-chromium alloy steels (5 percent chromium and above) are pres-

ently in wide use partially because they can have a useful life, and care during shutdowns is not required because polythionic acids and chlorides do not cause cracking of these ferritic alloys.

A more recent publication¹¹ presents corrosion rate data for hydrodesulfurizing units under conditions of pressure up to 2,000 psig, temperatures to 900 F, and hydrogen sulfide concentrations to 10.6 percent by volume in hydrogen. In addition to alloys of 9 percent chromium steel and the "300"-type stainless steels, corrosion rates for Types 410 and 430 stainless steels and Incoloy 800 are included.

Caution should be taken concerning the pyrophoric nature of the sulfide scales typically found on carbon and chromium-molybdenum steels in high-temperature, hydrogen sulfide-hydrogen atmospheres.

202.024 CARBON DIOXIDE:

a. General Discussion: Carbon dioxide combined with water causes corrosion in refining processes. Until the advent of reforming processes for generating a hydrogen-employing catalyst over which a hydrocarbon and steam are passed, the following paragraph covered most refining processes. Following this paragraph, the hydrogen plants are treated separately since the corrosion is no longer a rarity or of minor importance.

In some processes the carbon dioxide may come from two sources: 1, from the decomposition of bicarbonates contained in, or added to, the crude oil; and, 2, from steam used to aid distillation. The latter source is dependent on the type of boiler feed-water treatment used. In most cases the concentration of carbon dioxide in water is low, and corrosion rates are low relative to those associated with other corrodents. Data on actual corrosion rates for carbon dioxide are meager, but a corrosion rate of approximately 0.03 in. per year has been measured in steam-condensate systems operating at approximately 350 F. Corrosion rate from carbon dioxide depends on partial pressure and temperature. Severe steam-condensate corrosion is illustrated in Fig. 12. Inasmuch as other types of corrosion are so much more important than corrosion by carbon dioxide, this type of corrosion is often not recognized.

It may be of interest that the pH of streams does not give a good indication of anticipated corrosion when a weak acid, such as carbonic acid (carbon dioxide dissolved in water), is the corrodent. It has been found that appreciable corrosion can occur in carbonic acid solutions at a pH of 6.0. Corrosion by stronger acids, such as hydrochloric acid, is not particularly rapid in the absence of oxygen at a pH above 4.5, and serious corrosion occurs in refinery process streams containing hydrochloric acid generally if the pH value is less than 4.0. This is explained on the basis that total acidity, rather than pH, determines the extent to which an acid corrodes iron.¹²

In steam condensate systems, corrosion because of

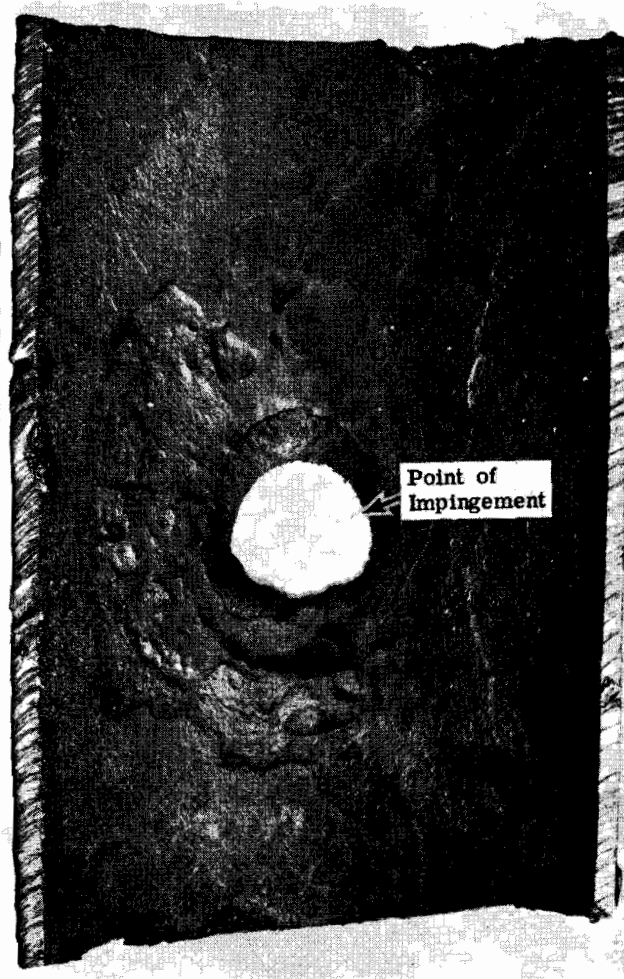


FIG. 12—Steam-Condensate Corrosion.

This is the lower half of a main steam-condensate line that failed from impingement of a lateral stream on the main line.

carbon dioxide can be prevented by injecting special corrosion inhibitors into the steam.

b. Hydrogen Plant Corrosion: Corrosion by carbon dioxide is very severe and can cause not only metal dissolution but also intergranular attack and can provide the environment for stress corrosion cracking. Corrosion by carbon dioxide in water (possibly containing impurities such as chlorides or alkaline substances) is typical of most corrodents in that the areas of condensation and impingement are the ones most severely attacked. In areas of condensation, corrosion rates exceeding 1 in. per year on carbon steel have been found. Alloys found resistant to attack are monel, aluminum, stainless steels, and cupro-nickel. Included in the stainless steel categories are the ferritic and martensitic as well as the austenitic stainless steels. Like hydrogen sulfide, the attack of wet carbon dioxide on steels is lessened by the addition of chromium. Normally, a reasonable amount of passivity is not

reached until the chromium content is about 12 percent, but the 5 to 9 percent chromium steels could be used for short-term life if any iron can be tolerated in the condensate.

Although Type 304 stainless steel is widely used and has been found most satisfactory in wet carbon dioxide environments of hydrogen plants, sensitized stainless steels (chromium carbides precipitated at grain boundaries) have been found to crack in the heat-affected zones. Lightly sensitized areas show the intergranular attack of weak acids, while highly sensitized areas have intergranular attack and have failed when overstressed in some reported cases. Plastic coating should be included in the list of stress-resistant materials. Both epoxies and phenolic-epoxies have been used as vessel coatings in temperatures as high as 300 F to 350 F.

202.025 DISSOLVED OXYGEN AND WATER: While moisture and oxygen in storage tanks may be introduced with the oil, much of it is drawn into the tanks by breathing during temperature changes and pumpings. The amount of moisture and oxygen, and consequently the corrosion rate, is therefore proportional to the number of temperature changes and the number of pumpings. The moisture condenses on the roof and the shell, and corrosion occurs in the vapor space.

Crude and heavy oils form a more or less permanent film on the working portions of the shell, and the corro-



FIG. 13—A Severely Corroded Cone-Roof Tank Roof.

sion in tanks handling these stocks always occurs above the upper working level, generally on the roof and top shell ring unless there is corrosive water present. Vapor-space corrosion in crude- and heavy-oil tankage is illustrated in Fig. 13 through 15.

Light stocks, such as gasoline, do not form such a protective coating, and corrosion in these tanks is generally more severe in the middle shell rings because



FIG. 14—Severe Corrosion of Cone-Roof Tank Roof.

Note corrosion at roof edges, along seams, and under water-spray header.



FIG. 15—Severe Vapor-Space Corrosion of Cone-Roof Tank Column.

these areas undergo more wetting and drying than others. Corrosion of the bottom and bottom shell ring of tanks handling light stocks is generally not severe unless a bottom layer of corrosive water is carried in the tank. Fig. 16 through 19 show corrosion in light-stock storage tanks.

Corrosion of light-stock storage tanks is generally of the pit type and is believed to be the result of entrained and dissolved water and of dissolved oxygen, the corrosion being proportional to the water and oxygen content. The rate of corrosion may also be accelerated by traces of other corrodents in the light oils.

Laboratory studies of this type of corrosion indicate that globules of water form on the metal, and corrosion occurs under each droplet in the form of a pit. The pits are so numerous, however, that corrosion appears to be general. The mechanism of corrosion is believed to be the initial conversion of iron to ferrous hydroxide, which is subsequently converted to the hydrates of ferrous or ferric oxide, depending on the amount of oxygen pres-

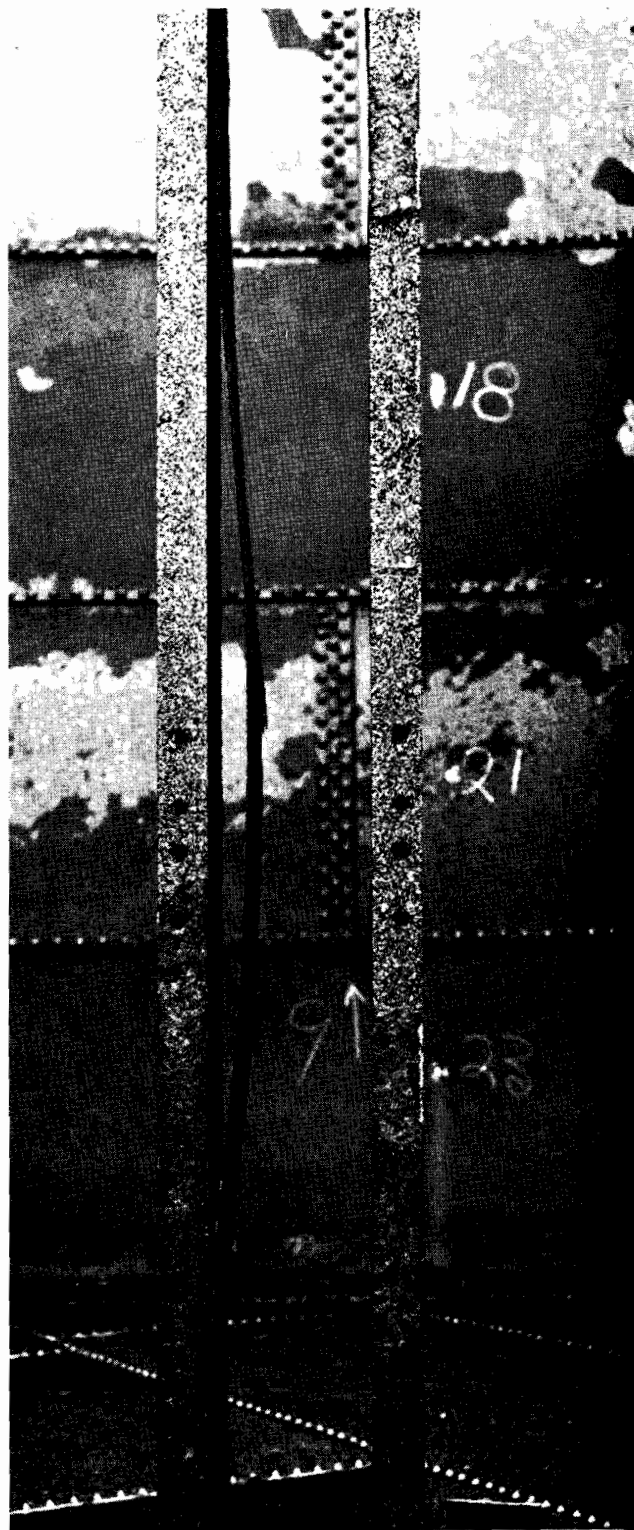


FIG. 16—Corrosion of a Column in a Light-Stock Storage Tank.



FIG. 17—Close-up of Corrosion of the Column Shown in Fig. 16.

Note loose heavy scale.

ent. The final residue is generally found to be ferric oxide, a red rust.

In all cases of storage tank corrosion, it should be recognized that mill scale will accelerate attack, particularly on the bottom of storage tanks. Cracks in mill scale form anodic areas with the remaining mill scale being highly cathodic.

202.026 ORGANIC ACIDS: Organic acids are not very corrosive at low temperatures. At their boiling temperatures, however, these acids are very corrosive, the most severe form of which generally occurs upon condensation. Under these conditions, corrosion rates as high as 0.35 in. per year have been reported on carbon steel.¹³ The rate decreases rapidly with temperature, and is only 0.025 in. per year at 20 F below the boiling point. The corroded surface of carbon steel is very smooth, and metal losses are not apparent from visual inspection.

California asphaltic crude oils contain naphthenic acids, and these acids may be very corrosive at high temperatures.¹⁴⁻¹⁶ The lower molecular-weight acids from light lubricating distillates appear to be more corrosive than the higher molecular-weight acids from heavy lubricating distillates. These organic acids are very corrosive above 500 F, and the reaction is most severe in the liquid phase just as the lubricating fractions are being condensed. Copper alloys are more resistant than steel and 5-9 chromium steels, but chromium-nickel stainless steel (Type 316) is normally very resistant to naphthenic acid. However, in areas of high velocity or impingement, Type 316 stainless steel has been found to be attacked $\frac{1}{16}$ in. to $\frac{1}{8}$ in. per year. Stainless Alloy 20 and aluminum (if securely held in place) are resistant.

Organic acids, such as acetic, propionic, palmitic, stearic, and oleic, react with aluminum at a very low corrosion rate at 200 F; but at 570 F the reaction is very rapid.¹⁷ The reaction rate at high temperatures is apparently independent of oxygen concentration, but is greatly influenced by the presence of water. The addition of 0.05 percent of water practically inhibits all corrosion as a result of formation of a stable oxide film; whereas in the anhydrous (dry) state, the rate of corrosion is very rapid near the boiling point of the acids.

202.027 NITROGEN COMPOUNDS: Nitrogen compounds in crude oil alone do not contribute to a corrosion problem. However, after decomposition in catalytic cracking, the ammonia and cyanides formed contribute to problems discussed in earlier paragraphs, such as high pH for hydrogen blistering in which the cyanides remove the protective polysulfide scale. In hydrocracking, the ammonia and hydrogen sulfide form ammonium hydrosulfide which causes serious corrosion problems at temperatures below the water dew point. Also, the presence of ammonium hydrosulfide in sour water stripping systems is becoming a widespread problem.

Ammonia formed in any cracking or hydrocracking unit limits the use of any copper alloys in product coolers because of their attack in areas where protective scale may have spalled. Both ammonia and cyanides attack copper and brasses (and probably other copper alloys) in a pitting or worm-holing type attack. With both chemicals present, there have been reported indications of reversal of anode and cathode where



FIG. 18—Close-up of Corrosion on Underside of Floating-Roof Tank in Light-Stock Service.

brass is in contact with steel, with the brass being corroded. Such locations have been where brass tubes pass through exchanger cross baffles and where copper gaskets contact steel floating heads and tube sheets.

Considering sources other than elements in crude oil, nitrogen compounds (oxides of nitrogen) can form at high temperatures in the flue gases of furnaces from the nitrogen in the combustion air. These compounds can be highly corrosive to steel if cooled to low or ambient temperatures in the presence of water condensate. A high percentage of excess air and sulfur trioxide in the flue gas can increase corrosion appreciably if these gases are pressurized. Stainless steel or plastic linings may be required for protection.

202.03 Corrosive Materials Added to the Process

202.031 INTRODUCTION: Although corrosion costs from corrodents naturally present in the crude oil rep-

resent a major portion of the estimated total corrosion cost of 11.25 cents per barrel of crude, the acids and other chemicals added and used as treating agents, absorbents, catalysts, and the like, in the various refinery processes probably cause the most rapid deterioration. Materials of this nature most widely used in the refining industry are:

- Sulfuric acid and hydrogen fluoride
- Phenol
- Phosphoric acid
- Caustic—sodium hydroxide
- Mercury
- Ammonia
- Chlorine
- Aluminum chloride

202.032 SULFURIC ACID AND HYDROGEN FLUORIDE

a. Alkylation Units: Alkylation units use sulfuric acid, in concentrations from 85 to 95 percent (b

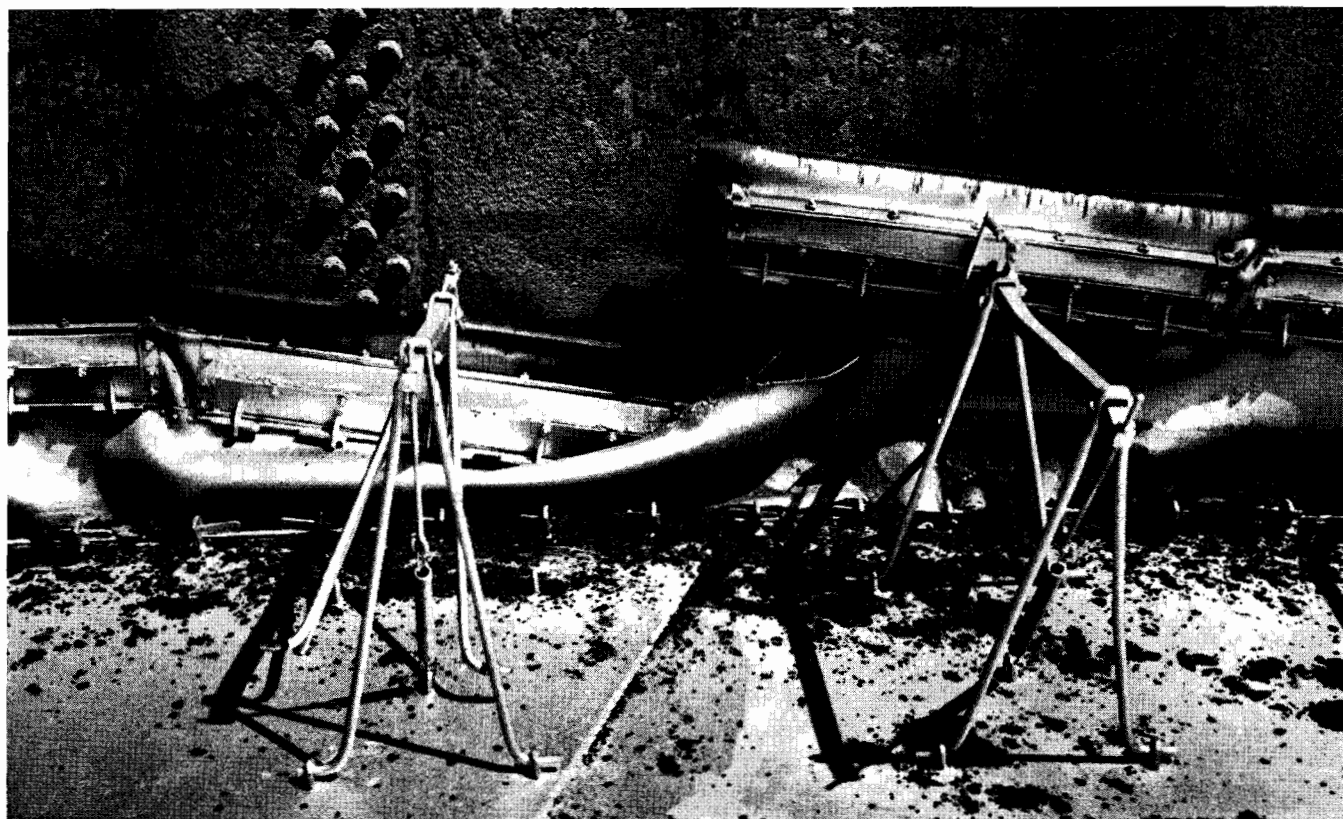


FIG. 19—Corrosion of the Top Shell Ring of a Floating-Roof Tank in Light-Stock Service.

weight), as a catalyst. Traces of acidic material in the product are scrubbed out by means of water, or neutralized by caustic, or both. This scrubbing step may not be complete, so that in alkylation units it is possible to have very high concentrations and very low concentrations of sulfuric acid present. The lower concentrations come as a result of either direct carryover into the fractionating equipment or breakdown of sulfuric acid esters. The corrosion occurring in the equipment may be very erratic, and it appears that there may be some very close correlations between corrosion and acid strength. Ester formation is a function of initial acid strength; that is, the lower the initial acid strength, the higher the ester content and, consequently, the greater the amount of sulfuric acid formed by ester breakdown. For the weaker concentrations, corrosion is generally found in the form of pits or general metal loss with pits. These may be found below the liquid level in the bottom of towers, drums, trays, and generally throughout the circumference of piping. The corrosion rate is affected by temperature, the corrosion being more severe at higher temperatures. Monel resists weak acid corrosion satisfactorily in the absence of air; thus thorough washing is required during shutdowns.

The higher concentrations of 85 percent or more are not usually very corrosive as long as the temperature is below 100 F and velocity is below 4 ft per second.

Carbon steel suffers little or no corrosion in this service. Attack that is a combination of corrosion and erosion will appear at the points of highest velocity or at points of turbulence. The latter type will normally be found at such locations as in or downstream of ells, and in or downstream of tees where a second stream enters at the tee, or where a high-alkaline material, such as caustic, is added for neutralization. The increase of corrosion at the neutralization point is probably the result of the increased temperature caused by the neutralization of acidic elements by caustic. In some instances, even Hastelloy B is attacked too rapidly to justify its expense. Linings, such as Penton, Teflon, and others, have been found most resistant in the neutralizing areas. Chromium-nickel stainless steels, such as Type 304 or Type 316, usually show negligible corrosion at points of increased velocity, except in pumps. Corrosion is usually slight in Alloy 20 (20 Cr-29 Ni) steel pumps. Although corrosion on carbon-steel valves is not usually very severe, the slight attack on the seating surfaces is sufficient to cause leakage. An Alloy 20 chromium-nickel valve trim is generally used in these locations.

In some alkylation units, hydrofluoric acid is used in place of sulfuric acid. Hydrofluoric acid is very corrosive to steel unless care is taken to keep concentration above 65 percent hydrogen fluoride, but if the

acid is air free, particularly in critical areas, monel can be used over a wide range of concentrations and temperatures. Otherwise, the more expensive materials, Hastelloy C or platinum, might be considered. Alloy 20 can possibly be used at ambient temperatures below 50 percent concentration with reasonable life. Alloy 20 should generally not be used above 175 F for a concentration of 15 percent or less.

b. Olefin-Extraction Units: In the extraction of olefins, sulfuric acid is used in concentrations from 45 to 98 percent (by weight), the temperature varying from atmospheric to 250 F. Because of the wide range of concentrations and temperatures, corrosion in these units may be very severe.

In these operations, olefins are absorbed in sulfuric acid of a suitable concentration. The attack of hot, strong acid on carbon steel is usually in the form of deep pits in any crevices or dead spots in the equipment and general etching of the surface. Although carbon steel is generally a satisfactory material for the higher concentrations, the heat generated during the absorption stage does not permit its use. Stainless steels, Type 304 or Type 316, are sometimes used in this service; and when corroded, they exhibit a rough-etched surface having the feel of emery paper. Stainless steels of the Alloy 20 (20 Cr-29 Ni) composition sometimes used in these locations will etch out so that they have the feel of "velvet." Cast iron has a relatively low corrosion rate in this service and is used for such parts as tower trays and accessories.

Following the absorption step, the olefin-acid mixture is hydrolyzed, and this may make it very corrosive to carbon steel. This is particularly true in areas where the carbon steel contains welds. The attack on steel is by deep grooving either in the weld proper or in the heat-affected zone on either side of the weld. In areas away from welds the corrosion in this service is very uniform, and visual inspection may be misleading.

In some units, materials such as monel, Hastelloy B, the copper-base alloys, and lead have been employed, together with the nonmetallics such as graphite and carbon brick. The corrosion found on monel is a general metal loss, and pits are very infrequent. Hastelloy B exhibits similar characteristics. The copper-base alloys may corrode severely at such points as Van Stone or flanged pipe joints where turbulence may be set up by gaskets. Where butt welds of copper-base alloys are involved, severe attack of the weld metal may occur when improper filler rod has been used. This material will generally have the appearance of a sponge.

Carbon brick shows no deterioration in this service. Acid brick will spall and require replacement after a service life of from 4 to 10 years.

The product of hydrolysis is generally both caustic and water-washed. Caustic-scrubbing facilities are normally fabricated from a material such as monel; and, where there is only a small amount of acid present, this material gives excellent service. Where unusually large

amounts of acid are permitted to enter the scrubbing equipment, monel will corrode uniformly with no pitting. Carbon-steel vessels can be used for water washing if the acid components are neutralized by prior caustic washing. Where quantities of acid enter this steel equipment as a result of inadequate neutralization, corrosion may be found in both the form of pits and thinning of large areas by general corrosion. The welds and the heat-affected zones on either side of the welds may be attacked in such a manner as described previously.

c. Acid-Concentration Facilities: Sulfuric acid used in the processes mentioned in the foregoing paragraphs must be concentrated from a lower strength to a strength at which it can be reused. There are several methods of performing this operation, but the most common is the use of a tank into which tubes supplying heat for evaporation of water are inserted. This is probably the most corrosive process in which sulfuric acid is handled. Initial concentrations may be as low as 45 percent (by weight), and the final concentrations may be as high as 95 percent (by weight). These tanks are generally made of a carbon-steel shell lined with either a loose lead lining or a homogeneously bonded lead lining which is also lined with acid brick, carbon brick, or carbon block. The heating elements through which the heating medium flows are made of Hastelloy D, high-silicon cast iron, or tantalum.

Attack of the carbon block or brick by hot acid is very moderate, and this material gives long, trouble-free service where proper joints are used. Acid brick, as in the case of pressure vessel linings, spalls and may require replacement about every five years. In addition, most acid brick exhibits a swelling characteristic which causes partition walls to arch, and which may exert enough pressure on the inside of the vessel to cause mechanical failure of the vessel wall. This is particularly noticeable where riveted angles are used to fasten the individual parts of the vessels together. The lead linings in these vessels, even though they are subjected to acids of various strengths, are not affected unless the inner brick or carbon lining deteriorates to such a point that circulation of hot acid against the lead occurs. Corrosion is in the form of pits or general thinning accompanied by a coating of white lead sulfate.

Tantalum heating elements, sometimes employed in sulfuric acid reboilers, are corrosion free where the temperature of the heating medium does not exceed approximately 350 F. Tantalum may suffer hydrogen embrittlement when placed in direct contact with other materials, such as lead or carbon, in the concentrator. This will usually result in a portion of the tube being very brittle and breaking. Vibration of the tubes may cause either fretting corrosion* or fatigue. Fretting corrosion is found under stiffening clamps which are

* "Corrosion at the interface between two contacting surfaces accelerated by relative vibration between them of amplitude high enough to produce slip."¹⁸

generally used on multiple-tube assemblies. High-silicon cast-iron heating elements exhibit almost complete resistance to all concentrations of sulfuric acid. Hastelloy D heating elements are very resistant to sulfuric acid, except in the range of 55- to 60-percent concentration (by weight) at boiling temperatures of the acid. At these concentrations, corrosion rates vary widely, depending on the contaminants that are present. Corrosion of Hastelloy D occurs in many forms. There may be a general thinning of the heater-element barrel, attack of the tube and cap on either side of the joining weld, deep grooving of the welded areas, and "island" type of corrosion on both the barrel and cap. A severely corroded Hastelloy D heater tube is shown in Fig. 20 and 21. Where vacuum-type concentration is employed, the corrosion of Hastelloy D tubes is of the general thinning type, while the pitting and grooving is severe where pressure concentration is used. The primary difference between the two methods (pressure and vacuum) is that of temperature, the vacuum process using the lower temperature.

Pipe used to convey the hot concentrated sulfuric acid to acid coolers is usually made of carbon steel with a lead and carbon liner. Corrosion in this pipe is nil, except at the joints where some general thinning may occur on the exposed lead gasket faces.

The shells of sulfuric acid coolers are generally constructed on the same order as the concentrators. Lead cooling coils are used at the higher temperatures and exhibit general thinning. Cast iron and carbon may also



FIG. 20—A Severely Corroded Hastelloy D Heater Tube.
Note hole near cap at end of tube.



FIG. 21—Close-up of the Tube Shown in Fig. 20.
Note how corrosion has concentrated near the cap and on the weld between cap and tube.

be used for this service. Pumps and valves for the hot concentrated acids are made from high-silicon cast iron, Hastelloy D, or carbon. The high-silicon cast iron and the carbon exhibit poor physical properties, but do not corrode. Hastelloy D is attacked in the same manner as described for the heating elements. Where velocities are in excess of 4 ft per second and the temperature is below 150 F in locations such as pumps and valves, Alloy 20 stainless steel is often used. The corrosion resistance of this material varies with the degree of heat treatment, and deep intergranular etching may be found on all surfaces exposed to the acid, as shown in Fig. 22; however, this condition is not usually serious.

202.033 PHENOL: Phenol (carbolic acid) is used in refinery operations in the manufacture of lubricating oils and aromatic hydrocarbons because of its affinity for naphthenes and aromatic hydrocarbons. A phenol-treating unit usually consists of three sections: treating, dephenolizing, and phenol recovery.

The treating section, where the feed is contacted with the phenol, operates at temperatures below 400 F. Carbon steel resists attack in this section provided that water is not present.

The dephenolizing section, which processes the lubricating stock-phenol mixture from the treating section, separates the phenol from the treated oil. No corrosion of carbon steel occurs in this section.

The phenol-recovery section processes spent phenol from the treating section and removes the extract. Although experience indicates that each piece of equipment in this section may have a completely different corrosion history during different periods of operation, corrosion on carbon steel is generally slight. The corrosion is very erratic, however; and, when it occurs, may be as severe as 0.12 in. per year, especially in turbulent

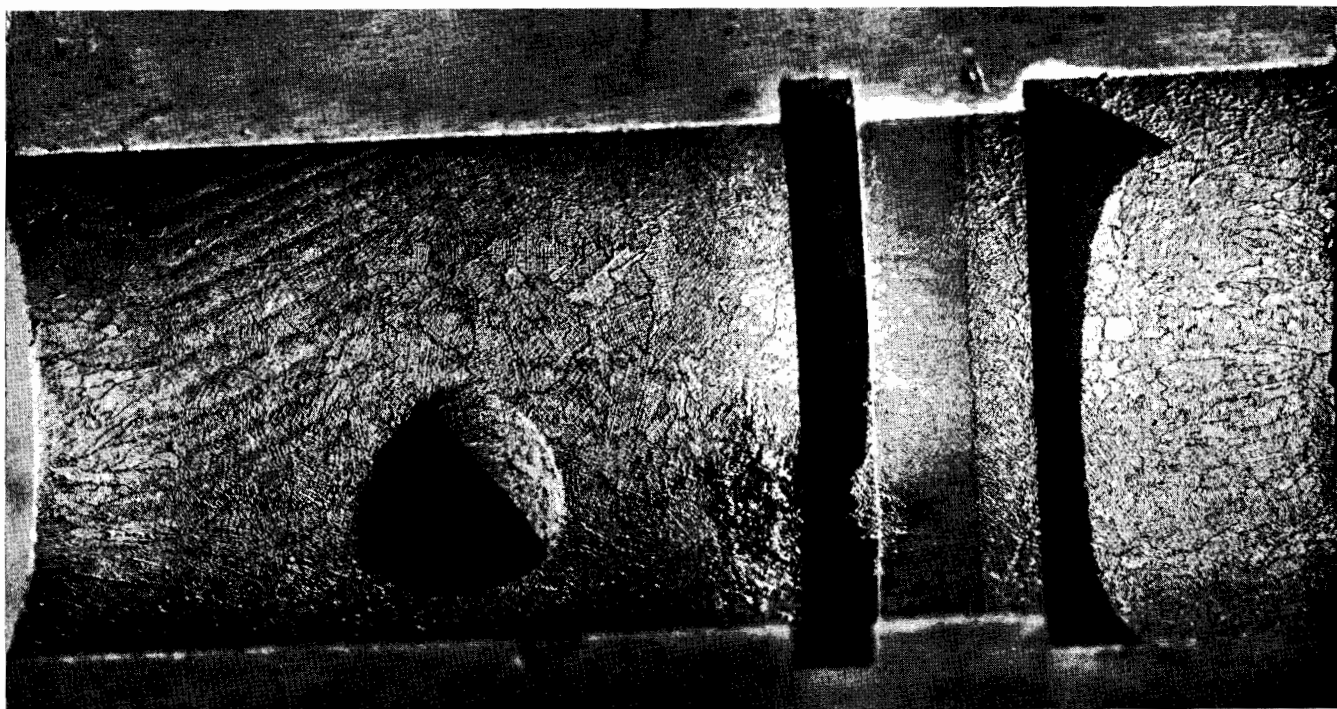


FIG. 22—Close-up of a Section of a 20 Chromium-29 Nickel Steel Pump Casting That Has Been in Sulfuric Acid Service. Note deep intergranular etching.

high-velocity service. Above 400 F, carbon steel may corrode rapidly in phenol service. In both liquid and vapor phases, Hastelloy C and Type 316 steel furnace tubes and headers are resistant to attack. Experience has shown that certain 18 chromium-8 nickel stainless steel suffers stress corrosion cracking in phenol drier towers, where the temperature is approximately 225 F. Very little corrosion occurs on copper-alloy heat-exchanger and condenser tubes.

202.034 PHOSPHORIC ACID: Phosphoric acid is used as a catalyst in polymerization units either in liquid form or as the pentoxide deposited on small clay pellets. Where water is permitted to contact the acid, severe corrosion of carbon steel, either of the general or pitting type or both, may occur. Corrosion rates increase with increasing temperature. Corrosion is usually found in dead spots in the equipment where circulation does not occur or is restricted. Such locations include piping manifolds, the bottom of kettle-type reboilers, welds without full penetration, and parts of exchangers where there is sufficient residence time to permit the settling of the acid particles. Contaminants such as chlorides may act as accelerators and increase the normal phosphoric acid corrosion.

Unless water in an amount above that required for hydration is present, corrosion is very rare. Most corrosion probably occurs during water-washing operations at shutdowns. Corrosion directly attributable to excess

water can penetrate a $\frac{1}{4}$ -in.-thick steel tube in approximately 8 hours. Fig. 23 shows a severely corroded exchanger tube. The copper-base alloys are not attacked in this service. Hastelloy B is unaffected by phosphoric acid.

202.035 CAUSTIC—SODIUM HYDROXIDE: Sodium hydroxide is widely used in refinery operations for the neutralization of acid components and for grease manufacture. This material at atmospheric temperature is noncorrosive and can be handled satisfactorily in carbon steel equipment. Carbon steel equipment that is not stress-relieved is subject to stress corrosion cracking due to caustic when the temperature exceeds approximately * the temperature obtained through the use of the following formula:

$$T_s = 170 - ^\circ\text{Be}$$

Where:

T_s = stream temperature, in degrees Fahrenheit.

$^\circ\text{Be}$ = density of the caustic water solution, in degrees Baumé.

This type of attack is discussed in more detail elsewhere in this section. Where caustic is encountered at temperatures greater than 200 F, it will also cause general corrosion of carbon steel. The 18 chromium-8 nickel stainless steel, Type 304, is subject to stress

* Time and stress level are factors.

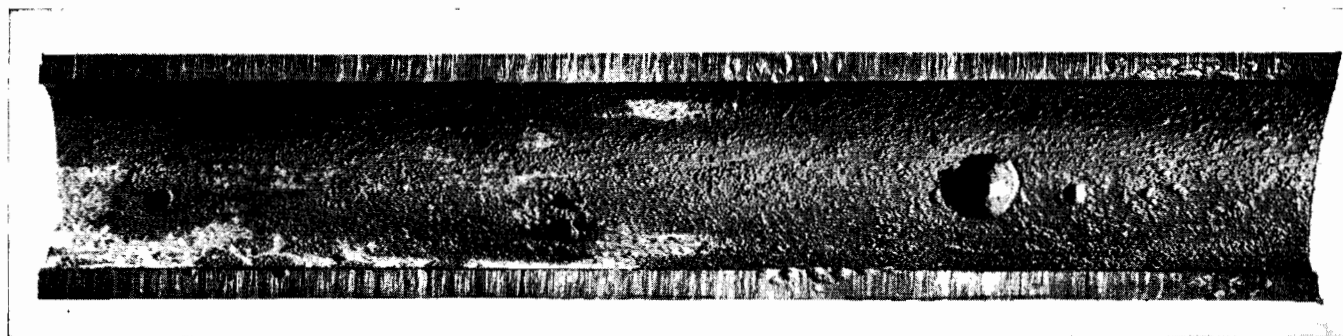


FIG. 23—Close-up of Phosphoric Acid Corrosion of a Carbon-Steel Reactor Feed Reactor Product Exchanger Tube in a Polymerization Unit.

This corrosion resulted from water in the reactor product.

corrosion cracking in or adjacent to welds or at other points of high stress concentration at temperatures over approximately 400 F. Monel and nickel are resistant to attack even at temperatures in excess of 400 F, provided the content of sulfur compounds is low.

202.036 MERCURY: Mercury is sometimes used in instruments in a refinery. Occasionally, it may be forced into the operating equipment through some malfunction of the instrument and will cause stress corrosion cracking of monel and copper-base alloys. This type of attack is discussed in more detail elsewhere in this section. Mercury is also extremely corrosive to aluminum.

202.037 AMMONIA: Ammonia is used in the refining industry as a refrigerant and for the neutralization of acidic components in such locations as the overhead streams from pipe stills and catalytic cracking units. Where this material is permitted to contact copper-base alloys in pH ranges of 8.0 and above, severe corrosion in the form of general metal loss and stress corrosion cracking will occur. The general attack may be identified by the appearance of a blue salt. Ammonia attack of copper-alloy equipment may result in severe fouling. An example of this could be a leaking safety valve in ammonia service discharging to a blowdown system serving other safety valves. If copper-base alloys are used in other safety valves in the same system, they may become inoperable as a result of fouling from corrosion products.

202.038 CHLORINE: Chlorine is used in refinery operations to treat cooling-tower water, for the manufacture of sodium hypochlorite for treating oils, and in special processes. For services in which no water is present, corrosion of carbon steel is slight. Where small amounts of moisture come in contact with chlorine, it becomes very corrosive, except on materials such as Hastelloy C, titanium, zirconium, rubber, polyvinyl chloride, saran, or other nonmetallics.

Where sodium hypochlorite is being manufactured, the point where chlorine and caustic are mixed will

suffer severe corrosion unless constructed of one of the materials listed in the foregoing paragraph. In other parts of the system, corrosion may be erratic, varying from nil to rates of more than 1 in. per year.

202.039 ALUMINUM CHLORIDE: Aluminum chloride is used as a catalyst in isomerization units and exhibits little corrosion so long as no water is present. In the presence of water it hydrolyzes, forming hydrochloric acid, and severe corrosion of carbon steel by pitting may occur. Austenitic stainless steels in a wet system handling this material will suffer severe intergranular and stress corrosion cracking.

In isomerization units the most corrosive environment is the molten aluminum chloride salt. In areas of high velocity, nickel corroded at rates up to 0.05 in. per year. Hastelloy B has been found to be resistant to corrosion except around cold-worked or unannealed welds where stress corrosion cracking occurs in the weld and heat-affected zones or stressed areas.¹⁹ Failures of this nature occur rapidly in strip lining, but piping in the as-welded condition is normally useful for 5 to 10 years before failures occur in welds. Since welding is difficult with coated electrodes and only satisfactory when TIG welded in the down-hand position, original weld flaws such as microfissures, probably contribute most to the failures. Both cold working and stresses contribute to failure by stress corrosion cracking.

Hastelloy overlays on steel appear satisfactory. Nickel overlays are normally attacked rapidly because of the iron dilution.

Hastelloy D in the as-cast or as-welded condition renders a useful life of several years for any wearing parts in this service.

202.04 Environmental Corrosion

202.041 REFINERY ATMOSPHERES: Inasmuch as carbon steel is the most common material of construction for refinery equipment, the discussion of atmospheric corrosion will be limited to this material. When

metals such as iron or steel are exposed to the atmosphere, they will corrode because of the presence of water and oxygen. It has been shown that below 60 percent humidity, corrosion of iron and steel is negligible,²⁰ and the lower the amount of oxygen absorbed in the water, the lower the corrosion rate.

Atmospheric corrosion is principally "galvanic," the base metal acting as the anode (electron provider) and a compound of the base metal, such as an oxide, acting as a cathode (electron receiver).¹² Thus the only other factor needed is water, which provides the electrolyte (electron path). If impurities are present in the water, it becomes a better electrolyte and the rate of corrosion is increased. Thus, to prevent atmospheric corrosion, it is necessary only to eliminate the water from the surface of the metal by means of a protective barrier or coating.²¹⁻²³

The normal rate of atmospheric corrosion of unpainted steel in rural atmospheres is low; it ranges from 0.00097 to 0.00734 in. per year.²⁴ However, in some atmospheres it corrodes much more rapidly, and a corrosion rate of 0.05 in. per year is common. The rate of corrosion is also accelerated at any break in a protective coating. At such breaks, deep pits will form and the steel will corrode at even greater rates because the base steel at the break will form a galvanic cell, the

steel acting as the anode and an oxide acting as a cathode. Fig. 24 illustrates the accelerating effect of breaks in a protective coating. There are usually certain areas that are subjected to accelerated corrosion. Equipment located adjacent to boiler or furnace stacks is subjected to corrosive gases, such as sulfur dioxide and sulfur trioxide. These gases, when dissolved in water, form acids. Thus dew from water vapor in the flue gas, rain, or mist in this area becomes a weak acid which acts as an electrolyte. In addition, chlorides, hydrogen sulfide, cinders, fly ash, and chemical dusts are also present in industrial atmospheres and may act in a like manner.

Corrosion rates of galvanized iron and aluminum in refineries vary greatly, depending on the location. In some locations galvanized iron fencing has a life of from 5 to 10 years, and penetration of aluminum weather coating has occurred in 2 years. If these materials are used together or with more noble metals, such as steels, without being electrically insulated from each other, severe galvanic corrosion may result.

202.042 DISCUSSION OF SPECIFIC PROBLEMS: Although atmospheric corrosion in the refining industry is ordinarily not as important from a safety standpoint as the other types of corrosion discussed, it is costly



FIG. 24—Faulty Paint Job on this Tank Roof has Resulted in Accelerated Corrosion.

and is often overlooked. The following paragraphs discuss specific examples of atmospheric corrosion.

a. Corrosion Beneath Insulation and Under Fireproofing: Cracks in insulation allow moisture to penetrate to the steel, and hidden corrosion takes place. This occurs in vessels and piping operating below approximately 250 F, and is often very severe in refrigeration systems. Cracks in fireproofing concrete, particularly at the top where the concrete ends, also allow moisture to penetrate to the steel and cause hidden corrosion (see Fig. 25 and 26).

If stainless steel is insulated, an inhibited insulation or one with very low content of water soluble chloride insulation material should be used to prevent stress corrosion cracking. Coatings may be useful especially in seacoast areas where the chloride can come from the air rather than from the insulation.

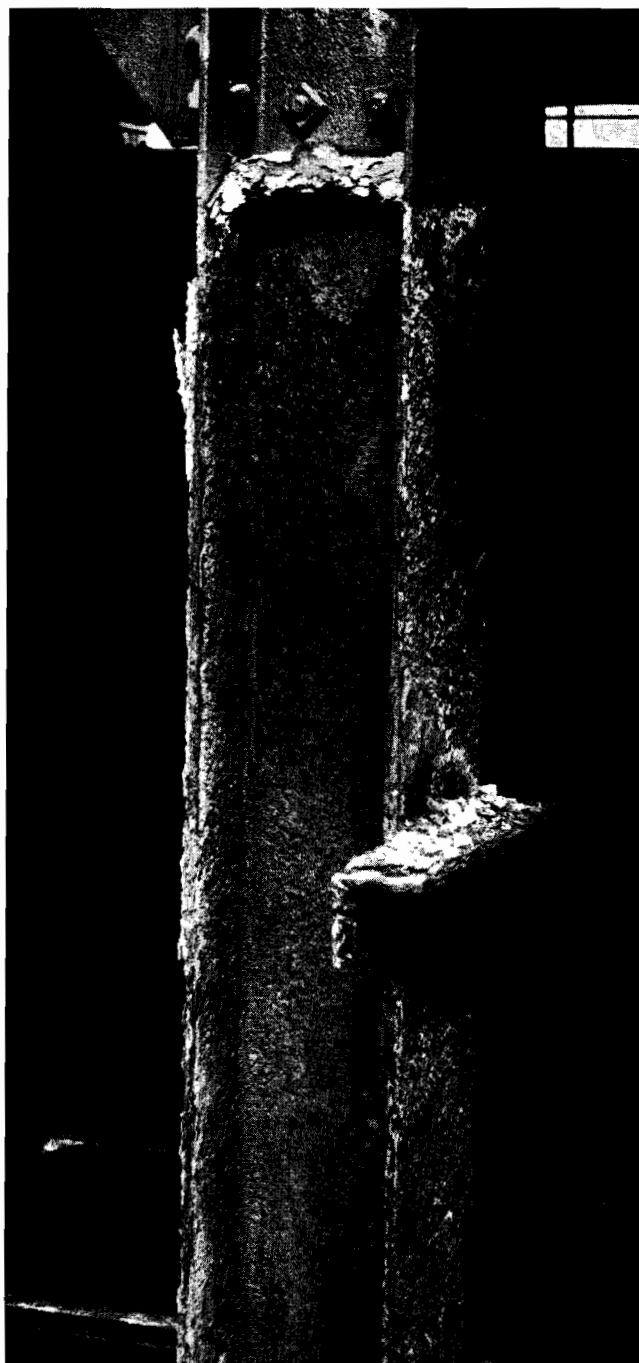
b. Corrosion of Pipelines: The installation of pipelines directly on the ground leads to severe corrosion on the bottom of the lines because of dampness. Fig. 27 and 28 illustrate the damaging effects on pipelines laid



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FIG. 25—Disintegration of a Concrete-Encased Beam Supporting a Heated Vessel, Resulting from Water Seepage Through the Concrete.

Note almost complete disappearance of web which was unknown before concrete insulation was removed.



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FIG. 26—Corrosion of a Steel Column on a Process Structure, Resulting from Water Seepage Behind Brick Insulation Over a Long Period of Time.

directly on the ground. If grass or weeds are allowed to grow beneath and around pipelines, the pipe will remain damp for long periods and corrode. Lines laid directly on supports or hung by clamps often corrode at the point of support because of crevice corrosion



FIG. 27—Half-Buried Lines Such as These Suffer Severe Corrosion of the Type Shown in Fig. 28.

(see Fig. 29 and 30). (See also references 25 and 26 for other pipeline problems.)

c. Corrosion of Structures: Structures that provide crevices where water may enter and remain for long periods may suffer severe corrosion. Examples of such construction are structural members placed back to back, and platforms installed close to the tops of towers or drums. Structures located near furnace stacks or near cooling towers are particularly susceptible to this type of attack.

d. Cooling Water Corrosion: Many engineers concentrate their corrosion protection efforts on the process

side of a refinery unit and do not concern themselves as much as they should with corrosion resulting from the use of cooling water. Equipment failure, downtime, and production loss caused by cooling water can be very costly.

The selection of neutralizers, chemicals for control of living microorganisms and scale, and the use of corrosion inhibitors depends upon the type of cooling system, once-through or recirculating, and the composition of the water. The economics of selection of proper treatment are generally minor compared with the savings that can be realized. The equipment construction materials exposed to cooling water must be carefully considered at all times along with any treatment of the waters.

Neutralization of water to proper pH level is essential for corrosion and carbonate scale control; generally sulfuric acid, caustic, or soda ash are used. Hardness (calcium carbonate, in parts per million), carbon dioxide and oxygen contents, and alkalinity of the cooling water are important considerations.²⁶ Living microorganisms in the cooling water are generally controlled by the use of chlorination or nonoxidizing biocides.

The most widely used corrosion inhibitors for cooling water systems are the polyphosphates, silicates, chromates, nitrites, and a combination of these chemicals with metallic anions. Sodium chromate or nitrite inhibitors in about 8 pH water are very effective if scaling is not a problem. However, these chemicals are generally restricted to closed-water systems (such as engine-jacket cooling) where leakage is nil and blowdown to disposal is unnecessary. Chromates and nitrites can be toxic when discharged in significant volume.

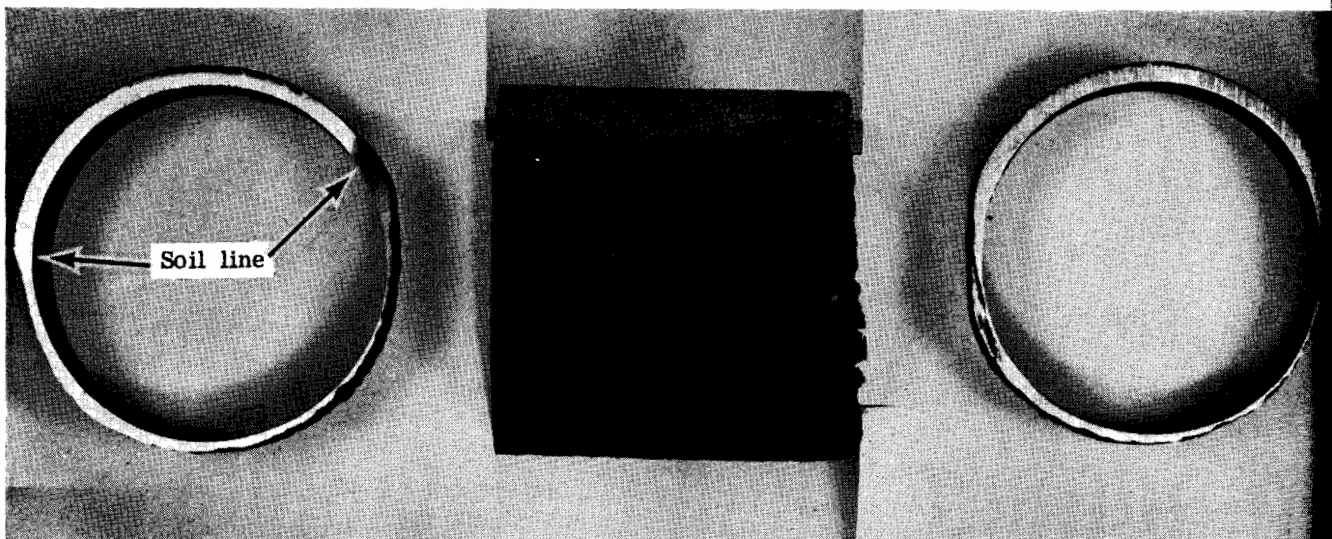


FIG. 28—Advanced Stage of Ground-Level Corrosion on Partially Buried Lines.
Note perforations in centerpiece.

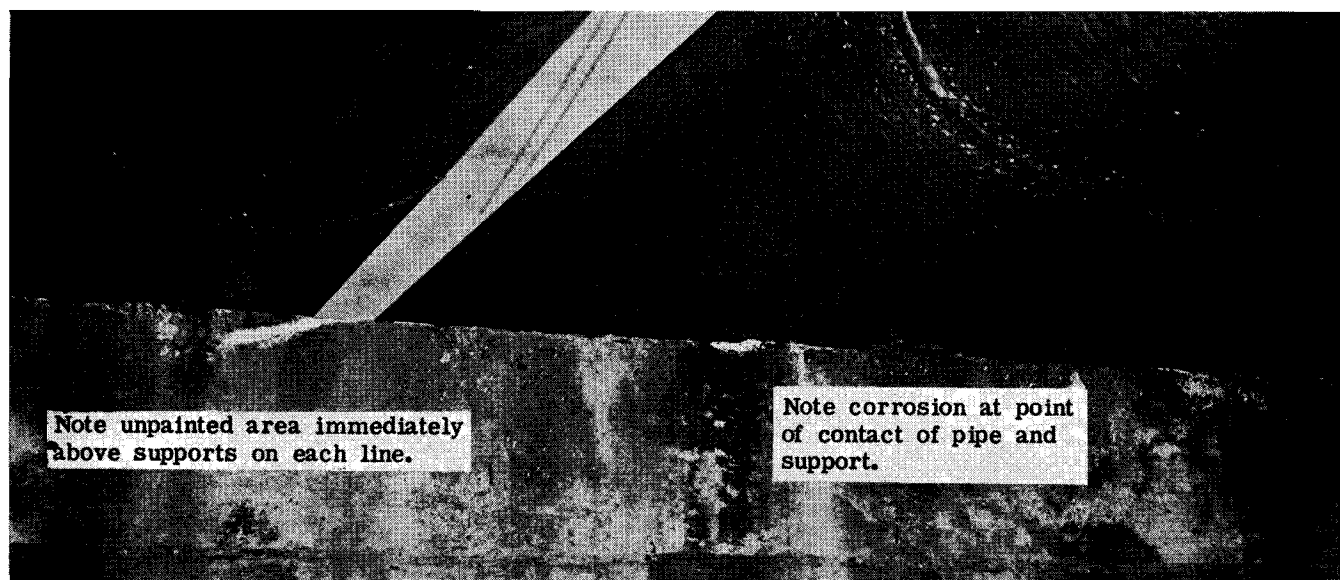


FIG. 29—Lines Resting on Concrete Pipe Supports.

In most treated cooling water systems, steel tubes, pipe or cast or wrought iron parts can be used if water velocities can be kept above 5 ft per second. Otherwise, inhibited admiralty tubes with water velocity below 10 ft per second have been found more effective if tube sheets are of copper alloy. In some systems aluminum bundles have been found to be effective.

Economic condenser tube materials for brackish or sea water are special problems, and velocity is an important consideration. Cupro-nickel (particularly the iron-bearing type) is widely used. Aluminum brass, monel, and stainless steels have had variable performances. The stainless steels can be subject to severe pitting and stress corrosion cracking. For piping, plastics and cement lining should be considered.

Wherever carbon steel is used and severe corrosion is encountered, properly applied coatings and cathodic protection may be used to extend equipment life.

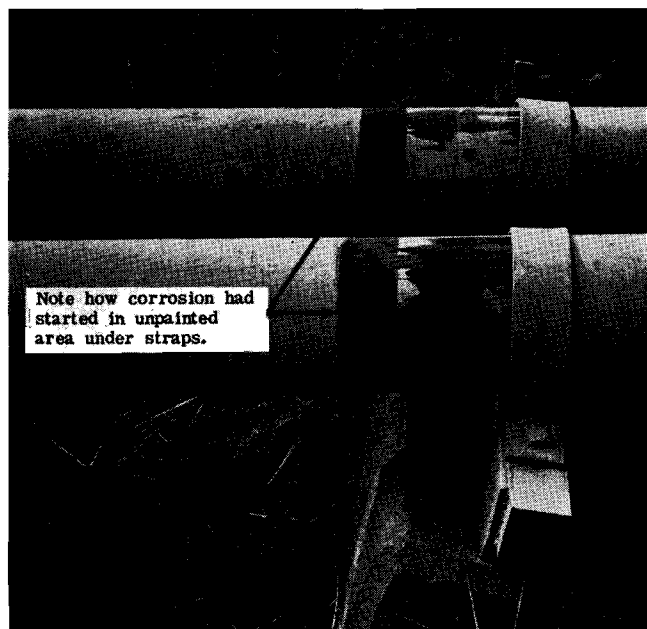
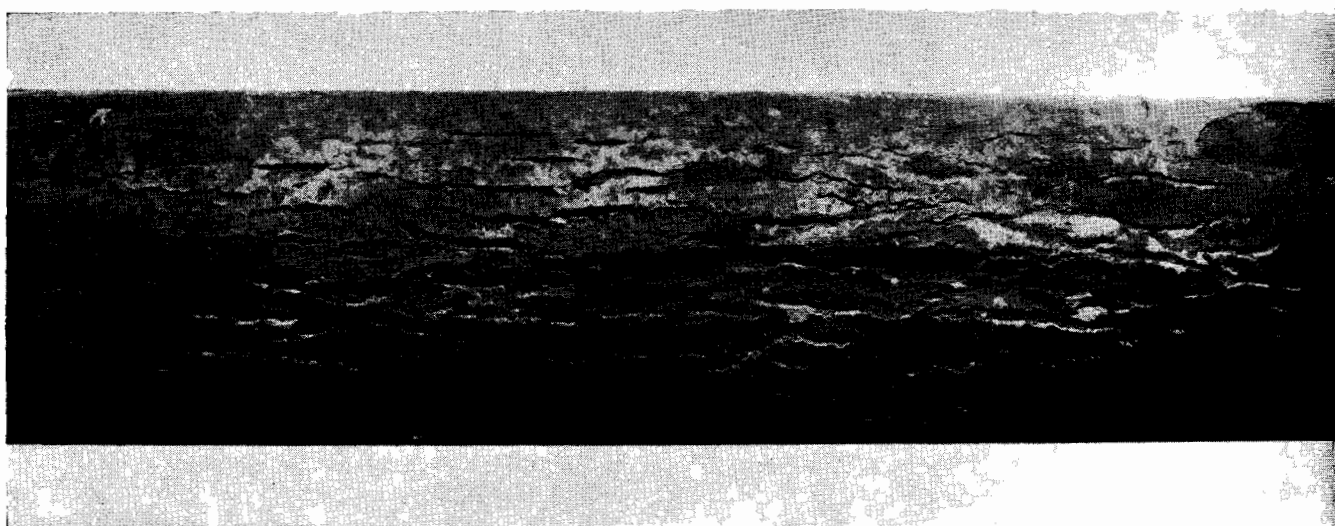


FIG. 30—Corrosion Under Clamps on a Pipeline.
Movement of lines has caused clamps to slip and support to tip.

202.05 Corrosion at High Temperatures

202.051 INTRODUCTION: Chemical elements that have little or no effect on metals and alloys at atmospheric temperatures may become extremely corrosive at high temperatures, resulting in severe scaling, cracking, disintegration, brittleness, or weakness. Oxygen, for example, which has relatively little or no effect (in the absence of moisture) on steel at atmospheric temperatures, can become extremely destructive at high temperatures where it unites with iron to change what was once steel into a weak, brittle mass of iron oxide. A discussion of the role of some of the more potent materials causing corrosion at high temperatures is presented in this section.

202.052 OXYGEN: Oxygen reacts with steel at high temperatures to cause scaling. In petroleum refining, the oxygen encountered is usually that in the surrounding air (which contains approximately 20 percent of oxygen). A severely scaled carbon-steel heater tube is



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FIG. 31—Example of a Heater Tube Badly Scaled as a Result of Overheating.

shown in Fig. 31. Oxidation in air increases with increasing metal temperatures and decreases with increasing chromium content of the metal. Maximum metal temperatures for low oxidation rates are given in the following tabulation. Above these temperatures oxidation becomes appreciable.^{18, 27, 28}

Material	Temperature (Degrees Fahrenheit)
Carbon steel	1,050
Carbon-molybdenum steel	1,050
½ percent chromium steel	1,075
1¼ percent chromium steel	1,100
2 percent chromium steel	1,150
2¼ percent chromium steel	1,175
3 percent chromium steel	1,175
5 percent chromium steel	1,200
7 percent chromium steel	1,250
9 percent chromium steel	1,500
12 percent chromium steel	1,500
18 chromium-8 nickel steel	1,600
25 chromium-12 nickel steel	2,000
25 chromium-20 nickel steel	2,100

Oxygen at high temperatures reacts with nickel alloys to cause scaling. Spalling, which depends on the expansion characteristics and composition of the oxide formed, and on temperature changes, accelerates oxidation of nickel alloys. The temperature above which oxidation in sulfur-free air becomes significant is given in the following tabulation for nickel and some of the common nickel alloys.^{18, 29-33}

Material	Temperature (Degrees Fahrenheit)
Nickel	1,900
Monel	1,000
Inconel	2,000
Incloy	2,000
Hastelloy A, B, D	1,400
Hastelloy C	1,800
Hastelloy X	2,000 +

Attack of copper and its alloys by oxygen is seldom a problem in refineries because these materials are not used where operating temperatures exceed 700 F. At considerably higher temperatures, such as might be encountered in fires, copper may be attacked by oxygen, with considerable scaling.

Like copper attack, oxygen attack of aluminum and its alloys is seldom a problem because these materials are not ordinarily used where operating temperatures exceed 400 F. Aluminum and its alloys are highly resistant to attack by dry air. This resistance is the result of the formation of a protective film composed of aluminum oxide. Above 700 F the presence of water vapor in air leads to internal oxidation, particularly in those aluminum alloys containing appreciable amounts of magnesium. The presence of small amounts of sulfur dioxide increases, and appreciable amounts of carbon dioxide inhibit this form of attack.¹⁸

202.053 HIGH-TEMPERATURE STEAM: Steam at high temperatures may be decomposed to hydrogen and oxygen, and the free oxygen may cause severe scaling of steels, which, in turn, will cause reduction of cross section and ultimate failure. The rate of scaling in-

creases with steam (and thus metal) temperature, while steam pressure seems to have little effect. In general, the steam temperature at which scaling becomes significant increases with increasing chromium content of the metal. Above the metal temperatures given in the following tabulation, scaling may become appreciable.^{18, 28}

Material	Temperature (Degrees Fahrenheit)
Carbon steel	950
Carbon-molybdenum steel	975
1/2 percent chromium steel	1,000
1 1/4 percent chromium steel	1,050
2 percent chromium steel	1,080
2 1/4 percent chromium steel	1,100
3 percent chromium steel	1,125
5 percent chromium steel	1,150
7 percent chromium steel	1,175
9 percent chromium steel	1,200

The austenitic chromium-nickel stainless steels resist steam oxidation to even higher temperatures, but as a result of their limited use in steam service, actual limiting temperatures are not available. The resistance of these austenitic steels to steam oxidation probably approaches to within 50 F or 100 F the maximum temperature to which good resistance to oxidation in air is obtained with them.

In general, where scaling is a problem, fluctuating temperatures increase the rate.¹⁸ A coating of scale often has some protective effect; it reduces the scaling rate after the initial period. However, on cooling or heating the scaled metal, differential contraction or expansion of scale and metal may cause spalling, thereby exposing the underlying metal to fresh attack. Alternating oxidizing and reducing conditions can also increase the rate of loss.

Above certain limiting temperatures, steam may cause embrittlement of nickel and its alloys from intergranular oxidation. In the following tabulation are listed the maximum steam temperatures at which use of high-nickel materials are suitable.^{18, 29, 30, 32}

Material	Temperature (Degrees Fahrenheit)
Nickel	800
Monel	700 to 800
Inconel 600	1,800
Incoloy 800	1,800
Hastelloys	No information

Steam is not damaging to aluminum and its alloys at temperatures up to 350 F to 500 F. Above this temperature range, steam may attack aluminum and its alloys to form aluminum oxide and hydrogen.¹⁸

Copper and its alloys are seldom used in steam service at temperatures above 560 F because their mechanical properties diminish markedly above these tem-

peratures. Although steam attack can occur at higher temperatures, it has no practical significance.

202.054 VANADIUM OXIDE: Vanadium exists in some fuels, such as the residual fuels derived from certain crude oils, and oxidizes to vanadium pentoxide when the fuel is burned. This oxide, or complex mixture of vanadium oxides and sodium sulfate, precipitates and forms a low-melting flux that prevents protective oxides from forming on steel parts of furnaces, gas turbines, and the like, and promotes accelerated oxidation attack. Apparently these compounds react directly with the steel in some manner, while atmospheric oxygen serves to regenerate the vanadium oxide.³⁴

Studies of the subject indicate that vanadium corrosion does not take place below approximately 1,100 F. This is because vanadium pentoxide compounds must be molten in order to cause the reaction. Although pure vanadium pentoxide melts at a temperature somewhat above 1,100 F, other substances in the fuel-oil ash, such as sodium compounds and sulfur oxides, unite with the vanadium pentoxide and lower the melting point considerably. The molten vanadium pentoxide forms a slag with steel. The molten slag runs off and exposes fresh metal to attack. Corrosive action of fuel-oil ash increases sharply with increasing temperature and vanadium content. For example, the tolerable level of vanadium in fuel oils is in the concentration of 20 to 150 ppm between 1,200 F and 1,550 F, depending on the sodium-vanadium ratio. Under the proper conditions, few, if any, of the steels seem to be immune to this type of attack, but the 60-40 and 50-50 chromium-nickels have proved more resistant to attack than other alloys.

Firing conditions in the firebox can be critical, as they can greatly affect the temperature of the tubes and tube supports. Poor flame patterns can result in high metal temperatures and hence high corrosion rates.

Combustion with low excess air also offers a means of reducing vanadium corrosion. With very low excess air levels, formation of sulfur trioxide in the firebox is minimized, and the resultant vanadium-sodium complexes are less corrosive.

A considerable amount of study has been devoted to this problem. Should a vanadium oxide corrosion problem be encountered, the current literature should be consulted for the latest information. The API has been very active in support of these studies.

202.055 EFFECT OF SULFUR DIOXIDE AND HYDROGEN SULFIDE: The presence of sulfur dioxide at high temperatures, as in furnace gases, increases the rate of scaling of steel through formation of a low-melting-point iron oxide-iron sulfur compound.¹⁸ Hydrogen sulfide has a similar effect in increasing scaling rates.

The extent of the corrosive attack of steels by hot sulfur compounds depends on concentration, temperature, and the oxidizing power of the environment. In combustion gases, minute quantities of salt increase

the corrosion rate. The sodium combines to form low-melting sodium sulfate (Na_2SO_4) and the corrosion rate from hydrogen sulfide or sulfur dioxide appears to increase. Actually, the increase comes with increased salt (normally sodium chloride but any sodium salt will do). Practical observations indicate that the higher the chromium content of the steel, the more severe the sulfur conditions that can be tolerated.

Sulfur in any form has a very detrimental effect on nickel and high-nickel alloys. Sulfur reacts along grain boundaries of nickel and nickel alloys to form a low-melting nickel–nickel sulfide mixture which causes brittleness.^{18, 32, 35–37} At temperatures above approximately 1,190 F this mixture, being molten, penetrates the grain boundaries and leads to disintegration of the metal.

At about 2,000 F, or lower temperatures if stainless steel is sensitized, sulfur corrosion of the austenitic stainless steels (Types 309, 310, etc.) takes the form of intergranular penetration. This can result in a serious loss of strength if the metal is being subjected to tensile loadings.

In oxidizing atmospheres the nickel sulfide is converted to nickel oxide which is a semiprotective oxide surface layer. In reducing atmospheres, however, the formation of sulfide is cumulative, and attack is more severe.

Additions of chromium, iron, and manganese to nickel alloys increase resistance to sulfur attack; in order to prevent or minimize it as service temperatures increase, the chromium content of the alloy is increased and the nickel content decreased.

The nickel materials are unsuitable for use in sulfurous atmospheres much above the maximum temperatures given in the following tabulation.^{18, 29, 30, 32, 33, 35}

Material	Temperature (Degrees Fahrenheit)	
	Oxidizing Atmosphere	Reducing Atmosphere
Nickel	600	500
Monel	600	500
Inconel 600	1,500	1,000
Incoloy 800	About 1,950 F *	. . .
Hastelloys B, C . .	Near 2,000 F	. . .
Hastelloy X	2,000 F	. . .

* The effect of creep at these high temperatures should also be considered.

Sulfur embrittlement of nickel and its alloys in the refinery may occur in equipment operating at high temperatures where a sulfur-containing fuel is burned (furnaces, flare stack tips, etc.), or where sulfur-containing process streams are being handled.

Nickel and high-nickel alloys, when heated in atmospheres that fluctuate between oxidizing (excess of air) and reducing (excess of carbon monoxide or hydrogen), suffer severe intergranular attack with result-

ing embrittlement, even though the atmosphere is sulfur-free.^{18, 35}

Embrittlement of nickel and high-nickel alloys, such as monel and the Hastelloys, often occurs during welding. Not only sulfur, but also lead, phosphorus, and some low-melting metals and alloys react with nickel-bearing materials at the high temperatures encountered during welding.³⁷ Grease, oil, machining lubricants, paint, marking crayons, pipe-thread dope, soap, dirt, and residues from process streams may contain one or more of the undesirable substances.

At temperatures for which copper alloys are employed in refinery service, they are resistant to attack by sulfur gases.

Aluminum and its alloys are highly resistant to attack by sulfur gases.

202.056 THE EFFECT OF HOT CORROSIVE GASES ON CAST IRON (GROWTH AND EMBRITTLEMENT): At temperatures above 800 F all gray cast irons begin to deteriorate, resulting in extreme brittleness, loss of strength, scaling, and growth. Growth results in a permanent increase in size. General scaling is, of course, caused by the same hot gases that cause scaling of steels, and it results in a general wasting away.

Growth of cast irons results both from graphitization and from infiltration of corrosive gases into the structure.³⁸ Graphitization is discussed elsewhere in this chapter. The infiltration of corrosive gases (oxygen, sulfur gases, etc.) apparently causes some sort of internal scaling accompanied by swelling. Such castings are weak, misshapen, and brittle. Some have been known to increase 50 percent in volume.³⁸ The amount of growth is ordinarily proportional to the maximum temperature reached and to the number of heatings. Growth may be found in burner and other furnace parts and, under unusual conditions, in compressor pistons.

Irons most resistant to growth are those with stable carbides and close grain structure, with low total carbon.³⁸ For this reason, low-carbon irons with 0.30 to 1.00 percent of chromium (a carbide former) are much more resistant to growth than unalloyed gray irons. The addition of more than 1 percent of chromium produces substantial improvement in oxidation resistance. Irons containing 1 percent of chromium have been used at temperatures up to 1,400 F, and irons with 35 percent of chromium have not been harmed by repeated short periods at temperatures as high as 2,100 F.¹⁸

The austenitic cast irons containing 14 percent or more of nickel, approximately 5 percent of copper, and 1 to 4 percent of chromium—that is, Ni-Resist—show good resistance to growth and oxidation up to 1,500 F.³⁸

202.06 Important Corrosion Phenomena

202.061 INTRODUCTION: There are a number of corrosion phenomena that are rather unique in that they occur only under certain conditions, or only in certain metals or groups of metals. The more important

corrosion phenomena of this type are discussed in the following paragraphs.

202.062 INTERGRANULAR CORROSION: When austenitic steels are heated in the temperature range of 750 F to 1,650 F, or cooled through this range, a complex carbide precipitates along the grain boundaries to form an envelope around the grains. Although carbide precipitation in itself is not particularly harmful, steels in this condition are susceptible to intergranular corrosion by relatively mild corrodents, especially the corrodents containing chlorine, fluorine, or iodine. Examples of intergranular corrosion are shown in Fig. 32 and 33. A further description of this type of attack is presented in another section of this chapter (see Par. 202.064 and Par. 202.065).

202.063 GRAPHITIC CORROSION OF CAST IRON: Graphitic corrosion of cast irons, sometimes unfortunately called "graphitization," should not be confused with graphitization (the decomposition of carbides at high temperatures) as discussed elsewhere in this chapter. Graphitic corrosion is low-temperature corrosion

of gray cast irons in which metallic iron is converted into corrosion products, leaving the graphite intact.¹⁸ (See Appendix I for the structure of gray cast iron.) This condition results in a porous structure, loss of density, and extremely low strength, but there is no outward appearance of any damage. This type of attack occurs in very dilute acid streams, salt waters, or in soils, particularly those containing sulfates. Graphitic corrosion has been found in distillation-tower internals, such as trays and bell caps.

202.064 STRESS CORROSION CRACKING: Stress corrosion cracking is the spontaneous failure of metals by cracking under the combined action of corrosion and tensile stress.^{18, 32, 39} The corrodent is, of course, some substance in the environment. Stress may be residual or applied. Residual stresses result from fabrication operations, such as bending and welding, and from unequal heating and cooling of a structure. Applied stresses are the working stresses that result from internal pressure or loading of a structure. In general, residual stresses, which may be of extremely high mag-



FIG. 32—Intergranular Corrosion in an 18 Chromium-8 Nickel Steel Pressure Vessel Head.

Carbide precipitation occurred during fabrication. The process stream contained inorganic aluminum chloride and organic methyl and ethyl chlorides. The oil seeping out of the cracks was applied during inspection by the fluorescent-penetrant method.

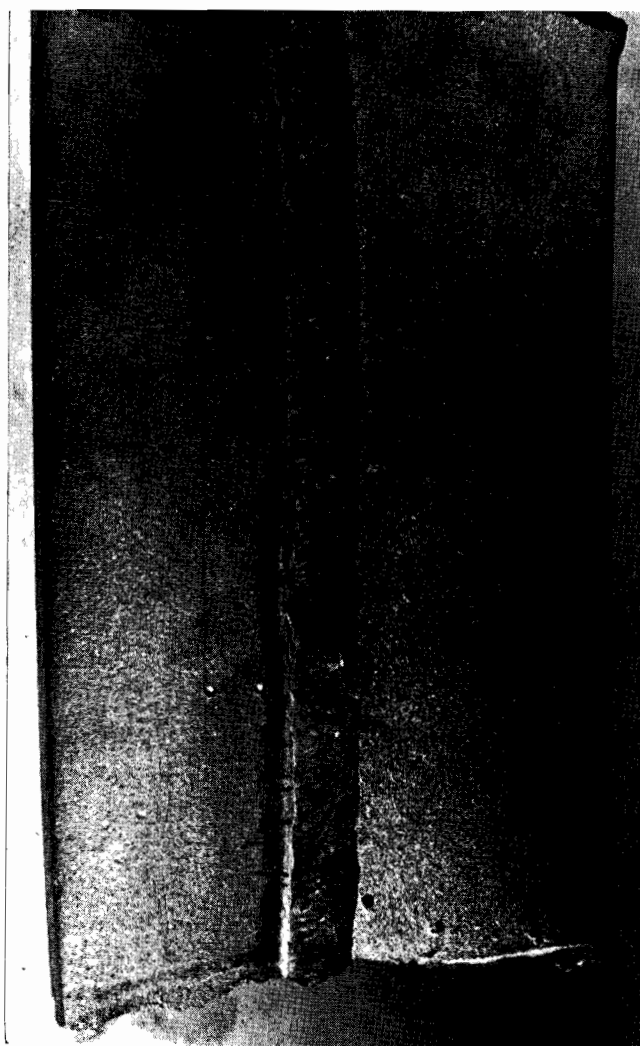


FIG. 33—Intergranular Corrosion in a Sample Removed from an 18 Chromium-8 Nickel Steel Drum.

Note how corrosion has occurred in the weld heat-affected zone.

nitude in localized areas, are of more importance than applied stresses in causing stress corrosion cracking, particularly in view of the factor of safety used in determining working stresses. However, applied stresses in corners or where stress raisers occur may be of considerable magnitude.

The mechanism of stress corrosion cracking is not clearly understood and is the subject of much debate, with various theories being offered. It has been noticed, however, that cracking seldom occurs where general corrosion is more than slight. More often than not there is no measurable general corrosion. This leads to the belief that corrosion resulting in stress corrosion cracking is highly concentrated in a minute area and produces an extremely sharp notch. This stress concentrator leads to cracking under tensile stress. If the

initial cracking does not proceed through the section, the cycle may be repeated until failure is complete.

In addition to a corrodent and stress, there is a third factor in stress corrosion cracking—time. The time required for cracking to occur may vary from minutes to years and depends on the combination of stress level, corrodent and corrodent strength, and the metal or alloy involved.

A common type of stress corrosion cracking that occurs in carbon steels in petroleum refineries is that caused by sodium hydroxide. This type is commonly called "caustic embrittlement" and sometimes "boiler embrittlement." Stress corrosion cracking by caustic is discussed further in an earlier portion of this section.

Hot nitrate solutions, concentrated and dilute nitric acid solutions, and hydrogen cyanide can also cause stress corrosion cracking of ferritic steels.⁴⁰

Hydrogen sulfide can cause stress corrosion cracking of ferritic steels containing martensite or tempered martensite. Particular difficulty has been experienced with the cracking of low-alloy steel bolting in equipment operating at temperatures up to 600 F. The fact that cracking has occurred in bolting is probably attributable to both high-stress level (particularly when bolts are installed with impact wrenches) and martensite contained in the ferritic steel. Low-alloy steels are not susceptible to cracking when compared to other equally stressed grades of steel if hardness and stress level are watched. Hardness reflects the amount of martensite and is detrimental in relation to susceptibility to failure—above $R_C=22$. Stress level also increases the susceptibility to cracking when stresses approach the yield point, therefore a safer level would be considered around 80 percent of yield.

Recent work indicates that hardness and stress levels are not the only important conditions. Alloying constituents, heat treatment, and microstructure must also be considered.

The most active media in producing stress corrosion cracking in the austenitic stainless steels (such as 18 chromium-8 nickel steel) are aqueous acid chloride solutions or solutions existing with oils below the water solution dew point. Even low chloride-ion concentrations of a few parts per million can produce cracking under the proper conditions^{18, 38} particularly when the salt water can be concentrated by boiling or evaporation. For this reason, atmospheric condensation may cause failures of this type. The tendency to crack increases with increasing temperature if stress remains constant.

Stress corrosion cracking has occurred in the support attachment areas in catalyst-recovery equipment of fluid catalytic cracking units, in entrainment screens and pressure vessel shells of phenol-treating units, and in the parts of instruments installed inside pipe still pressure vessels. Similar cracking may occur in any other service where even small concentrations of chlorides are present.

Stress corrosion cracking has also been experienced in austenitic stainless steel vessels handling caustic solutions in the temperature range of 400 F to 450 F. The range of corrodent concentrations, temperatures, and pressures causing stress corrosion cracking of stainless steels is wide, and the limits are unknown.

Stress corrosion cracking in the austenitic stainless steels may, at times, be difficult to distinguish from intergranular corrosion because both types of attack may occur adjacent to welds. At times, the two types of attack may be related in that intergranular corrosion may provide points of stress concentration at which stress corrosion cracking may develop. Stress corrosion cracking does not, however, depend on the precipitation of carbides, and may occur with or without their presence.

The only positive way to distinguish between intergranular corrosion and stress corrosion is by microscopic examination. Chloride stress corrosion cracks in austenitic alloys are usually transgranular and branching, while intergranular corrosion follows the grain boundaries.^{18, 38}

In general, nickel and nickel alloys show good resistance to stress corrosion cracking. Fused caustic solutions, and perhaps other very hot, highly concentrated solutions, may cause cracking of highly stressed nickel, monel, and Inconel.^{18, 32, 38}

In addition, monel only is subject to stress corrosion cracking in the presence of metallic mercury (which may enter a vessel from broken instruments) or mercury compounds.¹⁸

Stress corrosion cracks in nickel and nickel alloys are usually intergranular.

Stress corrosion cracking of the copper alloys is nearly always the result of the combined action of three substances: ammonia or ammonia-producing material (organic and inorganic substances containing nitrogen); water; and oxygen. Cracking of copper alloys occurs in pipe still overhead equipment, particularly in condenser bolting and tubing, as a result of improper control of ammonia injection rates. Cracking seldom occurs at pH values less than 8; therefore, efforts are normally made to control ammonia injection rates so as to maintain a pH of 5 to 7. Stress corrosion cracking of copper-alloy overhead equipment can occur in a matter of minutes or hours when ammonia injection rates are excessive.

Stress corrosion cracking of copper alloys may be accompanied by some general corrosion. The corrosion products that form are frequently dark blue, black, or dark brown, and only a small amount of metal is corroded.

Mercury and mercury salts are very potent in producing stress corrosion cracking in copper alloys. Mercury, in particular, may cause destruction of refinery equipment because it is occasionally introduced into process streams from broken instruments.

Stress corrosion cracks in copper alloys may be either intergranular or transgranular.

Pure aluminum is very resistant to stress corrosion cracking, but aluminum alloys containing copper, magnesium, and zinc are susceptible to cracking under mild corrosive conditions or in contact with mercury or molten solder.

Stress corrosion cracks in aluminum alloys are usually intergranular.

202.065 POLYTHIONIC ACID CORROSION: This corrosive is normally found during shutdowns as a result of the reaction of iron sulfide scale with oxygen and water. The oxidation of the sulfide forms acids of a family with a formulation $H_2S_xO_y$. Notice that sulfur dioxide in water also falls within this category. The acids attack sensitized stainless steel in the grain boundaries. Under stress, the failure is very much like the stress corrosion cracking of stainless steel covered in Par. 202.064 in that much of the failure is intergranular and slightly branched.⁴¹

This corrosion is treated separately because of its relative newness following the investigation of hydrogen-hydrogen sulfide corrosion whose rapid corrosion forced the use of stainless steels and Incoloy into a service that was susceptible to polythionic acid corrosion. Since the employment of stainless steel in light hydrocarbon service in catalytic reformers and hydrodesulfurizers, many recognized failures occurred during or immediately after shutdowns. Heavier oil units that previously required stainless steel probably protected the metal surface with an oil film in most cases so that moisture did not reach the scale. Protection of stainless steel is attempted by keeping the environment alkaline during downtime by washing with a soda ash solution or ammonia. Elimination of air from surfaces will also protect the stainless steels.⁴²

To avoid sensitization, piping and furnace tubes of stabilized austenitic alloys (Types 321 and 347) and low carbon grades (304L and 316L) have been either used or tested. Most of the service failures reported have been in furnace tubes or exchanger tubes; the next most frequent have been in thermowells and liners. Piping failures have been rare probably because of lower stresses and fewer areas of sensitization unless included in a regeneration cycle.

Investigations⁴¹ have shown that stabilization with alloy or use of low-carbon grades do not necessarily provide long-time stabilization. The time-temperature-sensitization performances developed using a Wachenroder solution or sulfur dioxide in water are similar to or developed from other tests of sensitizations. Thus, welding alone may not leave any or only a small amount of sensitized metal if time at temperatures in the 1,000 F to 1,300 F range is not sufficiently long. Long exposure at these temperatures will sensitize the alloy, but will ultimately leave it stabilized. Lower temperatures, particularly near 850 F to 900 F, will make the alloy most susceptible to attack and failure; thus most

furnace tubes can be susceptible to failure after being in long service regardless of alloying.

At present, the results of investigations on castings show that ferrite in stainless alloys adds to the resistance to stress corrosion cracking.⁴³ In some cases cracking was eliminated in the ferrite containing stainless so that this material looks promising in a service where polythionic acid could be expected. At the time of this writing, there are some field applications and no reported failures during this short period. However, the presence of large amounts of ferrite in austenitic stainless steels, followed by operation at a temperature over 800 F can lead to embrittlement. (Refer to Par. 204.02.)

202.066 DEZINCIFICATION: Dezincification is a type of corrosion that can occur in copper-zinc alloys (brasses) containing less than 85 percent of copper when used in water service. Zinc is lost from the brass and leaves as a residue, or by a process of redeposition, a porous zinc-free mass of copper having very little mechanical strength. Dezincification may be one of three types: plug, layer, or intercrystalline.

Plug-type dezincification occurs in localized areas. If the brass can be bent, the porous plugs of copper will pop out, leaving pits. Plug-type dezincification may be associated with white, brown, tan, or other colors of tubercles, caps, or flakes of corrosion products that form directly over the plugs. The plugs have a reddish appearance.

Layer-type dezincification covers larger areas. The copper layer has a rounded, nodular appearance and is adjacent to the brass surface. Thick layers of copper may build up in time and may be peeled from the brass, leaving an irregular surface. This type of dezincification may also be associated with the formation of colored corrosion products.

Intercrystalline dezincification occurs along the grain boundaries of the brass. In this type of dezincification the metal is weakened as a result of the brittleness of the intercrystalline deposit of copper.

Dezincification is most likely to occur in non-scale-forming fresh or salt waters. An increase in temperature accelerates the rate of dezincification.

Red brass, with 85 percent of copper, resists dezincification; brasses with less than 85 percent of copper, such as Muntz, naval brass, and admiralty brass, may be attacked. Many of the brasses used in modern refineries are alloyed with arsenic, antimony, or phosphorus. Such brasses are called "inhibited brasses" because alloying with arsenic, antimony, or phosphorus inhibits dezincification.

Other "dealloying" attacks such as removal of aluminum and nickel selectively from their alloys are less frequently encountered.

202.067 GALVANIC CORROSION: Much corrosion is the result of electrochemical action. The term "galvanic corrosion" is used to describe a much accelerated electrochemical type of corrosion that occurs

when two different metals are electrically connected, either by direct contact or by an electrical conductor, and are in contact with an electrically conductive solution called an "electrolyte." Probably the most common example of this is the ordinary wet or dry cell battery. If the positive and negative terminals of a battery are electrically connected, current flows and the anode (positive plate) corrodes rapidly. This is essentially what happens in operating units when metals having a considerable difference in potential are permitted to contact each other in electrolytes such as salt water or acidic solutions. Table 1 indicates, by the groupings, which materials can be coupled without experiencing corrosion. Metals from different groups of the table have significant differences of potential. The farther apart the materials appear in the table, the greater the corrosion rate of the corroded (anodic) end.

The relative position of a metal within a group sometimes changes with external conditions, but seldom does a metal change from group to group. It will be seen that several materials appear in two places in the table. The exact position is determined primarily by the oxidizing power and acidity of the electrolyte and by the presence of activating ions, such as chlorides.

Table 1, or any similar table of the electromotive series, indicates only the tendency to set up galvanic

TABLE 1—Galvanic Series of Refinery Metals and Alloys^{44, 45}

(Metals and alloys progress from the anodic, or least noble, to the cathodic, or most noble.)

Corroded end (anodic, or least noble)	
[Magnesium	[Nickel (active)
[Magnesium alloys	[Inconel (active)
Zinc	[Hastelloy A
	[Chlorimet 2
Aluminum 1,100	[Hastelloy B
Cadmium	[Brasses
Aluminum 2,017	[Copper
[Steel or iron	[Bronzes
[Cast iron	[Copper-nickel alloys
13 percent chromium	[Monel
iron (active)	[Silver solder
Ni-Resist	[Nickel (passive)
	[Inconel (passive)
[18-8 Stainless (active)	[Chromium iron (passive)
[18-8-3 Stainless (active)	[18-8 Stainless (passive)
[Chlorimet 3	[18-8-3 Stainless (passive)
[Hastelloy C	[Silver
[Lead-tin solders	[Graphite
[Lead	[Gold
[Tin	[Platinum
	Protected end (cathodic, or most noble)

corrosion. The actual amount of corrosion is determined by the ease with which current can flow and by how much current flows. These factors are generally controlled by the following five considerations:

a. Potential Between the Anode and Cathode: This is based primarily on the electromotive series, as indicated in Table 1.

b. Conductivity of the Circuit: The conductivity of the circuit is affected by the resistances of any metals in the circuit as well as the resistance of the electrolyte. The resistances of films which occur at every surface are particularly important and frequently determine whether or not corrosion will progress.

c. Polarization: This is the change in potential which occurs when the galvanic current starts flowing. Polarization tends to reduce the potential and thus reduce the amount of corrosion.

d. Relative Cathode and Anode Areas: Inasmuch as the anodic area is the area which corrodes, it is desirable to have it large, compared to the cathodic area. This has the effect of spreading the total corrosion over a large area. For example, the use of a carbon-steel pipe nipple in a monel vessel could lead to very rapid failure of the carbon steel, whereas a monel nipple in a steel tower would probably not present a problem.

e. Geometrical Relationship of Dissimilar Metal Surfaces: This can affect the areas that receive the most protection or that experience the greatest corrosion. Inasmuch as the galvanic current takes the shortest path through the electrolyte, if an undesirable couple cannot be avoided, its effect can often be minimized by proper location of the anodic material.

A study of galvanic corrosion leads to certain basic rules that will help prevent trouble. Following are some of these rules that can serve as a guide in corrosion work:

1. Select combinations of metals as close together as possible in the galvanic series given in Table 1.
2. Avoid making combinations where the area of the less noble material is relatively small. It is good practice to use the more noble metals for fastenings or other small parts in equipment that is built largely of less resistant material.
3. Insulate dissimilar metals wherever practical. If complete insulation cannot be achieved, materials such as paint or plastic coatings at joints will help to increase the resistances of the circuit.
4. Apply coatings with caution. For example, do not paint the less noble material without also coating the more noble, otherwise greatly accelerated attack may be concentrated at imperfections in coatings on the less noble metal. Keep such coatings in good repair.
5. In cases where the metals cannot be painted and are connected by a conductor external to the liquid, increase the electrical resistance of the liquid path by designing the equipment to keep the metals as far apart as possible.

6. If practical, add suitable chemical inhibitors to the corrosive solution.

7. If dissimilar materials well apart in the series must be used, avoid joining them by threaded connections, as the threads will probably deteriorate excessively. Brazed or welded joints are preferred, with the use of filler material more noble than at least one of the metals to be joined.

8. If possible, install relatively small replaceable sections of the less noble material at joints, and increase its thickness in such regions. For example, extra-heavy wall nipples can often be used in piping, or replaceable pieces of the less noble material can be attached in the vicinity of the galvanic contact.

9. Install pieces (sacrificial anodes) of bare zinc, magnesium, or steel so as to provide a counteracting effect which will suppress galvanic corrosion.

202.068 CONTACT CORROSION (CREVICE CORROSION): This type of corrosion occurs at the point of contact or in a crevice between a metal and nonmetal or between two pieces of metal in the presence of a corrodent. An electrolytic cell is established because the concentrations of the corrodent inside the crevice and outside are different. A difference in electrical potential is established, and the resultant current flow causes accelerated attack which often results in pitting.

Contact or crevice corrosion may occur at washers; under barnacles, sand grains, or applied protective films; and at pockets formed by threaded joints. Examples of contact or crevice corrosion are shown in Fig. 24, 28, and 29.

202.069 BIOLOGICAL CORROSION: Certain primitive living organisms may influence corrosion in one of the following ways: by directly influencing the rate of corrosion; by permitting the development of an environment corrosive to the metal; or by producing electrolytic concentration cells leading to contact or crevice corrosion. Organisms that influence corrosion may be divided into: 1, those of microscopic proportions, such as bacteria, slime, and fungi; and, 2, those of macroscopic size, such as marine organisms (barnacles, etc.).

The most important microorganisms that directly influence the rate of metallic corrosion are the sulfate-reducing bacteria found in many soils. There are many species and strains of these bacteria, but they all have one common characteristic in that they use hydrogen to reduce sulfate contained in the soils. Corrosion of metals always results in the release of hydrogen at some point on the metal surface. If this hydrogen is not removed in some way, it forms a blanket over the metal and reduces the rate of corrosion. Sulfate-reducing bacteria consume this hydrogen, thus speeding up the rate of corrosion. The reduction of sulfate results in the formation of hydrogen sulfide; this, in turn, causes further corrosion. This type of biological corrosion may result in severe pitting of underground pipelines

and other equipment. Local colonies of sulfate-reducing bacteria may develop at small isolated points on the surface of a buried pipe where organic debris has been included in the backfill.¹⁸ Control of such bacterial corrosion can be accomplished by keeping the pH of the environment above 9.0 by electrical (cathodic) or chemical means.²⁶

The most important microorganisms that permit the development of corrosive environments are the bacteria that have the power of changing sulfur or sulfur compounds into strongly corrosive sulfuric acid. Corrosion by sulfuric acid is discussed earlier in this chapter.

The damaging effect of microorganisms, such as slimes and fungi, and macroorganisms, such as barnacles, is the formation on the metal surfaces of encrustations, with poor adhesion and/or irregular thickness, consisting of living and dead organisms that lead to contact or crevice corrosion. This type of corrosion is discussed earlier in this section.

202.07 Corrosion Occurrences with Attempts at Corrosion Control

The inspector should be aware that attempts to control one corrosion problem can cause another if precautions in installation or application are not taken.

202.071 INHIBITORS: Corrosion can be caused by inhibitors under some conditions. Some have been reported to be corrosive, particularly at the point of injection, if allowed to run down the pipe wall undiluted. Most are known to have the ability to clean a surface of corrosion product. This can cause corrosion, if the amount of the inhibitor added is sufficient to scavenge the corrosion product as it is formed, but is insufficient to coat the metal surface and retard the corrosion. Also, the use of too little inhibitor can accelerate corrosion by coating only a part of the surface area, thus concentrating all the attack in the uncoated region.

202.072 NEUTRALIZATION: Ammonia and caustic have been discussed as corrosives. Since they are corrosive in certain locations and with certain materials, the inspector should be aware that any time they are used for neutralization there is a possibility that copper alloys, aluminum, and the like, can be attacked downstream unless good neutralization has occurred.

Soda ash is sometimes used for neutralization and water is sometimes used for dilution and removal of dissolved gases such as ammonia, hydrogen chloride, hydrogen sulfide, hydrogen cyanide, and salts. If temperatures are high enough to flash the water, plugging can occur from the solids with resultant corrosion-erosion downstream. Occasionally, corrosion has been caused by introduction of both moisture and oxygen into the acid gases in the system.

202.073 CATHODIC PROTECTION: Cathodic protection is used as an impressed current system or a

sacrificial anode system. Both have the ability to destroy protective coatings if the voltage is too high. About -0.85 v to copper-copper sulfate half-cell is generally induced on the corroded surface so that corrosion of iron can be minimized. An impressed current system naturally has the ability to apply too much potential. Magnesium can also apply too much potential if the corrosion product on the magnesium does not slow down its dissolution or there is too much exposed area. Both zinc and aluminum are incapable of impressing enough potential to destroy a coating. Coatings are used to protect the surface from corrosion. Since some pinholes that exist in the coatings or thin areas are permeable to diffusion of water, cathodic protection can be used to protect these weak areas. Once the main coating is destroyed, the cathodic protection system is normally not adequately designed to protect the larger bare areas. Coatings are destroyed by high impressed voltage because hydrogen bubbles are formed more rapidly than they can diffuse away and an alkaline environment is also created. As the alkalinity is increased it becomes strong enough to destroy the coating. Certain zinc alloys have been known to reverse the potential in hot water and cause corrosion to accelerate rather than diminish.

203 EROSION

203.01 Introduction

Erosion is a common form of deterioration of refinery equipment. It is the physical wearing away of vessels, piping, and other equipment by moving streams of liquids or gases and is particularly severe if solids are also present in the stream. Erosion is generally found in locations where the flow is restricted or its direction changed, where a gas stream contains a small amount of solids or liquid, or where there is excessive turbulence. Typical areas are pump cases, valve seats, nozzle necks, condensers, furnace tube inlets, pipe fittings, and thermowells. Where a mild corrodent is present, a slight tendency toward erosive conditions may cause severe metal loss because the normal protective metallic oxide film is eroded away, exposing fresh metal to the corrodent. Generally, erosion does not cause rapid deterioration in equipment unless solids are present in the flowing stream.

203.02 Discussion

203.021 SOLIDS IN FLOWING FLUIDS: Erosion is frequently a problem in equipment utilizing the fluidized-solids principle.* Various linings are employed to protect equipment from erosion.⁴⁶ One type of lining consists of heavy carbon-steel wear plates welded directly

* If a gas stream of sufficient velocity is passed through a mass of finely divided solids, such as a powder, the mass of particles will behave very much like a true liquid. This is the fluidized-solids principle. A common example of its application is in fluid catalytic cracking units in which the finely divided catalyst is handled as a liquid.

over the interior surface of the equipment. This type of lining can become severely eroded in service; in some cases, attack will penetrate a heavy plate in a small area, leaving most of the lining untouched. Alloy plates and alloy hard-faced materials are only slightly more resistant than carbon steel. Linings of reinforced, hard, dense refractory materials are probably more widely used than metal wear plates. The refractory linings are considered superior because, with them, wear is more uniform than with the metal wear plates and, as a result, longer life is obtained.

In refractory linings the refractories are generally held in place with a steel grating welded to the vessel or pipe wall. The erosion often attacks only the refractory, if inferior or improperly applied, leaving the reinforcing steel intact. One type of steel reinforcing material is a $\frac{3}{4}$ -in.-thick mesh made of $\frac{3}{4}$ - by $\frac{1}{8}$ -in. steel strips fabricated to give $1\frac{3}{4}$ -in., face-to-face hexagonal openings. This material has also been used satisfactorily without the refractory, the principle being that the solids, such as catalysts, build up in the hexagonal

opening and act as a cushion, thus reducing erosion. Experience with this type of installation has been limited but it has been found that the following four factors generally control the rate of erosion:

1. Velocity. The rate of erosion increases with the cube of the velocity.
2. Angle of impingement. Angles of 20 deg to 30 deg have proved to be the most destructive.
3. Solids concentration in the stream (e.g., catalysts). The rate of erosion increases as the solids concentration in the stream increases.
4. Temperature. The erosion resistance of steel generally decreases as the operating temperature increases.

Erosion is usually localized; but at times it is very general, and this makes it difficult to detect visually. Large eroded areas have a bright, shiny appearance and feel slick and irregular. Localized eroded areas are likely to occur where the streams change direction or are restricted, such as at slide valves (Fig. 34 and 35),

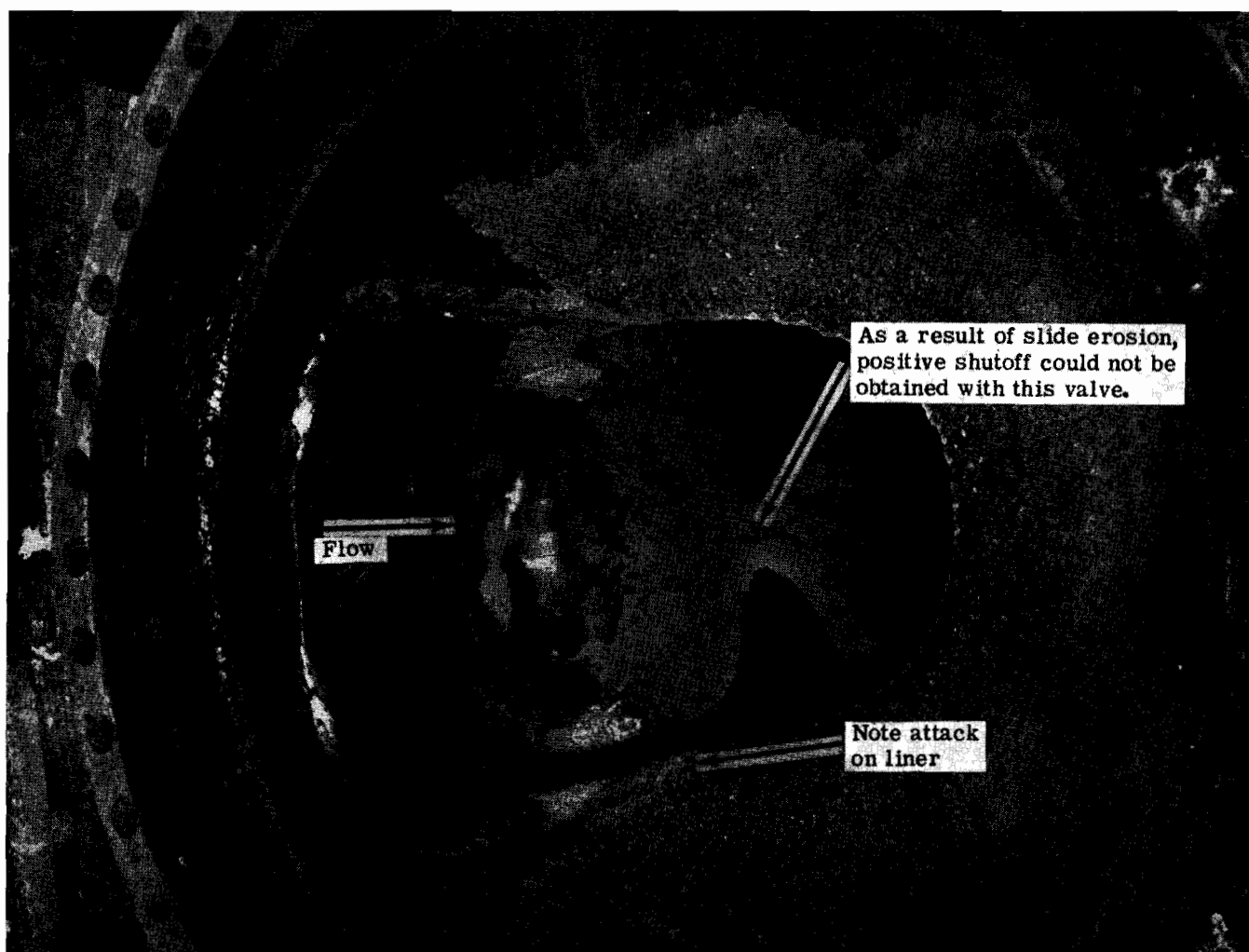


FIG. 34—Erosion of a Slide Valve in a Catalytic Cracking Unit.

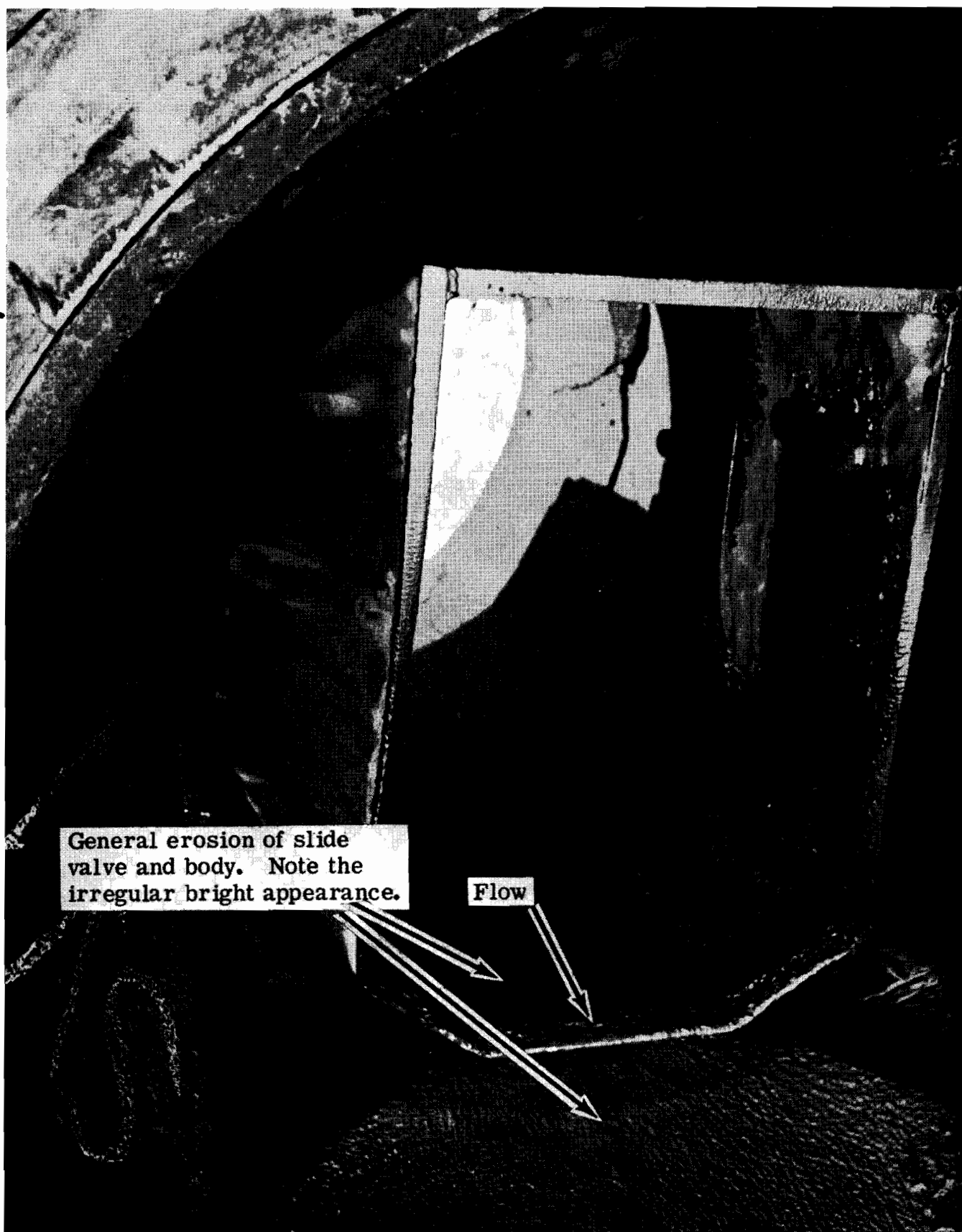


FIG. 35—Slide Valve from a Catalytic Cracking Unit.

orifices, vessel inlet and outlet nozzles, and vessel grids (Fig. 36 and 37). Areas such as aeration connections, thermocouples, steam nozzles, pipe bends, cyclone separator internals, grid seals, exchanger internals, impingement baffles, and mixing columns are also subject to localized erosion. Fig. 38 shows the combined effects of erosion and corrosion in a large flue-gas line. Water sprays were used during the run, and this added to the deterioration of the liner. Fluidized solids, leaking through small cracks or pinholes at high velocities, cause severe erosion and cracks, and the pinholes rapidly grow in size. Serious attack may occur on internal equipment, that is, on cyclones and plenum chambers, which contains cracks or other small leaks.

203.022 HIGH FLUID VELOCITIES AND EDDY CURRENTS—CAVITATION: Cavitation erosion is associated with the formation and collapse of cavities in a liquid at the metal-liquid interface.¹⁸ Most frequently affected by cavitation are the suction side of pump impellers and the discharge side of regulating valves. In pumps, cavitation results in a decrease in pump head, capacity, and efficiency, and causes vibration and noise.

The cycle of cavitation action is as follows:

1. Extreme low-pressure areas are produced by flow irregularities.
2. Pockets or "cavities" of vapor form.
3. Pressure and flow conditions change abruptly.
4. Pockets or "cavities" collapse, and resultant shock pressures reach several hundred atmospheres in local areas.

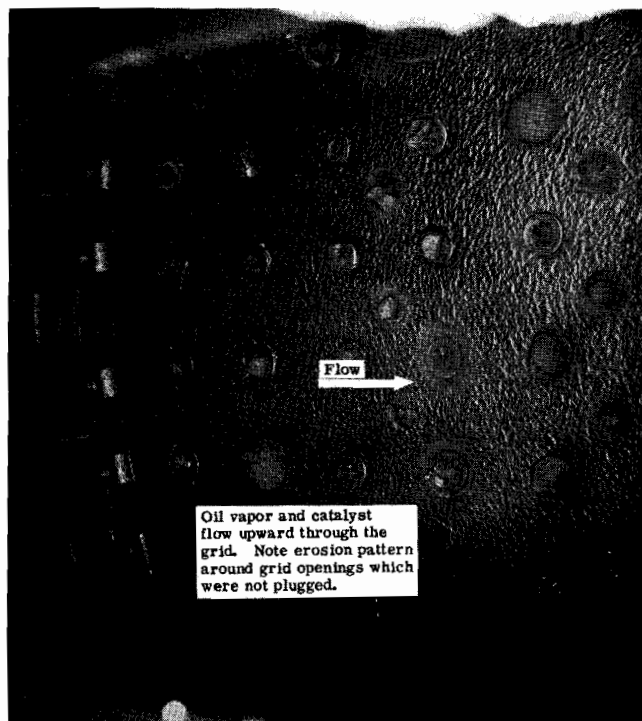


FIG. 36—Reactor Grid from a Catalytic Cracking Unit.

The resultant impact tears out sections of porous or brittle material, or causes plastic flow or deformation which leads to cracking and breaking out of material. Work hardening may occur in the surface layer of some metals, with a corresponding change in physical characteristics.

The cavitation cycle repeats many thousands of times. Ductile metals may resist erosion for a period of time, but breakdown of large areas that take on the appearance of hard, hammered surfaces eventually occurs. If the metal is brittle and of relatively low strength, such as cast iron, the appearance of pitting will be very pronounced. If the material is dense and with high fiber strength, there will be only a roughening of the surface.

Where corrosive conditions exist in the presence of cavitation, the damage is accelerated because the products of corrosion are removed more rapidly than in static conditions, and new and fresh surfaces are exposed to the corrodent. Such conditions are found in sea water with cast iron or steel, where more rapid loss of metal occurs than would be experienced with the same cavitation conditions in fresh water.

204 EFFECTS OF HIGH TEMPERATURES

204.01 High-Temperature Strength

204.011 INTRODUCTION: Room-temperature physical properties used so frequently in engineering design are based on the elastic properties of metals and alloys. Such designs are generally based on the tensile strength, yield strength, or elastic limit as determined at room temperatures. At ordinary service temperatures, stresses are normally within the elastic range of the material. Thus no permanent deformation results when the member is loaded.

Once the temperature exceeds a certain level, the elastic properties no longer give a true picture of behavior. Instead, plastic properties dominate. Under plastic conditions, permanent deformation occurs, with time, at stresses below the apparent elastic limit defined by the room-temperature tests. A somewhat similar, although not exactly analogous, phenomenon is the flow of tar under its own weight on a warm day. Creep and stress-rupture data are commonly used to evaluate the high-temperature strength of metals and alloys.

204.012 CREEP: Creep is defined as the flow or plastic deformation of metals held for long periods of time at stresses lower than the normal yield strength. Creep strengths are usually expressed as the stress producing a creep rate of 1 percent in either 10,000 hr or 100,000 hr at the metal temperature. When equipment is being designed for long-time service at high temperatures where appreciable deformation cannot be tolerated, current design practice is to use creep values at the metal temperature expected to exist in service.

204.013 STRESS RUPTURE: In many high-temperature applications, stresses are selected to ensure a certain

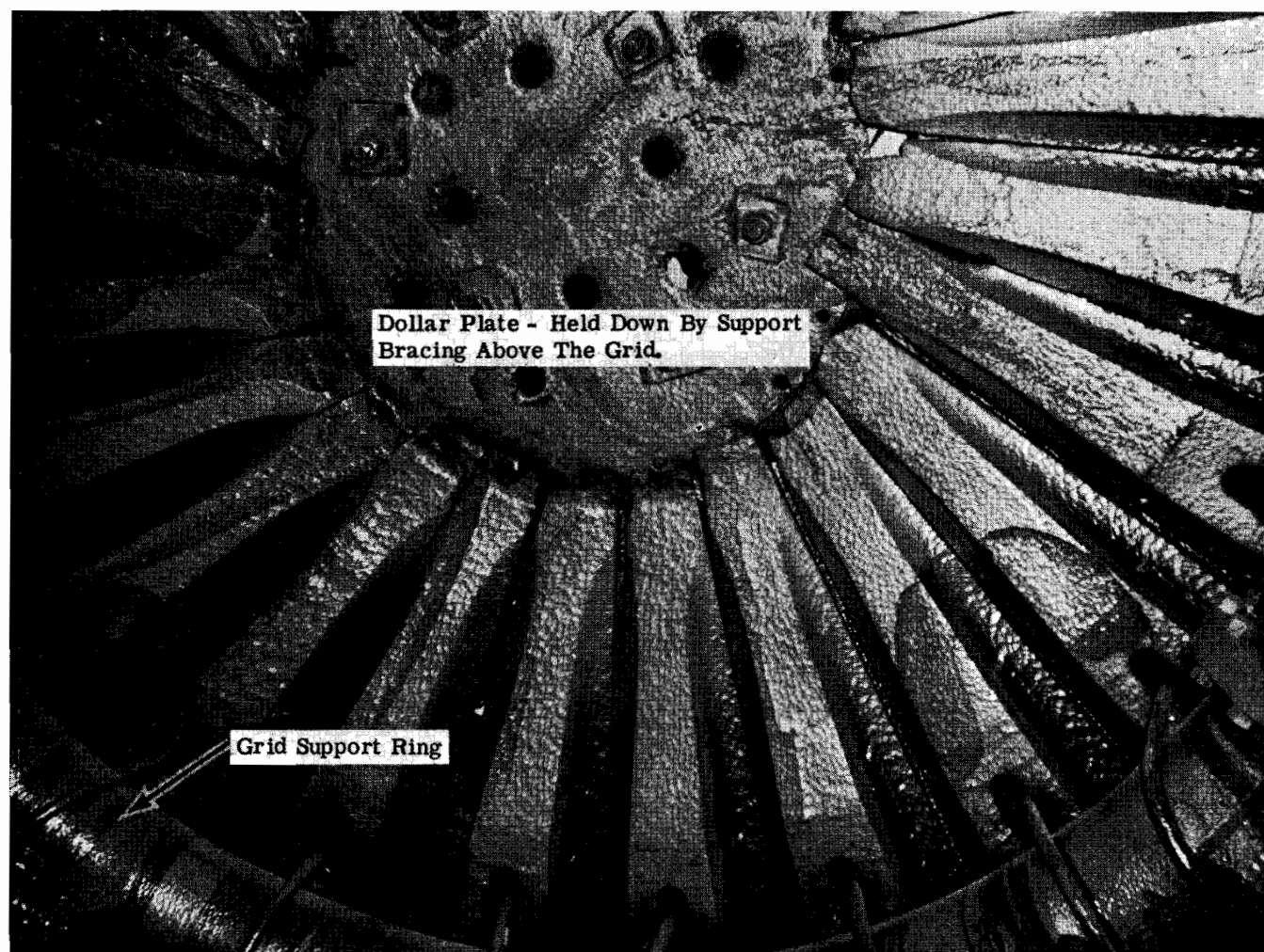


FIG. 37—Regenerator Grid from a Catalytic Cracking Unit.

service life rather than to limit deformation. In these cases, stress-rupture data are more valuable than creep data. Stress rupture relates the time-to-failure with temperature and stress. Actually, stress-rupture tests are very similar to creep tests, except that the loads—and, consequently, the creep rates—are higher and the tests are carried to failure. These data are usually expressed as the stress to cause rupture in 100 hr; 1,000 hr; 10,000 hr; or 100,000 hr at different metal temperatures. However, in many instances, the longer time stress rupture data (10,000 and 100,000 hr) values are extrapolated for shorter time tests. Stress-rupture techniques are used extensively in the design of furnace tubes. In this application the mode of failure is of particular interest. A stress-rupture failure is a brittle type of failure. This means that there may be very little, if any, noticeable deformation prior to failure in such instances. Normal visual inspection does not reveal an impending failure. Fortunately, most furnace tubes fail by localized overheating. In these cases such

obvious indications as bulging and hot spots give early warnings of failure. API RP 530 has both stress rupture information and instructions for its use in design and retirement of furnace tubes.

204.014 PROPERTIES FOR HIGH-TEMPERATURE STRENGTH: Temperature and chemistry control during manufacture of metals can affect the grain size of the finished product and the high-temperature properties of the material. Standards (ASTM or ASME) for finished products have been revised to include limits on the properties of end products, such as plate, pipe, and the like. Standards, such as ASME Code Case 1325 for Incoloy, include two classes of materials: Class I—fine-grained for temperatures nearer atmospheric temperature, Class II—coarse-grained for elevated temperature service. ASTM B 407 covers only Class II for Incoloy. Both creep and stress rupture properties are improved in the coarse-grained materials. The description as “coarse-grained” is used since it is the

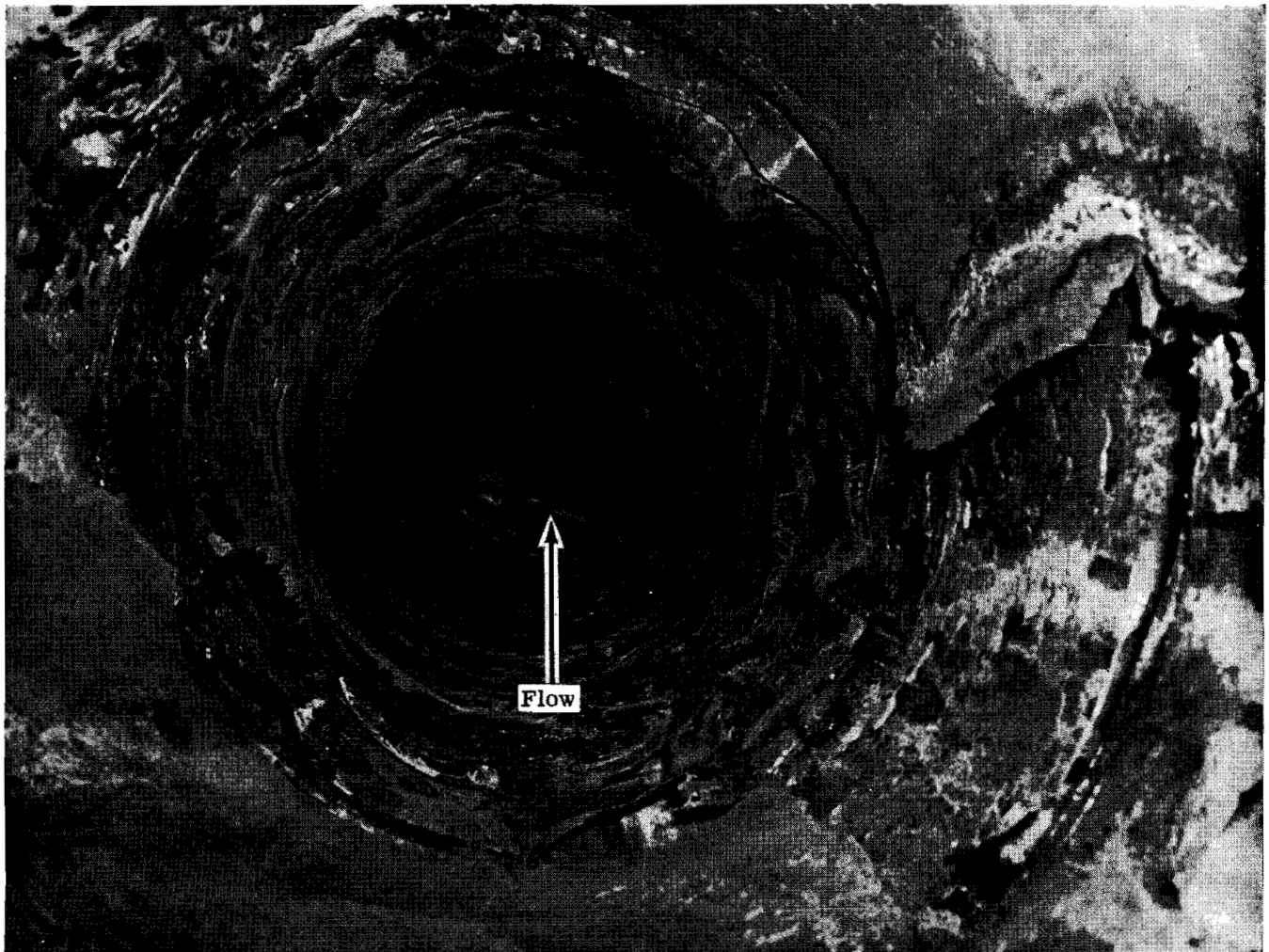


FIG. 38—Deterioration of Liner in Flue-Gas Line on a Catalytic Cracking Unit.

most available method of determining if material has been solution-annealed. The actual effect on high temperature is that the carbides have been taken into solution. While this is occurring, grain coarsening generally occurs. The solution annealing increases high-temperature strength of most materials and usually at the expense of high-temperature ductility.

204.02 Metallurgical Structural Changes

204.021 INTRODUCTION: All metals and alloys undergo changes when heated above a certain temperature. These changes may be classified into two broad categories: structural changes and compositional changes.

Metals and alloys are composed of one or more types of tiny crystals, often called "grains." Structural change refers to any change that occurs in the crystals or grains.

In order to understand how excessive temperatures cause harmful structural changes and what these changes

are, the reader should refer to Appendix I for a general discussion of the common refinery metals and alloys.

204.022 STRUCTURAL CHANGES: The most serious structural changes that may occur in refinery metals and alloys are discussed in the following paragraphs.

a. Grain Growth: In general, the smaller the grain size in a metal or alloy, the higher the tensile strength and the lower the rupture and creep strengths (generally at highest creep temperatures). Metals are, therefore, produced with a grain size best suited to the operating conditions under which each metal is to be used, and any change in this size is detrimental.

When ferritic steels are heated above a certain temperature (above 1,100 F for mild steel depending on cold work), grain growth occurs and leads to a general lowering of the tensile strength. For this reason, any mild-steel equipment that has been heated above 1,100 F for some time—for example, in a fire—may have an increased grain size, with the result that the

original strength of the part may have been lowered and the original factor of safety reduced. The amount of deterioration depends on the maximum temperature encountered (which sets the maximum possible grain size) and the length of time at this temperature (which determines whether there was sufficient time to reach maximum size). Note that the above temperature level cannot be firmly established because of type of steel, degree of cold work, and time of exposure. Temperatures even above 1,350 F may be required for grain growth to occur.

The austenitic stainless steels and the higher nickel-chromium alloy steels suffer grain growth when heated above approximately 1,650 F. The exact temperature required depends on the carbon content as well as the manufacturing practice used when making the steel, and may be slightly lower or considerably higher than 1,650 F. The effects of time and temperature on grain growth are the same as discussed in the foregoing paragraph for the ferritic steels.

Cast irons and nickel, copper, aluminum, and their alloys are used principally in relatively low-temperature service (with the exception of the nickel-chromium alloys), and structural changes due to excessive temperatures will occur only in unusual circumstances, such as fires.

b. Incipient Melting (Burning): If the ferritic steels are heated above approximately 2,600 F, melting and oxidation will begin at the grain boundaries. Steel in such a condition is called "burned" and is very likely to part intergranularly under its own weight. Should failure not occur at the high temperature, the steel will be very weak and brittle upon cooling.

A similar condition will occur in the austenitic stainless steels when they are heated above approximately 2,500 F.

Cast irons and nickel, copper, aluminum, and their alloys can also suffer incipient melting.

c. Graphitization: Certain ferritic steels, when operated for long periods in the range of 825 F to 1,400 F, may suffer a type of structural change called graphitization. The cementite or carbide which gives ferritic steels their strength is unstable and, in this temperature range, may decompose into iron (ferrite) crystals and graphite (carbon) nodules. This decomposition is known as graphitization.⁴⁷ Replacement of the hard, strong carbide with soft, weak iron and graphite lowers the strength of the steel.

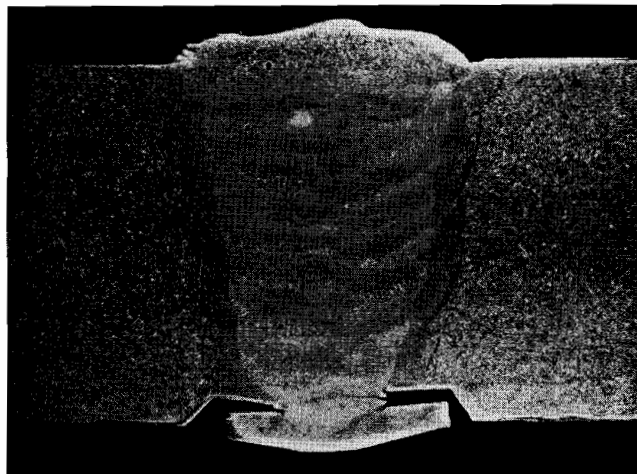
Some steels are much more susceptible to graphitization than others, and graphitization seems limited, for all practical purposes, to carbon and carbon- $\frac{1}{2}$ molybdenum steels. Exactly what causes some steels to graphitize while others are resistant has not yet been determined; however, various correlations have been found which indicate that small amounts of minor constituents can influence the tendency to graphitize. Thus, steels with more than 0.015 percent aluminum tend to be prone to graphitize.⁴⁸ It has been hypothe-

sized that plastic straining of the ferrite lattice allows interstitial carbon migration, but that the presence of nitrogen inhibits such migration. The role of aluminum may be one of "gathering" nitrogen, thereby enhancing carbon mobility and graphitization. With the current emphasis being placed on steels having high notched impact strength for low-temperature use, increasing amounts of aluminum are being used in deoxidation practices in order to render these materials more fine grained. Such steels should be avoided for use at temperatures in the graphitization range.

There are two general types of graphitization.^{49, 50} The first is random graphitization, in which the graphite nodules are distributed uniformly throughout the steel. While this type of graphitization lowers the room-temperature tensile strength, it does not usually lower the creep resistance. The high-temperature strength is, consequently, seldom affected because the creep resistance of the steel is the dominant factor at high temperatures.

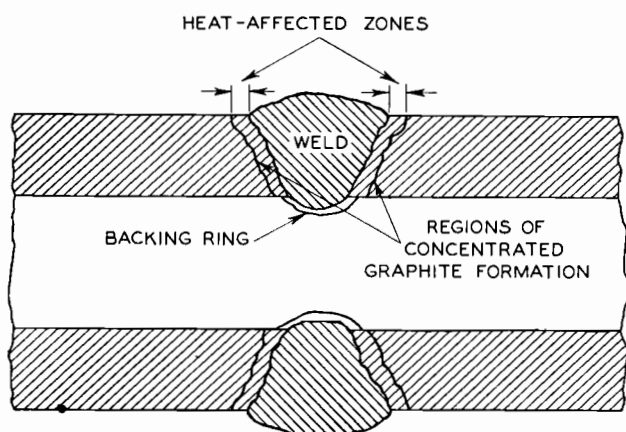
The second type of graphitization is that which results in highly concentrated graphite-nodule formation in local regions. In this situation, mechanical failure is likely to occur through these areas of graphite concentration.

Localized graphitization has most frequently been found in a narrow band which corresponds to the low-temperature edge of the zone of the parent metal which was heat-affected during welding, as illustrated in Fig. 39, 40, and 41. In multipass welded butt joints the zones of the parent metal heated by each welding pass overlap all across the section. Graphite nodules can form at the low-temperature edge of these heat-affected zones and link together to form a zone of weak graphite which extends through the section and results in ulti-



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FIG. 39—Graphitization of Welded Carbon-Molybdenum Steel Piping at the Low-Temperature Edge of the Heat-Affected Zone (Pittsburgh Piping and Equipment Company).

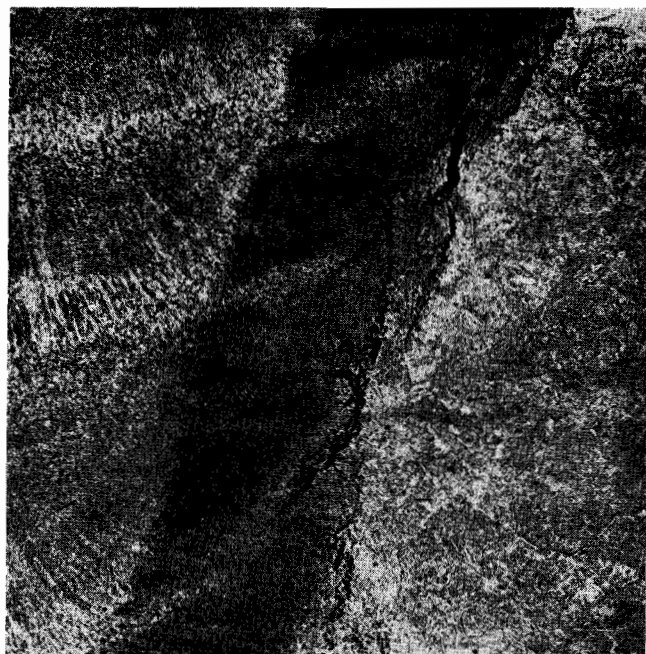


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FIG. 40—Schematic Longitudinal Median Section Through a Single-V Butt-welded Pipe Joint.

mate failure. Because of its appearance, graphite formation at the low-temperature edge of heat-affected zones is called the “eyebrow” type. Another type of localized graphitization sometimes occurs along planes of localized yielding in steel, called Luder’s lines. Such lines are formed in cold-working operations like bending.

Temperature has an important effect on the rate of graphitization. Below 825 F the rate is extremely slow. The rate increases with increasing temperature to a maximum at 1,150 F to 1,200 F. At higher tempera-



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FIG. 41—Graphitization at the Low-Temperature Edge of the Heat-Affected Zone of a Welded Pipe Joint.

tures the rate decreases, and graphitization probably ceases above 1,350 F to 1,400 F.

To date, no failures directly attributable to graphitization have occurred in the refining industry; however, graphitization has been found in cases where failure was primarily because of other causes and may have contributed to such failures. Several serious cases of graphitization have appeared in the reactors and piping of catalytic cracking units, and there has been one case in carbon-steel thermal cracking-unit furnace tubes. In another case, failure of seal welds by graphite occurred in a catalytic cracker waste heat boiler at the bottom tube sheet of the vertical boiler. The power industry has experienced failures caused by graphitization of both carbon and carbon-molybdenum steam piping.

Where concentrated “eyebrow” forms of graphite occur along heat-affected zones, the creep rupture strength may be drastically lowered; however, slight to moderate amounts of graphite along the heat-affected zones do not appear to lower room- or high-temperature properties materially.³

d. Hardening: When the ferritic steels are heated above 1,350 F, austenite, a solid solution of iron and carbon, begins to form. On slow cooling, austenite transforms again to form ferrite and cementite. If the steel is cooled rapidly—and this critical rate of cooling varies widely with the steel composition—martensite, rather than ferrite and cementite, is formed. Martensite is an extremely hard, brittle substance, the formation of which is the object of hardening heat treatments.

In general, the cooling rate required to harden becomes less with increasing carbon and alloying-element content, that is, the steels become easier to harden. The plain high-carbon (above approximately 0.35 percent of carbon) and low-alloy steels require a rapid cooling rate, such as is produced by plunging into water or oil. This is called quenching, and water cools more rapidly than oil. Water-quenched steels are called water-hardened, and oil-quenched steels are called oil-hardened. The intermediate- and high-alloy steels, particularly the straight chrome steels, will harden just by cooling in air and are called air-hardened.

Martensite has its uses in cutting tools, wear surfaces, and the like, but may be objectionable in refinery piping, furnace tubes, pressure vessels, and the like, because of its extreme brittleness, which results in failure under bending stress or impact loading. As a matter of fact, martensite is so highly strained internally that a fully martensitic piece of steel may crack of its own accord without any external load. This characteristic makes welding difficult on most hardenable grades.

Martensite is produced in several ways in refinery equipment made of steel that is hardenable in any degree. Any type of heating to a sufficiently high temperature, followed by rapid cooling, can produce martensite. In welding, a zone of the steel next to the weld is heated well above this temperature. However, the

rest of the parent metal is relatively cold and, by conduction, rapidly cools the zone adjacent to the weld and causes hardening. This effect occurs to a lesser extent in low-carbon-content, plain carbon steels because the cooling rate is not fast enough. In plain carbon steels with over 0.35 percent of carbon, and in most of the alloy steels, the cooling rate is fast enough to cause hardening and the accompanying brittleness. This is particularly true of the straight chromium steels because even air cooling hardens them.

In welding, hardening may be prevented by preheating and postheating. Preheating the surrounding metal keeps the cooling rate, by conduction, down to the point where complete hardening of the oil- and water-hardening grades is usually prevented. Preheating does not keep the air-hardening grades from hardening, but it does keep them from cracking from stresses resulting from the contraction of the surrounding metal by rapid cooling. Postheating reduces the brittleness and can be done in two ways. The first method is to use a full annealing treatment in which the metal is heated to a high enough temperature to convert the martensite to austenite, followed by very slow cooling to produce ferrite and cementite. The second method is to heat the metal to a lower temperature which allows the martensite to transform to a less brittle constituent. This second method is called "stress relieving," or subcritical annealing. These treatments are really tempering or drawing treatment similar to those given to heat-treated steels.

Another way in which refinery steels may become hard and brittle is from heating to facilitate bending. In fabricating pipe and plate, for instance, it is often the practice to heat portions of the steel in order to make bends. Sometimes the heating and bending is followed by cooling with water. From the foregoing discussion it can be seen that although this practice may not result in hardening low-carbon steel, it will surely cause hardening of the high-carbon steels and straight chrome steels. If the high-carbon steels and straight chrome steels are heated for fabrication and not properly heat-treated to restore mechanical properties, they may crack or fail in service.

Similar to heating for bending is the heating that may result from fires. This heating may be followed by rapid cooling by water from fire fighting, while even cooling in air is enough to cause hardening of many of the ferritic alloy steels.

Hardening of the ferritic alloy steels may also result from overheating in service—as a result of human error, steam-air decoking of furnace tubes, overfiring, coking, or upsets—followed by rapid cooling. Although chromium-steel furnace tubes are particularly susceptible to this type of damage, they do not ordinarily harden in service because of the very slow rate of cooling in a furnace. However, under certain conditions the phenomenon of carburization, which will be discussed later, actually increases the carbon content of

the steel. If carburization has occurred previously, the increased carbon content changes the properties of the metal so that even the slow cooling of the furnace box is fast enough to cause hardening. Such hardening is often accompanied by cracking through the tube wall or by spalling of the bore.

Similar overheating of piping, pressure vessels, and other equipment fabricated of ferritic alloy steels, particularly the chromium steels, may well result in hardening and cracking when they are cooled in air at atmospheric temperatures or in any faster medium.

Some steels, mostly the low-alloy steels, are used in the refinery in the heat-treated condition. These steels are almost fully hardened, followed by a tempering treatment to produce certain required mechanical properties. Any further heating above the tempering temperature will result in a modification of the original properties. Depending on the temperature encountered and on the method of cooling, heating will result in either a soft, weak material or a hard, very brittle material, neither of which is satisfactory for the intended uses. For this reason, such steels should not be welded, heated for bending, and the like, unless heating can be followed by proper heat treatment to restore the required properties.

Bolting of quenched and tempered 4140 steel (A-193, grade B7) is the most common example of refinery use of heat-treated steels. However, an increasing number of pressure vessels for high-pressure, high-temperature service are being made of quenched and tempered steels. Since vessels to be economically made of quenched and tempered steels are large, a substantial decrease in wall thickness can be achieved by use of the higher strength steels. This principle is being used in the design of nuclear power reactor vessels with high-strength steels, such as ASTM A-533 and A-542. In the refining industry low chromium-molybdenum steels made to A-543 or Q and T, and N and T, A-387 specifications have proved equally feasible for heavy wall vessels. As previously mentioned, proper welding procedures are extremely important to follow in order to have a satisfactory piece of equipment. The warnings in the preceding paragraph about welding not only apply for these vessels because of the heat treatment but because of the thickness also. However, such "quenched and tempered" steels can be susceptible to hydrogen stress cracking if used at high strength levels.

e. Sensitization (Carbide Precipitation): Sensitization is a phenomenon that occurs in the austenitic stainless steels, and is believed to be the precipitation of a complex chromium carbide at the grain boundaries. It takes place when the austenitic steels are heated in the range of 750 F to 1,650 F.

When a sensitized steel is exposed to corrosives, rapid solution of the metal occurs at the grain boundaries and causes the steel literally to disintegrate into individual grains. This phenomenon is called intergranular corrosion and is shown in Fig. 32 and 33. There are a number of theories to explain this phe-

nomenon, but the chromium-impoverishment theory is probably the most popular.⁵¹ This theory proposes that as chromium carbides are precipitated from the grains, the portions of the grains adjacent to the grain boundaries are depleted of chromium and lose their corrosion resistance. The effect of intergranular corrosion is much the same as that which might be expected if some corrodent dissolved all the mortar in a brick building. There would be nothing to hold the bricks together.

In order to prevent intergranular corrosion, austenitic stainless steel for corrosive applications is supplied in the solution heat-treated state. The solution heat treatment involves heating the steel to approximately 2,000 F for a long enough time to ensure that all the carbides are dissolved. The steel is then rapidly cooled (usually in water). Inasmuch as it takes time for the precipitation to occur in the sensitizing range, rapid cooling through this temperature range prevents any significant amount of precipitation. The final structure is a supersaturated austenite, and all the carbides are in solution. Austenitic steels do not harden when quenched.

If the solution heat-treated steel is heated into the sensitization range, carbide precipitation occurs and the steel becomes susceptible to intergranular corrosion. Such heating occurs during welding, and a narrow sensitized zone may develop on each side of the weld. Inasmuch as austenitic stainless steel is often used at high temperatures because of its superior strength at such temperatures, many structures operate in the sensitization range.

Sensitization in itself is not particularly damaging to the properties of the steel.* It is only after intergranular corrosion occurs that difficulty is encountered. Because the corrodents causing intergranular corrosion are most frequently found in aqueous solutions, intergranular corrosion in high-temperature applications does not occur, except during shutdown periods when condensation may take place in or on the equipment (see Par. 202.065 on polythionic acid corrosion). Sensitized equipment operating at lower temperatures can, of course, suffer corrosion at any time in the presence of the proper corrodent.

Methods employed to prevent intergranular corrosion are generally aimed at limiting the amount or type of precipitated carbides.⁵¹ One method is to keep the total carbon content of the steels low (the ELC grades). Another method changes the type of precipitate by adding titanium or columbium to the steel (such steels are called "stabilized"). These preventive methods have some merit, such as preventing sensitization during welding, but no austenitic stainless steels are immune to carbide precipitation, particularly after long service in the sensitizing range.

Intergranular corrosion will appear as cracks which

* Other than loss of some ductility and slight embrittlement at room temperature (about 20 ft-lb impact compared to 30-50 ft-lb originally).

sometimes outline the grain boundaries so closely that a geometrical pattern, known as "sugaring," results. In equipment that operates in the sensitizing range, corrosion may show up anywhere. In equipment operating at lower temperatures, intergranular corrosion may be limited to areas adjacent to welds.

Intergranular corrosion is often discovered when welding repairs are attempted. If present to any extent, cracking during the welding operation will make repairs difficult, if not impossible.

The nickel-molybdenum-iron alloys are also susceptible to sensitization when heated into or cooled slowly through the temperature range of 930 F to 1,300 F.

f. Sigma Phase: This damaging phase can form in austenitic stainless steels as well as in straight chromium steels. The most susceptible of the austenitic stainless steels appears to be the 25 chromium-20 nickel type.⁵²⁻⁵⁴ The susceptible straight chromium steels are those containing 17 percent or more of chromium.

The formation of sigma increases room temperature tensile strength and hardness, and decreases ductility to the point of extreme brittleness. The short-time elevated-temperature strength and ductility are decreased. Because of the extreme brittleness, cracks are very likely to develop during cooling from operating temperature, during handling, and especially during welding (see Fig. 42). Inasmuch as sigma dissolves above 1,800 F, the original properties of the austenitic stainless steel can be restored by heat treatment if cracking has not occurred.

Sigma is most likely to be found in furnace tubes, furnace parts (particularly in castings), and other equipment operating between 1,200 F and 1,400 F. Types



FIG. 42—A 25 Chromium-20 Nickel Steel Furnace Tube Header Embrittled by Sigma.

The small crack developed during cooling when the furnace was removed from service. When welding repairs were attempted, the large crack developed.

304 and 316 stainless steels have been found to have maximum sigma formation from exposure near 1,200 F, while Types 309 and 310 have maximum sigma formed near 1,400 F. A research investigation was made on sigma formation of Type 310 and it was found that a chemistry balance could minimize sigma formation. Most centrifugally cast tubes for service at 1,200 F or over are now made of higher carbon so that optimum properties may be maintained.

For heat-resistant cast alloys, particular attention should be given to their contents of silicon and carbon. Static castings of Type 309 used particularly for tube hangers have been available as low ferrite grades to minimize the amount of ferrite available for formation of sigma.

g. Embrittlement (885 F): A change occurs in some normally ductile steels when exposed to temperatures of around 750 F to 1,000 F. Upon cooling from these temperatures the steels are brittle at ambient temperatures (under 200 F). This so-called embrittlement occurs most rapidly near 885 F, but requires more time to reach maximum embrittlement at temperatures above or below 885 F. This embrittlement can be eliminated by annealing the steel to restore original physical properties.

Ferritic chrome steels are quite susceptible to 885 embrittlement. Thus Types 430 (17 percent chromium) and 446 (27 percent chromium) are not deliberately used in temperature ranges where embrittlement might occur. The lower chromium alloys, such as 9 chromium-1 molybdenum, 7 chromium- $\frac{1}{2}$ molybdenum and lower, are not susceptible to embrittlement because of the molybdenum addition. The straight chromium stainless steels, such as Types 410 and 405, have occasionally embrittled, with Type 405 being more susceptible than Type 410. This susceptibility is thought to be proportional to chromium equivalent where, in the 11 to 14 chromium range as Types 405 and 410 are, the higher the chromium the greater the susceptibility.

A similar type of embrittlement has been reported in austenitic chromium-nickel stainless steel weld metal containing over 10 percent ferrite.⁵⁵

Other than in laboratory tests, most cases of embrittlement are found in the form of cracking occurring during turnarounds. This cracking appears in both wrought and cast (weld) structures. The high stress level in exchanger tubes leads to rapid failures in these structures.

204.03 Metallurgical Chemical Changes

204.031 INTRODUCTION: Chemical change refers to a change in the chemical composition of a metal or alloy as opposed to a strictly structural or phase change. Chemical changes and structural changes cannot always be dissociated because chemical composition changes can produce entirely new structures or change old ones, with accompanying changes in properties.

At high temperatures, chemical elements and compounds that have little or no effect on metals and alloys at atmospheric temperatures may become extremely destructive, resulting in severe cracking, disintegration, brittleness, or weakness. For example, carbon and hydrogen at high temperatures can actually be dissolved into a steel structure and thus cause serious changes in properties. A discussion of some of the more common chemical changes is presented in the following paragraphs.

204.032 CARBURIZATION: The diffusion of elemental carbon into solid steel in contact with a carboniferous material (such as oils being processed) at high temperatures is called carburization.^{38, 56} Such an increase in carbon content results in an increase in the hardening tendency of ferritic steels. Thus, if a carburized steel is cooled from a high enough temperature, hardening is likely to occur, and this results in a brittle structure. The presence of such a hard, brittle structure may result in spalling or cracking.

Carburization depends on the rate of diffusion of elemental carbon into the metal, and increases rapidly with increasing temperatures.^{38, 56} Some of the unsaturated hydrocarbons may greatly accelerate this process.⁵⁶ Cracks and the presence of a scale layer sometimes catalyze the reaction. Carburization is often found where coke is present; however, when furnace tubes are coked, metal temperatures are increased. For this reason, it is difficult to determine whether the presence of coke or the higher metal temperatures lead to carburization. Carburization is also found when carbon is present (see Par. 204.033).

All steels are susceptible to carburization under the proper conditions; however, susceptibility decreases with increasing chromium in the steel.* The austenitic stainless steels appear to be more resistant to carburization than the straight chromium steels, partly because of their higher chromium content and partly because of the nickel content.

204.033 METAL DUSTING: A carbon monoxide-carbon dioxide environment may promote carburization as noted in the preceding section. This environment as well as high-temperature hydrocarbon gases may also cause a catastrophic localized corrosion called metal dusting. It is so called because pits are found filled with carbon, often with some metal in the carbon. Usually the surface of the pit is carburized while adjacent uncorroded areas are not carburized or pitted.

Metal dusting was originally found in ethylene furnaces where feed was pure. Few metals resisted the corrosion for long, but it was found that trace amounts of sulfur arrested the corrosion. This corrosion, or a similar appearing phenomenon, has been found in other services where hydrogen-carbon monoxide-carbon di-

* As a generality, this varies with the environment. For example, chromium steels have been found more carburized in catalytic cracking unit regenerators than carbon steel.

oxide mixtures are involved, with or without hydrocarbon. Temperature ranges involved are 1,400 F to 2,000 F. Furnace tubes are normally affected and can often be inspected for this corrosion by checking for magnetism of the carburized area if tubes are austenitic. Metal dusting is a specialized attack that could also be increased by alternating oxidizing and reducing atmospheres, if suspected reference to the latest experiences should be made.

204.034 DECARBURIZATION: Decarburization may be defined as the loss of carbon from the surface of a ferrous alloy as a result of heating in a medium that reacts with the carbon. So far as refinery equipment is concerned, decarburization is usually the result of restricted high-temperature oxidation^{38, 56} (see Par. 204.035 for an exception). When carbon is removed from the surface of a steel, the surface layer is converted to almost pure iron, which results in considerably lower tensile strength, hardness, and fatigue strength. The appearance of the decarburized layer is usually not serious unless fatigue is a problem. However, its occurrence in operating equipment is evidence that the steel has been overheated, and other effects may be present. Decarburization can be found only by metalurgical examination. For all practical purposes, decarburization is limited in refinery service to the ferritic steels, and is most often found in steam and hydrogen services.

Although decarburization of refinery process equipment is in itself not usually harmful, it can be quite detrimental in some applications. Heat treating of steels without the use of a proper atmosphere may result in a thin, decarburized layer. This soft, weak layer has very poor fatigue properties and may result in failure of springs, shafts, gears, and the like. Also, the presence of a decarburized layer on a cutting tool will preclude proper surface hardening and result in poor performance.

204.035 HIGH-TEMPERATURE HYDROGEN ATTACK: Some refining operations involve the use or production of hydrogen at high temperatures and pressures. Hydrogen at elevated temperatures (above 450 F) can have a very destructive effect on steels.

At high pressures and temperatures, hydrogen dissociates into atomic hydrogen which can penetrate a metal. Likewise, carbon in steel will migrate at high temperatures. Thus, at low pressures but high temperatures, carbon can migrate toward the surface and combine with hydrogen to form methane.^{57, 58} Under these conditions the hydrogen attack is confined to decarburization. However, if the stress level is high, cracking may result from overstressing.

As pressure is increased and the temperature is still high, the dissociation of hydrogen and the penetration of hydrogen into the metal is more rapid than the migration of carbon to the surface. Under these conditions carbon migrates to the grain boundaries, dis-

locations, and the like, and combines with hydrogen to form methane. This methane reaction causes internal pressure that can crack the metal intergranularly. Under externally applied stress the cracks form and propagate more readily.

An important reference, *API Publication 941: Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*, presents safe operating limits, solely as a guide for use of different steels in hydrogen service. A basic "Nelson" chart shows curves, drawn for different steels, that are the limits for use in hydrogen service. It can be noted that as the amount of carbide stabilizers, such as chromium and molybdenum, are increased the resistance to hydrogen attack is increased. Thus, the curves shown on the chart are for commercially available alloys. For interpolation of these curves, a separate chart shows the effect of molybdenum equivalent when added to steel.

Generalities that apply to hydrogen attack on steel are:⁵⁹

1. Additions to the steel composition of carbide-forming alloying elements, such as chromium, molybdenum, tungsten, vanadium, titanium, and columbium increase resistance to hydrogen attack. Noncarbide formers, such as nickel, copper, silicon, and manganese, have no effect to decrease hydrogen attack.
2. Susceptibility to attack increases with increasing carbon content; thus these curves are meant for wrought alloys primarily, but are a good guide for castings also.
3. Coarse-grained steels are more susceptible to attack than fine-grained steels. Note that the welded and hot-worked carbon steels have been separated by about 75 psi partial pressure of hydrogen from the fine-grained seamless steel. The same differentiation probably holds true to some extent for any alloyed steel, but information is not available at this date to refine these curves.
4. Approximate selected operating limits to avoid severe attack, based on long-time experience in operating equipment, are given in Table 2 for a few steels.⁵⁷

TABLE 2—Approximate Maximum Operating Limits

Steel Type	Selected Temperature * (Degrees Fahrenheit)	Hydrogen Partial Pressure (Pounds Per Square Inch)
Carbon (not welded)	575	300
½ Percent molybdenum	750	1,100
1 Percent chromium-		
½ percent molybdenum	775	1,300
2 Percent chromium-		
½ percent molybdenum	850	1,600

* Somewhat higher temperature limits exist at lower pressures, but some surface decarburization is likely to occur.

These data are given only as a basis for estimating the probability of hydrogen attack under these specific conditions and should not be used for any other purpose. Reductions in hydrogen partial pressure would increase temperature limits (see Nelson chart).⁵⁷

Oxygen-bearing copper and copper alloys, such as tough-pitch copper, are subject to attack by hydrogen at temperatures of 750 F and greater.^{18, 38} Such materials contain particles of cuprous oxide. Hydrogen diffusing inward reacts with this oxide to form water which ruptures the metal. This form of attack is sometimes called "hydrogen disease" or hydrogen embrittlement. Where it is necessary to use copper or its alloys in hydrogen service, such as gaskets, oxygen-free alloys are resistant to hydrogen attack; however, these can become slightly sensitive to hydrogen embrittlement should they be heated in an oxidizing atmosphere. Welding on copper that is to be used in hydrogen service produces cuprous oxide and renders the copper susceptible to hydrogen attack.

204.036 MISCELLANEOUS HIGH-TEMPERATURE ATTACK: Somewhat new specific problems that may be potential trouble areas are:

1. Attack of weld flux on Incoloy tubes.
2. Boiler carryover deposit corrosion.

These are too new and not completely resolved to be discussed in this Guide.

205 SUBNORMAL AND AMBIENT TEMPERATURE EFFECTS

205.01 Brittle Fracture

Notch toughness is a property of metals defined as the amount of energy necessary to cause fracture in the presence of a sharp notch or stress concentrator. In general, the tougher the material, the more energy required to cause fracture. High energy requirements indicate a ductile material, and low energy requirements indicate a brittle material. For most metals and alloys, notch toughness does not change greatly from ambient or intermediate to extremely low temperatures. The ferritic steels are an important exception to this general rule.⁵⁹⁻⁶¹

The ferritic steels usually have good notch toughness at moderate temperatures; that is, they fail in a ductile manner with high energy absorption, even in the presence of a notch. However, it is the nature of all ferritic steels, especially for thicker sections in rigid structures (e.g., 5/8-in. plate and above), that at and below a certain temperature, notch toughness suddenly falls to an extremely low level; that is, failure occurs in a brittle manner with low energy absorption. The temperature at which the type of failure changes from ductile to brittle is called the "transition temperature." The transition temperature varies markedly with differences in chemical composition, hardness or strength level,

heat treatment, microstructure, and steel-making practices. Steel with the proper combination of the above factors may have a transition temperature that is satisfactorily low (refer also to Par. 204.02).

It is not the purpose of this chapter to discuss all the factors related to brittle fracture, nor to discuss the relative merits of the various commonly used steels. Excellent information can be obtained from the current literature in the use of aluminum-killed steels for grain refinement and of ASTM steels designated specifically for low-temperature service.

Important research and development on fracture toughness and fracture-safe design have been undertaken in recent years by the Naval Research Laboratory. Also, the API has long been in the forefront of promoting fracture-safe designs through the use of notch-tough materials (refer to API Standard 650, Appendix D). These sources should be contacted for information on brittle fracture. From an inspection standpoint, except for steels selected especially for their low-temperature properties, most of the commonly used pressure vessel steels probably have transition temperatures between 100 F and -40 F. Some steels may have even higher transition temperatures.

Brittle failures, unlike most ductile failures, occur without warning (no bulging, distortion, etc.), and the cracks propagate with a loud report at a speed near that of the speed of sound. Once such a crack starts, it will very likely continue through more than one plate. Lack of warning and the rapid and extensive propagation of cracks account for the fact that such failures are often catastrophic. Fig. 43 shows a serious brittle failure.

For brittle fracture to occur, there must be present, in addition to a susceptible steel operating below its transition-temperature range, a notch or stress concentrator. Such notches are most likely to be present in the form of welding defects. In most pressure vessel failures to date, a welding defect has apparently acted as a stress concentrator to start the failure. However,



FIG. 43—One of Two Cone-Roof Storage Tanks That Failed During Hydrostatic Testing.
Ambient temperature was +40 F.

notches in the form of plate defects; welders' strikes; cracks resulting from punching, shearing, and other fabrication operations; and sharp geometrical changes present in the design have initiated failures in other structures, such as ships and bridges.

Some of the brittle failures of tanks and pressure vessels have occurred during hydrostatic or pneumatic testing. For this reason, it is generally the policy to refrain from testing tanks and vessels while ambient temperatures are low, particularly if the testing medium is also cold. In any case, the test pressure is applied as slowly as practicable in order to avoid sudden increases in stress.

Brittle fracture can be recognized by several characteristics, as follows: 1, cracks propagate at high speed; 2, there may be a loud report or sharp rending sound; 3, there is almost complete lack of ductility; and, 4, the fractured surface has a brittle or faceted appearance.⁶² The fractured surface often has a characteristic "chevron" or "herringbone" appearance, and the apexes of the chevrons or herringbones point to the origin of the fracture.

Of all of the common metals and alloys used in the refinery, only the ferritic steels exhibit low-temperature brittleness. Some of the ferritic steels, such as SAE Type X1020, the 2½ percent and 3½ percent nickel steels and several other steels, have quite low transition temperatures. The austenitic chromium-nickel stainless steels (18-8, 25-20, etc.) and nickel, copper, aluminum, and their alloys maintain ductility down to the lowest temperatures man has been able to produce.

206 EXCESSIVE PRESSURES

206.01 Introduction

Excessive pressures may be defined as those in excess of the maximum allowable working pressures of the equipment under consideration. When the excess pressure is low, the result may not be serious; but when it is high, the result may be loss of life and property. Therefore, every effort should be made to prevent excessive pressures. Although explosions constitute one type of overpressuring, they are not covered in this discussion. It should be kept in mind, however, that some explosions have been prefaced by what may be considered minor failures, some of which were caused by overpressured equipment.

206.02 Causes of Excessive Pressures

High pressures may develop in a number of ways, several of which are discussed in the following paragraphs.

206.021 ADDED HEAT IN EXCESS OF NORMAL OPERATION: Excess heat can come from an outside source, such as a fire in the area, or it can be the result of upset or abnormal operating conditions. Another cause of excess heat is the failure of control facilities on the

heat-input source, which may allow a higher than normal heat input.

206.022 BLOCKING OFF AGAINST A PRESSURE SOURCE: As a general rule, all parts of pressure systems are designed for the maximum pressure which can be developed by pumps, compressors, and the like, or are protected by pressure-relieving devices. There are some exceptions, however, such as the exhaust side of steam turbines, which are seldom designed to withstand high-pressure steam pressure. Blocking off the outlet before closing the inlet may cause failure of the turbine case.

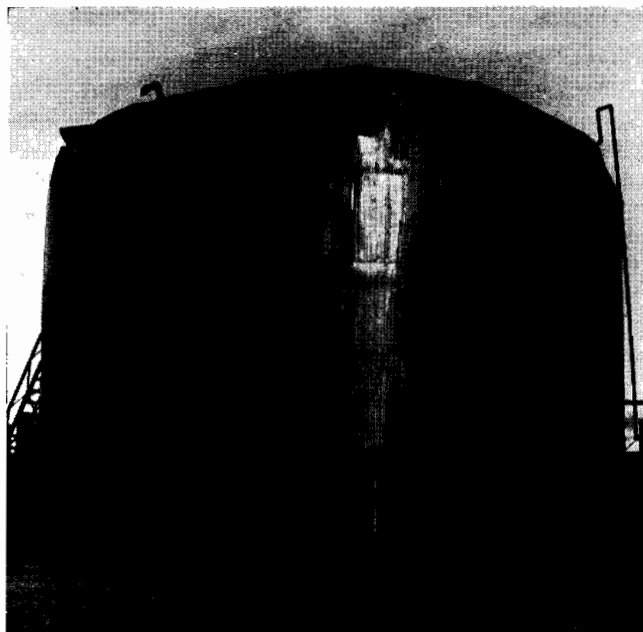
206.023 THERMAL EXPANSION OF TRAPPED LIQUID: There is a good possibility of overpressure in heat-exchange equipment if the inlet and outlet of the colder liquid are closed before the flow of the hotter liquid is stopped. Long pipelines exposed to sun heat can also be subjected to excess pressures by thermal expansion.

206.024 HYDRAULIC HAMMER OR RESONANT VIBRATION: Hydraulic hammer or resonant vibration can occur with relatively low pressures under conditions that make the results of pressure surges additive. Shutting off long lines may result in failures of fittings or gaskets from hydraulic hammer.

206.025 INADEQUATE OR DEFECTIVE VENTS ON STORAGE TANKS: Cone-roof tanks are vented to the atmosphere in order to prevent overpressuring. When these vents are undersized, or when they become plugged with ice, debris, and the like, overpressuring may result. This may occur during pumping (air must escape from the tank during filling, and air must be taken into the tank when pumping out), or during variations of the vapor volume because of fluctuations of atmospheric or hydrocarbon temperatures. The pumping of hot oil into a tank that contains water may result in overpressuring because of the generation of steam. Roof rupture of a tank may occur because of overpressuring if the tank is overfilled. Excessive pressures may be either internal or external. Fig. 44 illustrates excessive internal pressure that developed during the filling of a tank with a plugged vent. Fig. 45 illustrates excessive external pressure. Failures because of excessive external pressure may occur when a vacuum is created in an inadequately vented tank, either by pumping out or by condensation of hydrocarbon vapors. Failures caused by the latter sometimes occur when a cold rain suddenly falls on a tank partially filled with a hot hydrocarbon.

206.03 Effects of Excessive Pressures

Overpressuring usually causes buckling and bulging of the vessel shell, generally in the area of the shell-to-head joint. If the overpressuring is severe enough, rupture occurs. Such ruptures can be explosive in nature if the vessel contains gaseous fluids. If the vessel is

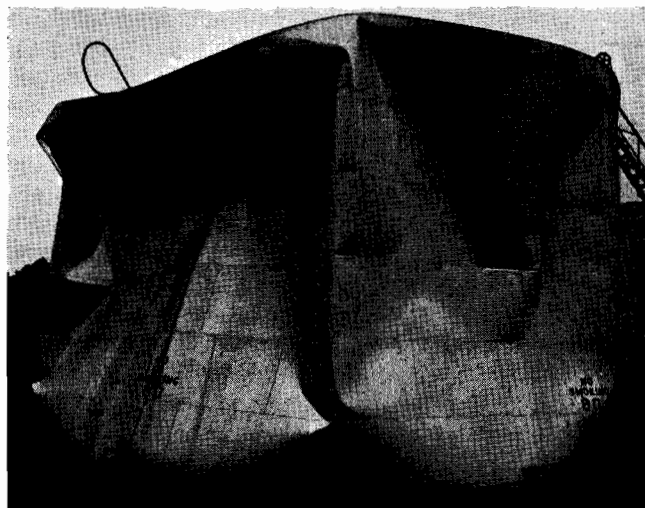


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FIG. 44—Tank Ruptured as a Result of Internal Pressure.
Note small vent pipe and failure of roof and shell joint at upper left.

completely full of liquid, ruptures are generally in the nature of leaks because the overpressuring is relieved as soon as a small amount of liquid escapes. If the liquid is flammable, however, fire is a distinct possibility.

Overpressuring of piping and pumping equipment is a more common occurrence because such equipment is



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FIG. 45—Collapse of an Atmospheric Storage Tank as a Result of Inadequate Vacuum-Venting Capacity.

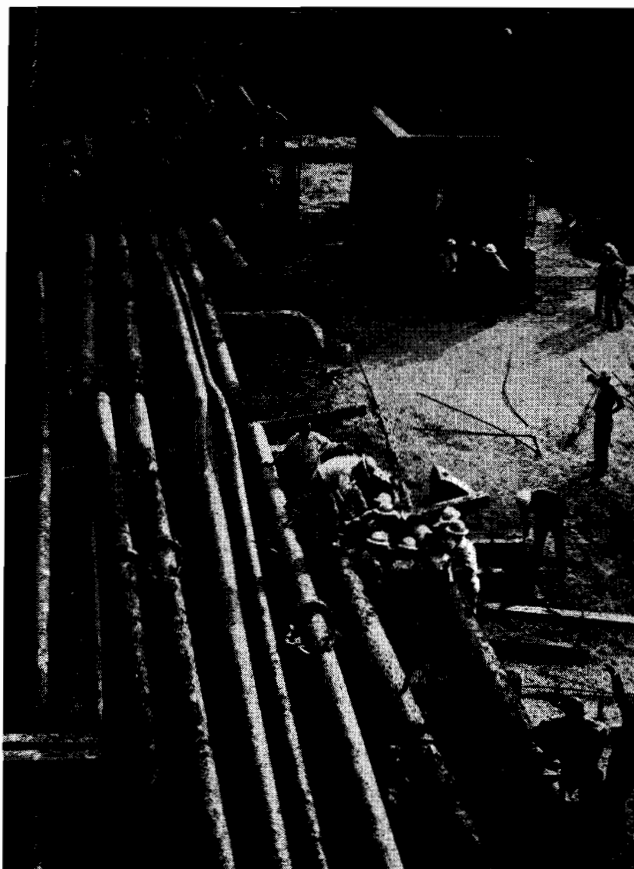


FIG. 46—Overpressured Natural Gas Line Rupture.
Gas ignited and the resulting fire caused the damage shown. Note damaged power and communication lines.

often remotely located and receives less attention than equipment intimately associated with operating units. Furthermore, pipe systems frequently are very complicated and interconnected, and leaky valves may overpressure parts of such systems. Overpressuring of lines is generally evidenced by gasket leaks or the pulling apart of pipe joints. Overpressuring of pumps also causes gasket leaks, but sometimes results in complete casing failure. Fig. 46 shows the results of overpressuring a natural-gas line serving a large refinery. A cast-iron booster pump that failed because of overpressure is shown in Fig. 47 and 48.

207 OVERLOADING

207.01 Introduction

Overloads may be defined as loads in excess of the maximum permitted by the design of the equipment under consideration.

Structures and equipment, including foundations, are normally designed with a factor of safety to carry static loads imposed as well as certain live loads and wind loads. In some cases, a structure or foundation may have been deliberately designed to support the normal

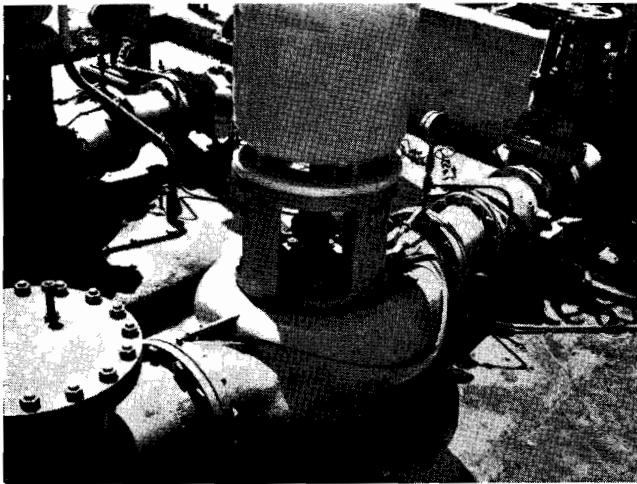


FIG. 47—Failure of an Overpressured Cast-Iron Hydrocarbon Booster Pump.

operating load only; therefore, it will not be sufficiently strong for the hydrostatic test loading of a vessel, or for the hydrostatic test loading of all vessels on a single structure at the same time. The weight of water used in testing is usually greater than the weight of fluids used in petroleum operations. During tests of a tall, vertical vessel, there is the possibility of overloading the bottom head if the weight of water is not considered in test pressures gaged at the vessel top.

Overloading may result if equipment and materials are added to existing vessels and structures, either temporarily or permanently. For example, the application of gunite fireproofing can double the foundation and structural loading. Guniting applied as metal protection under tank roofs or inside pressure vessels may cause failure of supports. Excessive bending stresses may be induced in vessel shells when support brackets, such as those used for piping, are attached to the shells.

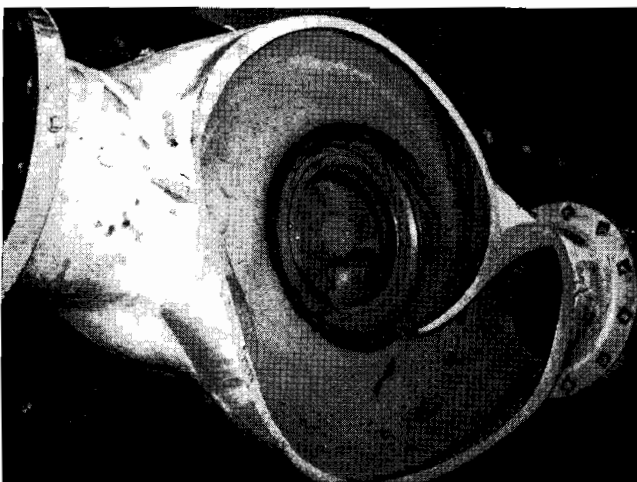


FIG. 48—Bottom Half of the Overpressured Booster Pump Shown in Fig. 47.

The same may be true when oversized manways are installed. The addition of piping to existing pipe supports, or piping that is left overhanging on supports, may present overloading problems. Pipes used as beams may not have sufficient strength to hold loads which may be applied between the pipe supports. A concentrated load applied at mid-span of a simple beam will stress the beam twice as much as the same load if it were uniformly distributed along the beam. Also, deflection of piping may be excessive if unsupported lengths are great.

Overloads occur where metal members have been weakened as a result of corrosion, wear, fire, or change in shape or position. Supports are sometimes bent or shifted in position by accidents, or by use of the supports as hitches.

Thermal expansion and contraction cause many overloading problems, unless flexible-type connections are properly provided. The problems arise where straight piping is rigidly connected between hot vessels and the pipe-supporting structures, or between two pieces of equipment that move in relation to each other. Piping subject to thermal expansion may force a centrifugal pump or steam turbine out of line and warp the shaft, unless the pipe is anchored near the equipment. The commonly used overhead pipe supports may not be strong enough to securely anchor piping that is subject to thermal movement. Guides will normally permit sufficient movement of piping to compensate for thermal expansion or contraction, but may present problems at pipe bends.

Vibration loads on structures and equipment generally require special treatment because the vibration effects may be shifted when a vibrating section is anchored. Special studies may be necessary before anchors or dampeners are provided, unless the vibration is eliminated by removing the source. Failures result from fatigue stresses that are built up at supports, piping, and equipment in which sharp corners exist and in which anchoring attachments are undersized for vibration loading.

There are also miscellaneous locations where overloading may occur. Exchanger foundations or piping may be damaged by pulling bundles that are stuck in the shells, unless the shells are firmly secured. Gaskets between flanges may be crushed by uneven or over-tightened bolting. Furnace stacks, flare stacks, or similar structures are subject to overstressing by unevenly tightened guy lines. Failure of equipment may result where wooden supports decay or burn. Severe impact loads occur in machinery, such as compressors, when bolts become loose or defective parts fail. Underground washouts from water lines and sewers, including acid sewers in particular, affect the allowable loading of foundations in the vicinity. Retaining walls and end dams on separators can be overloaded by washouts. Non-load-bearing tile or similar building construction may not be suitable for additional weight.

Other temporary and permanent installations that may have damaging overloads are not covered herein.

207.02 Evidences of Overloading

Indications of excessive loading are usually apparent because of visible distortion, change of shape, change of position, or other visible signs. An overloaded condition may not be readily apparent when a distortion has not occurred, such as when weak bolted or welded joints, or even poor soil conditions, exist.

The following are some typical observations which give evidence of overloading:

1. An unlevel horizontal cross beam on a pipe support indicates soil overloading.
2. A noticeably sagged support beam.
3. A support column found bent out of line or leaning (Fig. 49).
4. A support column made of pipe that can be dented with a hammer is generally corroded and is probably overloaded.
5. At structural joints the slippage of bolts may be noted on the bolted surface, or a weld may have cracks.

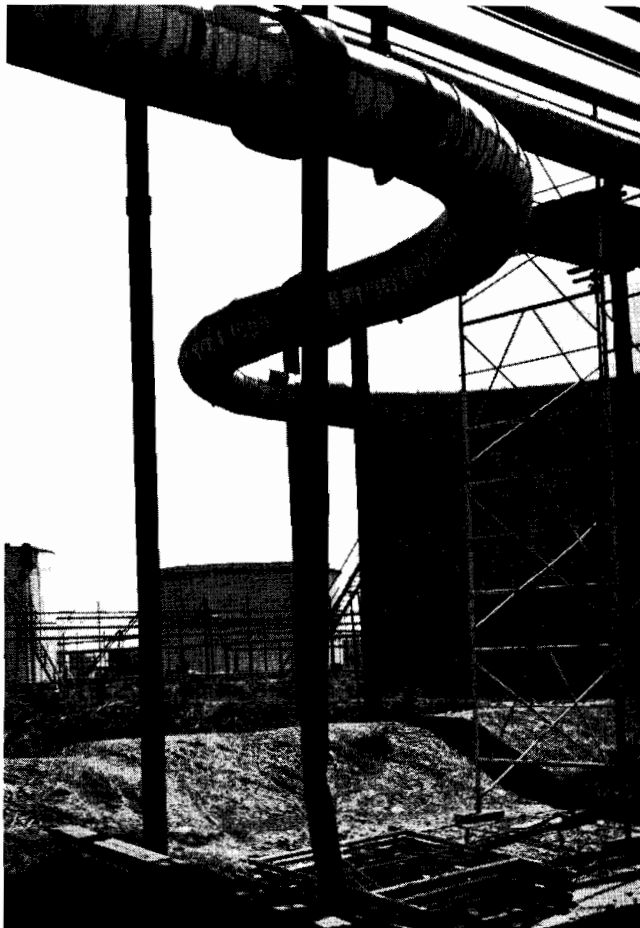


FIG. 49—Overloaded Pipe Support.

6. Substantial springing of piping may be observed when disconnected from a pump being removed for repairs.

7. A thermal expansion overload may be indicated when a leak develops in drain piping serving a hot vessel if the piping is anchored some distance from the vessel connection.

8. Failure of one or two similar supports on a discharge header serving gas-engine-driven compressors is indicative of vibrational overloading.

9. A loose guy line observed on a furnace stack that has become distorted indicates too much pull by the other guy lines.

10. A compressor shaft or flywheel failure may result from an overloaded bolt. For example, one of two bolts holding a shaft counterweight may not be seated because of faulty tightening. The other bolt, though properly installed, may not be adequate, and the counterweight may become loose.

11. Overloading, because of deterioration from heat, of a concrete pedestal supporting a masonry stack may become evident by subsequent leaning of the stack.

Other evidences of overloading are shown in Fig. 50 through 55.

208 EARTHQUAKES AND EARTH SETTLEMENTS

Earthquakes will cause severe vibration in equipment, and may cause it to sway so far out of line as to place excessive eccentric loading on supports. It may result in broken lines, broken connections, bent parts, and even actual collapse of a structure. As a result of ground movement, uneven settlement may occur. Also, most of the results listed under Sect. 207 may follow. Most serious damage from earthquakes can be determined by a careful and close visual inspection.

209 MECHANICAL AND WIND DAMAGE

209.01 Introduction

Operating equipment and structures may suffer damage from several sources, including the following:

1. Trucks, tractors, and handling equipment.
2. Misuse of equipment.
3. Wind.

Mechanical and wind damage is almost always of such a nature that it can be found by visual inspection.

209.02 Examples of Mechanical and Wind Damage

Following are some examples of mechanical and wind damage. Much of this damage resulted from improper equipment location, failure to provide adequate barriers and guards where necessary, and improper material-handling procedures.



FIG. 50—In Dismantling Structure, Side Sway of Load Apparently Caused this Crane-Boom Failure.

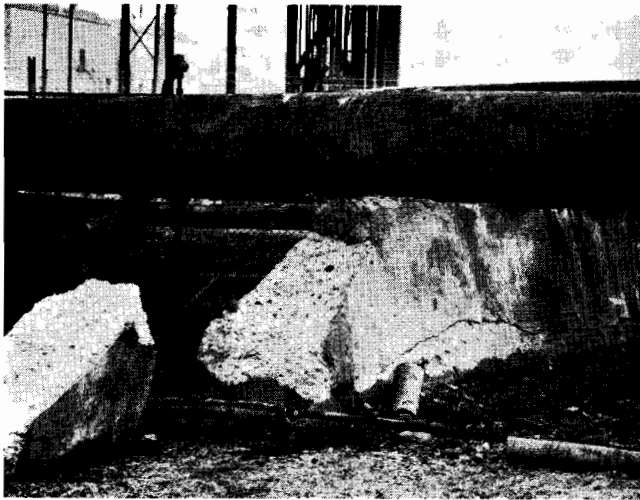


FIG. 51—Fire Has Reduced the Load Capacity of this Concrete Pipe Support.

1. An air-powered winch, anchored to a structural column, caused bending of the column when a load was applied to the winch (Fig. 49).
2. A truck, or other motorized equipment, collided with a structural column. The column was deformed, and its concrete foundation was damaged (Fig. 56).
3. A truck collided with a small bleeder connection on

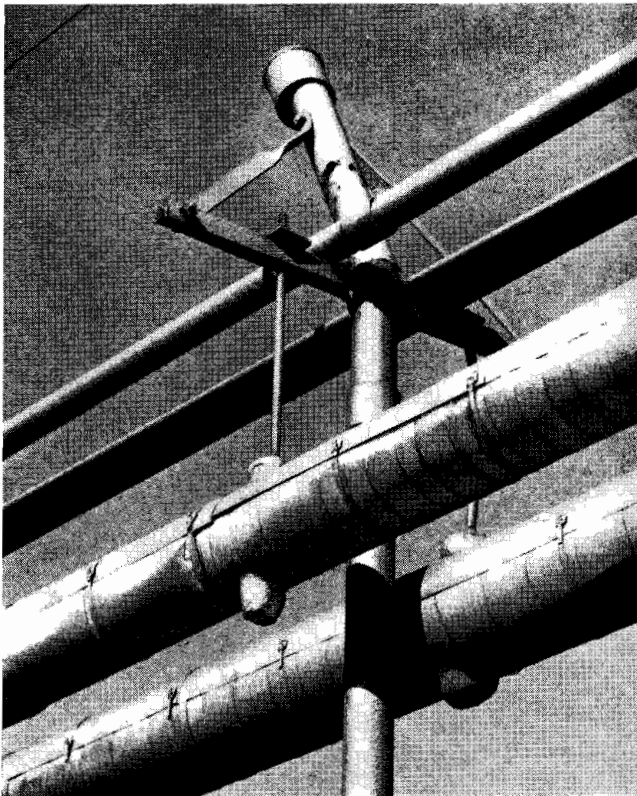


FIG. 52—Pipe Support Overloaded as a Result of Corrosion.

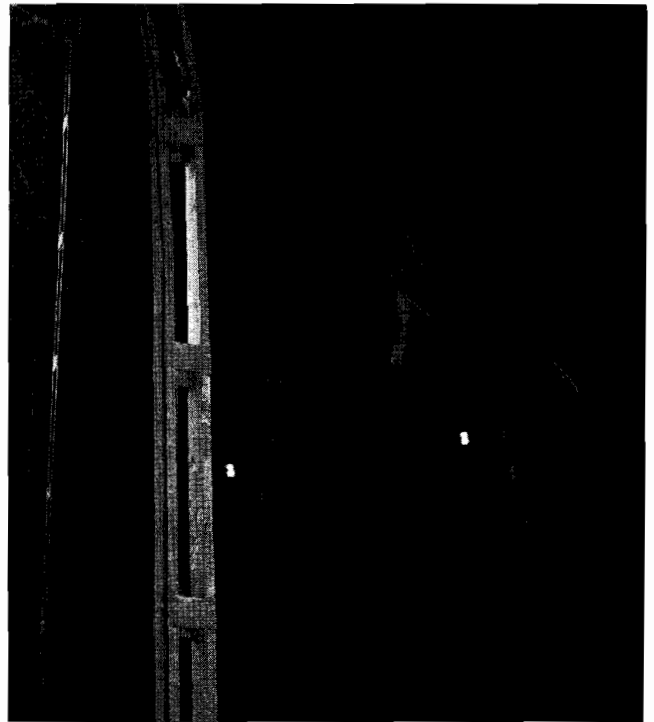


FIG. 53—Tank-Roof Supports Are Overloaded After Corrosion Has Occurred.

a high-pressure steam line. The connection was broken off, and an important refinery unit had to be shut down while repairs were being made (Fig. 57).

4. A truck collided with a fire hydrant, breaking it off at ground level.
5. A bulldozer severed an underground gas line, and leaking gas ignited. The plant served by the gas line was shut down while repairs were made.
6. Fabricated piping was thrown off a delivery truck, and a groove was cut across the face of a flange when it struck a sharp object. The flanged joint leaked when tested and had to be replaced.
7. A tube bundle was being pulled from the shell of a heat exchanger with a winch. The heat-exchanger shell was improperly secured and was pulled off its foundation.
8. A heat-exchanger tube bundle was being lifted with a wire-rope sling. The tubes were crushed by the single turn of wire rope.
9. Several scaffold boards were not lashed securely to a scaffold. High winds picked up the boards and threw them into adjacent piping. The piping was damaged and required replacement.
10. A tank shell was being erected. The plate for the top ring had been installed, but had not been guyed or reinforced. A strong wind collapsed the top shell ring.

209.03 Causes of Mechanical and Wind Damage

Fire hydrants, valves, piping, and structural supports may be located too close to accessways, especially near



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FIG. 54—Deterioration of the Concrete Foundation Pedestal in One of the Areas of Maximum Stress.

The structure was reinforced with steel, as shown underneath.

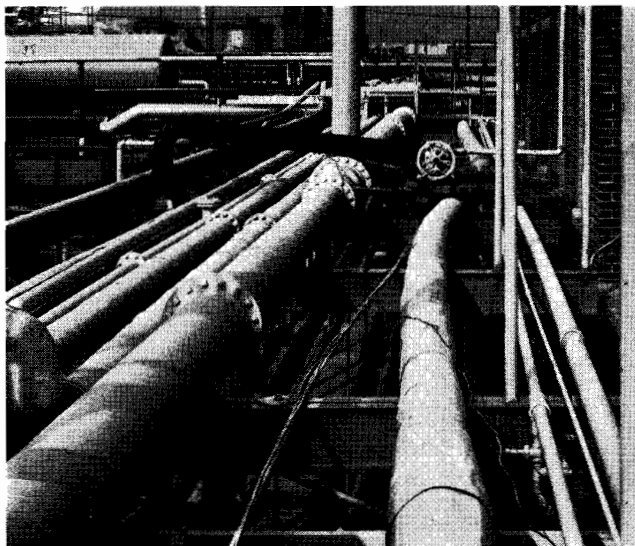


FIG. 55—Wooden Support is Inadequate to Support Overhanging Piping.

The steam line underneath has moved out of position as a result of expansion loading.

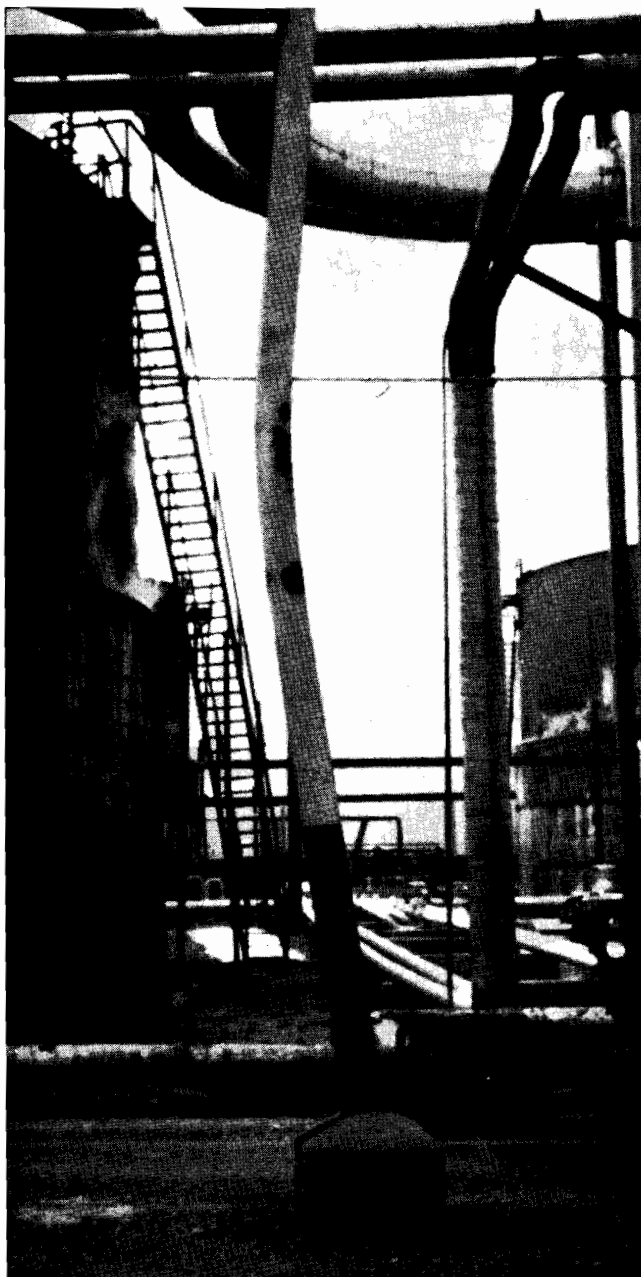


FIG. 56—Pipe Support Column Damaged by Motorized Equipment.

This column is now very susceptible to collapsing from an overload.

sharp corners. Guards may be inadequate where it is necessary to locate equipment near an accessway. Structural support columns are normally designed for compressive loading, and other types of loading may lead to bending. Supports may be damaged when used as anchors for winches. During earth-moving work, underground pipelines and electrical conduits may be damaged if they are not carefully located and properly identified.

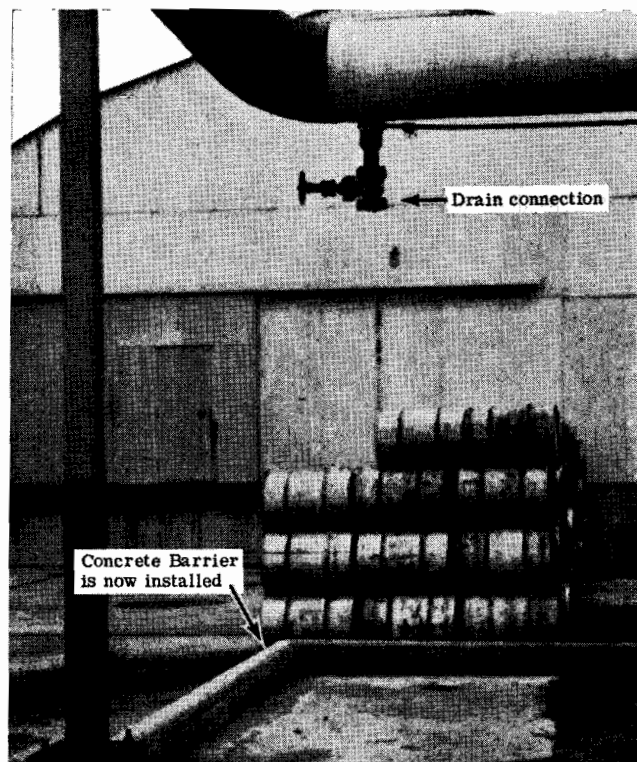


FIG. 57—Drain Connection on High-Pressure Steam Line was Broken Off When a Truck Used the Space Between the Pipe Support Columns as a "Turnaround Area" for Access to Warehouse Doors.

Note that a concrete barrier has now been installed.

Flange faces and other machined seating surfaces may be damaged when not protected with covers, or when not handled with care. Material may be thrown from truck beds in such a manner that it is bent, crushed, or cracked. Tubes of heat-exchanger tube bundles may be crushed if the bundles are not lifted with proper slings. Foundations of heat-exchanger shells may be damaged when an attempt is made to pull the bundles without adequately anchoring the shells.

Equipment and structures are normally designed to withstand any anticipated wind loading. During construction or repairs, however, wind damage may result if they are not properly guyed or reinforced. Loose sheets of metal, boards, and the like, may be blown about by high winds if they are not properly secured.

The foregoing is not a complete list of damage that may be caused by mechanical means or by wind, but is quoted to illustrate the wide variety of damage that may be experienced.

210 FAULTY MATERIAL AND EQUIPMENT

210.01 Introduction

Many advances have been made in the past decade in the field of material and equipment selection. Instances of failures attributable to poor selection of ma-

terial and equipment have become the exception. Nowadays, unit shutdowns are caused primarily by corrosion or erosion, overpressuring, or poor operational techniques. However, the possibilities of poor material or equipment selection must not be minimized.⁶³

210.02 Situations Leading to Improper Selection of Material and Equipment

Three principal means still exist whereby improper material and equipment selection may be made: error, designing for new processes, and use of low-cost materials.⁶⁴

210.021 ERRORS: These may occur either during construction or during repairs. Adequate plans and specifications and careful supervision and inspection should prevent the installation of wrong material during construction. Repairs that require replacement of parts are more liable to error. For example, a carbon-steel part may be used to replace an alloy part, thinner material may be used than required for the service, unsuitable welding rod may be used when making repairs, and other similar substitutions may occur. Examination of the original drawings and specifications before any part is replaced or any repair is made, and inspection while the work is in progress, should prevent such errors.

210.022 NEW PROCESSES: New processes always present a multitude of material and equipment prob-

lems. Even with good pilot-plant data, it is often difficult to determine the various contingencies that will arise. Several excellent examples have arisen with some of the newer gasoline octane-improvement processes. Fig. 58 indicates how high-hydrogen recycle gas streams have carburized transfer piping. Inasmuch as this was a new process, this attack was not anticipated. Other problems, such as the failure of flue-gas-stack muffler sections (see Fig. 59), have arisen. Reducing the 200-psig regenerator pressure to atmospheric pressure creates unusual flue-gas flow patterns that tend to loosen and pulverize the refractory attached by metal reinforcing to the stack. Process modification on existing units generally presents more problems than new plants. Conversion of existing units generally implies a "rush" program to get some new product on the market; and in the haste to complete construction, material and equipment selection may be influenced by the availability of existing equipment.

210.023 USE OF LOW-COST MATERIALS: The third opportunity for improper material and equipment selection, the use of low-cost items, becomes increasingly important as the industry gets more investment conscious. If a judicious economic review of all cases is not made, improper materials or equipment may result. It is generally more costly to rectify an error than to build quality into the original installation. Therefore, efforts are usually directed toward getting quality in equipment that is critical to a unit or very expensive

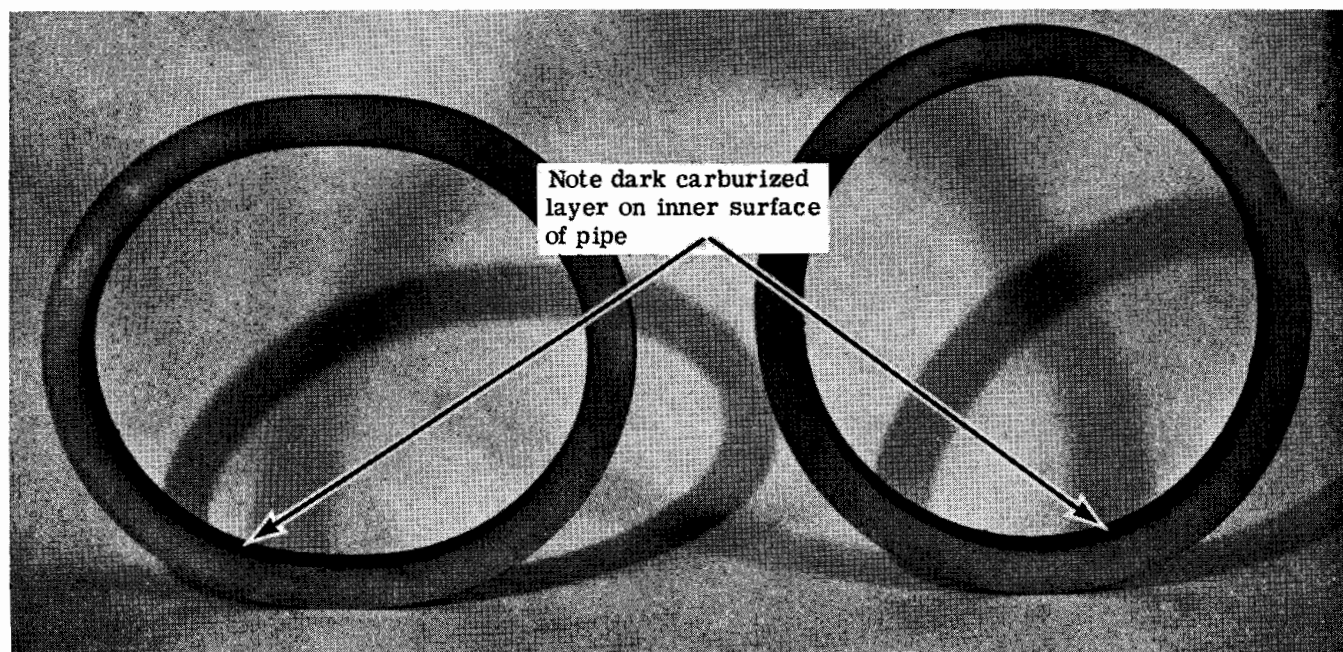


FIG. 58—Ring Samples of 5 Percent Chromium Steel, 8 in.-Schedule 120 Pipe Removed from Recycle-Gas Piping in Fluid Hydroformer Unit.

Ring on left was flattened during ductility tests.

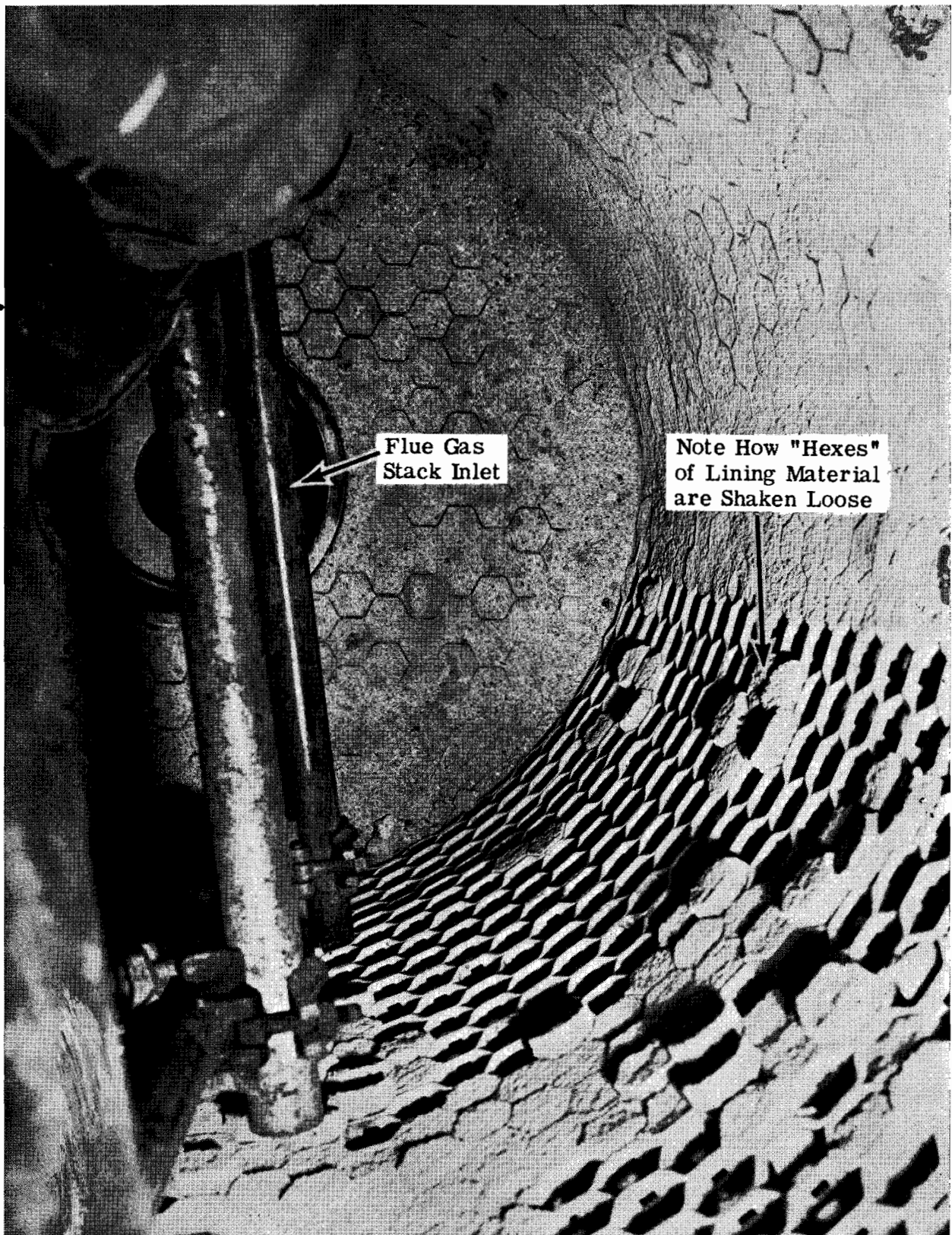


FIG. 59—Failure of the Lining in a Flue-Gas Stack.

to replace. Examples of the former are furnace tubes and unit piping; tower internals are a good example of the latter.

210.03 Evidences of Faulty Material and Equipment

Faulty or improper material and equipment manifest themselves in a number of ways. Cracks, bulges, and excessive corrosion or erosion are the more prominent ones. Cracks may be caused by such things as shrinkage, sand holes, and blowholes in castings, and by sub-surface laminations at points of high stress in wrought materials. Shrinkage cracks occur in castings and are often found in the thinner sections where the metal cools faster. Sharp corners and abrupt changes in cross-

sectional areas are stress raisers, and shrinkage cracks also occur at such points. Sand holes are caused by molding sand trapped within the casting. Blowholes are caused by gas trapped within the casting during solidification. The sand and gas create crevices or holes that are often within the metal and may not be visible from the exterior of the casting.

Discontinuities, when subjected to high stresses, are excellent crack initiators. The discontinuities in the material may be laminations, crevices, abrupt changes in thickness, sharp corners, and the like. Cracks may also occur without a discontinuity under excessively high stress.

Bulges may result if the materials selected do not have adequate strength for the intended service.

APPENDIX I

COMMON REFINERY METALS AND ALLOYS

A. Ferrous Alloys

The ferrous alloys are the alloys of iron, principally steels and cast irons. Steel is an alloy of iron and carbon, with a carbon content ranging from 0.01 to 1.7 percent. Usually refinery construction steels have less than 1 percent of carbon, and steels for welding generally have a maximum of 0.35 percent of carbon.⁶¹ Steels containing only iron and carbon are called carbon steels. Mild steel is one type of carbon steel. In addition to iron and carbon, some steels have other metals (called alloying elements) added, in which case the steel is called an alloy steel. Steels with a total alloying-element content of up to 5 percent are called low-alloy steels. Studs and bolts for high-temperature service are made of such steels. Steels with a total of 5 to 10 percent of alloying elements are called intermediate-alloy steels. Examples are the chromium steels, such as 4 to 6 percent and 8 to 10 percent, used in furnace tubes. Steels with a total of more than 10 percent of alloying elements are high-alloy steels. Examples are the stainless steels, such as 12 percent chromium or 18 percent chromium-8 percent nickel steels.

In the ferrous-alloy sense, iron refers not to the chemical element, but to high-carbon alloys of iron. These are the cast irons and contain 2.7 to 3.6 percent of carbon and 1.0 to 2.75 percent of silicon. There are various alloy cast irons which, besides the high carbon and silicon contents, contain various percentages of other metals, such as chromium and nickel.

There are two general types of steels, the ferritic steels and the austenitic steels. Ferritic steels include the ordinary carbon steels, low- and intermediate-alloy steels, and the high-alloy steels such as the straight chromium steels. The austenitic steels are the chromium-nickel stainless steels, such as 18-8, 25-20, 25-12, and 20-29.

The ordinary cast irons (gray cast irons) are ferritic; some of the alloy cast irons, such as Ni-Resist, are austenitic.⁶⁵⁻⁶⁷

1. **FERRITIC STEELS:** The normal structure (often called microstructure because of the relatively small size of the constituents) of ferritic steels consists of two types of crystals or phases called ferrite and cementite. Ferrite is practically pure iron and is quite soft and ductile. Cementite is a chemical compound of iron and carbon, with the approximate chemical formula Fe_3C . It is fairly hard and brittle. The combination of soft, weak ferrite and hard, brittle cementite accounts for

the high strength and plasticity of steel. The strength and ductility of any given steel depend on the relative amounts of these two phases which, in turn, depend on the chemical composition. For instance, the more carbon there is present, the more cementite will be present; and the less carbon, the less cementite. Certain alloying elements tend to strengthen the ferrite.

When ferritic steels are heated above a certain temperature, the ferrite and cementite crystals start to dissolve into one another to form a new phase called austenite, which is a solid solution of iron, carbon, and any other element present. The temperature at which this begins depends on the steel composition; it ranges from approximately 1,350 F for mild steel to approximately 1,500 F for the straight chromium steels, up to and including the 12 percent chromium stainless steels. On slow cooling, austenite transforms back to ferrite and cementite.

Stainless steels are those that contain more than 12 percent of chromium. They are high-alloy steels. This figure of approximately 12 percent of chromium and the name "stainless" are based on the fact that corrosion resistance, which improves as increasing amounts of chromium are added to a steel, suddenly achieves a noticeably high level when the amount of chromium reaches approximately 12 percent. Further additions of chromium continue to increase corrosion resistance gradually.

The ferritic steels are not intended to be used at temperatures near or above the temperature at which austenite forms, partly in order to avoid structural changes which seriously affect mechanical properties, and partly to avoid severe oxidation. However, as a result of upset conditions of operating equipment, fires, neglect, coking, poor design, and the like, excessive operating temperatures are sometimes encountered.

2. **ALLOY STEELS:** In ferritic steels the normal microstructure is composed of ferrite and cementite. These phases (crystals) are formed by the transformation of austenite below a certain temperature. There are certain steels in which the chemical composition is such that the austenite is stable down to room temperature; that is, it does not transform to ferrite and cementite. Such steels are called austenitic steels.

Although there are a number of types of austenitic steels, almost the only ones found in the refinery are the austenitic stainless steels.

The austenitic stainless steels contain more than 12 percent of chromium (in general) and 6 percent or

more of nickel to stabilize the austenite. Typical refinery austenitic stainless steels are 18 chromium-8 nickel steel (AISI Types 301, 302, 303, 304, 316, 321, and 347), 25 chromium-12 nickel (AISI Type 309), 25 chromium-20 nickel (AISI Type 310), and 20 chromium-29 nickel (various proprietary alloys, usually bearing the numeral "20" after the trade name).

The normal microstructure of the austenitic stainless steels consists only of austenite grains. Austenite, it will be remembered, is a solid solution of iron, carbon and, in this case, chromium and nickel. On normal heating and cooling, no phase changes occur (i.e., no new type of crystals are formed).

Inasmuch as these steels do not normally undergo phase changes and consist entirely of austenite, there is no problem with graphitization and hardening.

3. **CAST IRONS:** Cast irons are characterized by a high carbon content. While the carbon content in steels is so low that the carbon is fully dissolved in the structure, there is a surplus of carbon in the cast irons. This surplus carbon is usually found as graphite stringers in a matrix of metal crystals. The presence of these soft, weak graphite stringers, which may be considered discontinuities, partly accounts for the low tensile strength and the brittleness of the cast irons. The presence of the black graphite gives a newly fractured surface a gray appearance, thus the name "gray iron."

There are two general types of cast irons commonly used in refineries: ferritic and austenitic. In the ferritic irons, graphite is found in a matrix of ferrite and cementite. In the austenitic irons, graphite is found in a matrix of austenite.

Because of the brittleness and low strength of cast irons, there has been a general reluctance to employ these materials inside battery limits in the petroleum industry for the handling of hydrocarbons. The use of cast iron in refineries may increase as a result of the development of the new "ductile irons." These are cast irons in which the graphite has been formed (by additions of certain materials to the molten metal) as nodules, instead of as stringers as in ordinary cast irons. These ductile irons have properties intermediate between cast irons and steels; they will probably be used in the future in applications for which ordinary cast irons have been undesirable.

B. Nonferrous Metals and Alloys

The nonferrous metals and alloys are all those which contain less than 50 percent of iron. Thus all the common metals and alloys, except iron and steel, are in this group.

The nomenclature of nonferrous alloys is based on a consideration of which metal makes up 50 percent or more of the total. Thus monel (70 percent of nickel, 30 percent of copper) is a nickel alloy, and a cupronickel (such as 70-30, which is 70 percent of copper and 30 percent of nickel) is a copper alloy.

1. **NICKEL AND NICKEL ALLOYS:** Commercially pure nickel and the only common refinery nickel-copper alloy, monel, are single-phase metals used for relatively low-temperature corrosion resistance.

Nickel-molybdenum-iron alloys of varying compositions are single-phase alloys marketed under trade names, such as Hastelloy, Chlorimet, and Illium. They are used in petroleum refining mostly for their excellent corrosion resistance at moderate temperatures, although they do, because of high molybdenum content, have good high-temperature strength properties.

A nickel-silicon alloy, sold under trade names such as Hastelloy D and Illium S, is used in the refining industry for its sulfuric acid corrosion resistance. This alloy is a hard, brittle cast material.

Nickel-chromium alloys, such as Alloy 20, Incoloy, or Inconel sold under a number of trade names, are used both for their excellent resistance to chemical attack at moderate temperatures and for their high-temperature properties. Alloy 20 (20 Cr-29 Ni) and Incoloy 800 (21 Cr-32 Ni) are usually used for resistance to chemical attack, whereas Inconel 600 (15 Cr-76 Ni) and Incoloy 800 are commonly used for high-temperature strength purposes. In structure these alloys are similar to the austenitic stainless steels.

Nickel and nickel alloys are sometimes used in the cold-worked (called "tempered," half-hard, cold-drawn or -rolled, etc.) condition for increased strength. Certain nickel alloys, such as K monel and Inconel X, are used in a heat-treated condition for increased strength.

2. **COPPER AND COPPER ALLOYS:** The major uses of commercially pure copper in refineries are for electrical conductors, for gaskets, and for corrosion resistance. The copper alloys—which consist of the various brasses, bronzes, and cupronickels—are, in general, single-phase alloys [exceptions are Muntz and naval brasses, which are two-phase alloys (alpha and beta)] used for corrosion resistance.

Copper and copper alloys are sometimes used in the cold-worked (called "tempered," half-hard, cold-drawn or -rolled, etc.) condition for increased strength. Beryllium copper is used in a heat-treated condition for increased strength.

3. **ALUMINUM AND ALUMINUM ALLOYS:** The major uses of aluminum and its alloys in refineries are for corrosion resistance and for structures in which light weight is a necessity. Aluminum alloys may be single-phase or multiphase alloys, depending on composition.

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INDEX

Acid (s):

- acetic, 202.026, **21**
- concentration facilities, 202.032c, **24**
- hydrofluoric, 202.032a, **23**
- hydrogen chloride, 202.021, **8**; 202.022, **9**
- hydrogen sulfide, 202.021, **8**; 202.023, **13**; 202.055, **33**
- naphthenic, 202.026, **21**
- oleic, 202.026, **21**
- organic, 202.021, **8**; 202.026, **21**
- palmitic, 202.026, **21**
- phenol (carbolic), 202.033, **25**
- phosphoric, 202.034, **26**
- propionic, 202.026, **21**
- stearic, 202.026, **21**
- sulfuric, 202.032, **22**
- Acid brick, 202.032c, **24**
- Admiralty, corrosion rates for, 202.022, **11**
- Adsorption systems, 202.022, **12**
- Air-hardened steels, 204.022d, **47**
- Alkaline agents, in corrosion control, 202.022, **12**
- Alkylation units, sulfuric acid corrosion of, 202.032a, **22**
- Alloy 20 stainless steels, 202.026, **21**; 202.032a, **24**; 202.032c, **25**

Alloys:

- cast irons, Appendix I, **64**
- ferrous, Appendix I, **64**
 - cast irons, Appendix I, **64**
 - steels, Appendix I, **64**
- nonferrous, Appendix I, **65**
 - aluminum and aluminum alloys, Appendix I, **65**
 - copper and copper alloys, Appendix I, **65**
 - nickel and nickel alloys, Appendix I, **65**
- Alloys and metals, galvanic series of refinery (Table 1), 202.067, **38**

Aluminum and aluminum alloys, Appendix I, **65**

- corrosion rates of, 202.041, **28**
- corrosion resistance of, 202.024b, **18**
- Aluminum chloride, corrosion by, 202.039, **27**
- Ambient temperature effects, 205, **52**

Ammonia:

- corrosion by, 202.027, **21**; 202.037, **27**
- as neutralizer, 202.022, **12**

Anhydrous ammonia, 202.022, **12**

Aqueous ammonia, 202.022, **12**

Asphaltic crude oils, 202.026, **21**

Atmospheric corrosion, *see* Environmental corrosion

Austenite, 204.022d, **47**; Appendix I, **64**

Austenitic steels, Appendix I, **64**

- carbide precipitation in, 204.022e, **48**
- carburization of, 204.032, **50**
- grain growth in, 204.022a, **46**
- intergranular corrosion, 202.062, **35**
- resistance to corrosion, 202.023c, **17**; 202.024b, **18**
- sensitization in, 204.022e, **48**
- sigma phase in, 204.022f, **49**
- stress corrosion cracking in, 202.064, **36**

Bacteria, 202.069, **39**

Bibliography, **67**

Biological corrosion, 202.069, **39**

Blistering, hydrogen, 202.023b, **14**

Blocking off against pressure source, 206.022, **53**

Boiler embrittlement, 202.064, **36**

Brass, corrosion of, by ammonia and cyanides, 202.027, **21**

Brine, in crude oil, 202.022, **9**

Brittle fracture, 201.02, **8**; 205.01, **52**

Burning (incipient melting), 204.022b, **46**

Calcium hydroxide, 202.022, **12**

California asphaltic crude oils, 202.026, **21**

Carbide precipitation (sensitization), 204.022e, **48**

Carbolic acid (phenol), 202.033, **25**

Carbon block, 202.032c, **24**

Carbon dioxide, 202.021, **8**; 202.024, **18**

general discussion, 202.024a, **18**

hydrogen plant corrosion, 202.024b, **18**

Carbon steel:

- corrosion of, 202.022, **10**; 202.023c, **15**
- corrosion rates for, 202.022, **11**
- hardening of, 204.022d, **47**
- hydrogen sulfide corrosion of furnace tubes of, 202.023c, **15**
- susceptibility to brittle failure, 201.02, **8**

Carbonic acid, 202.024a, **18**

Carburization, 204.022d, **48**; 204.032, **50**

Cast irons, Appendix I, **64**

austenitic, Appendix I, **64**

ductile, Appendix I, **64**

ferritic, Appendix I, **64**

gases, hot corrosive, effect on, 202.056, **34**

graphitic corrosion of, 202.063, **35**

Catalysts, 203.021, **41**

Catalytic cracking units, hydrogen sulfide corrosion of,

202.023c, **15**

Cathodic protection, 202.073, **40**

Caustic:

corrosion by, 202.035, **26**

embrittlement, 202.064, **36**

Caustic soda, 202.022, **12**

Cavitation, 203.022, **43**

Cementite, 204.022d, **47**; Appendix I, **64**

Chemical changes, metallurgical, 204.03, **50**

carburization, 204.032, **50**

decarburization, 204.034, **51**

hydrogen attack, 204.035, **51**

metal dusting, 204.033, **50**

Chemical components, corrosion problems caused by, 202.021,

9

Chemicals, in corrosion control, 202.022, **12**

Chlorides:

organic and inorganic, 202.021, **8**; 202.022, **9**

stress corrosion cracking caused by, 202.064, **36**

Chlorine, corrosion by, 202.038, **27**

Chromium-improvement theory of intergranular corrosion,

204.022e, **49**

Chromium steels:

carburization of, 204.032, **50**

hardening of, 204.022d, **47**

hydrogen attack of, 204.035, **51**

hydrogen sulfide corrosion of furnace tubes of, 202.023c,

15

sigma phase in, 204.022f, **49**

Coking processes, hydrogen sulfide corrosion in, 202.023c, **17**

Condensers, hydrogen chloride corrosion of, 202.022, **10**

Contact (crevice) corrosion, 202.068, **39**

Coolers, sulfuric acid, 202.032c, **25**

Cooling rate for hardening, 204.022d, **47**

Cooling water, corrosion resulting from, 202.042d, **30**

Copper and copper alloys, Appendix I, **65**

corrosion of, by ammonia and cyanides, 202.027, **21**

dezincification, 202.066, **38**

stress corrosion cracking, 202.022, **12**; 202.064, **37**

Corrosion, 202, **8**

causes of, 201.02, **7**

control of, 202.021, **9**

cost of, 202.01, **8**

effects of, 201.02, **7**

low-temperature, 202.022, **9**

in overhead equipment, 202.022, **10**

rates of, 202.022, **10**

reduction of, 202.022, **12**

Corrosion by:

acetic acid, 202.026, **21**

aluminum chloride, 202.039, **27**

ammonia, 202.037, **27**

carbolic acid, 202.033, **25**

carbon dioxide, 202.021, **8**; 202.024, **18**

- caustic, 202.035, **26**
- chlorine, 202.038, **27**
- components in crude oil, 202.021, **8**
- dissolved oxygen and water, 202.025, **19**
- environment, 202.04, **27**
- gases, on cast iron, at high temperature, 202.056, **34**
- high temperature with oxygen, 202.052, **31**
- hydrochloric acid, 202.022, **9**
- hydrogen chloride, 202.022, **9**
- hydrogen fluoride, 202.032, **22**
- hydrogen sulfide, 202.023c, **14**; 202.055, **33**
- mercaptans, 202.023, **13**
- mercury, 202.036, **27**
- naphthenic acid, 202.026, **21**
- nitrogen compounds, 202.027, **21**
- oleic acid, 202.026, **21**
- organic acids, 202.026, **21**
- organic sulfur compounds, 202.023, **13**
- oxygen, 202.025, **19**; 202.052, **31**
- palmitic acid, 202.026, **21**
- phenol, 202.033, **25**
- phosphoric acid, 202.034, **26**
- propionic acid, 202.026, **21**
- salts and hydrochloric acid, 202.022, **12**
- sodium hydroxide, 202.035, **26**
- steam, at high temperature, 202.053, **32**
- stearic acid, 202.026, **21**
- sulfur, 202.023a, **13**
- sulfur dioxide, at high temperature, 202.055, **33**
- sulfuric acid, 202.032, **22**
- vanadium oxide, at high temperature, 202.054, **33**
- Corrosion inhibitors for cooling water systems, 202.042d, **30**
- Corrosion occurrences with attempts at corrosion control, 202.07, **40**
 - cathodic protection, 202.073, **40**
 - inhibitors, 202.071, **40**
 - neutralization, 202.072, **40**
- Corrosion phenomena, 202.06, **34**
 - biological corrosion, 202.069, **39**
 - contact (crevice) corrosion, 202.068, **39**
 - dezincification, 202.066, **38**
 - galvanic corrosion, 202.041, **28**; 202.067, **38**
 - graphitic corrosion, 202.063, **35**
 - intergranular corrosion, 202.024b, **18**; 202.062, **35**; 204.022e, **48**
 - polythionic acid corrosion, 202.065, **37**
 - stress corrosion cracking, 202.022, **12**; 202.024b, **18**; 202.064, **35**
- Cracking units:
 - catalytic, hydrogen sulfide corrosion, 202.023c, **15**
 - thermal, hydrogen sulfide corrosion, 202.023c, **15**
- Cracks, fatigue, 201.02, **7**
- Creep, 204.012, **43**
- Crevice (contact) corrosion, 202.068, **39**
- Crude oil, corrosive components of, 202.02, **8**
- Cupro-nickel, corrosion resistance of, 202.024b, **18**
- Cyanides, corrosion of copper and brass by, 202.027, **21**
- Decarburization, 204.034, **51**
- Desalting equipment, 202.022, **12**
- Deterioration:
 - erosion as cause of, 203.01, **40**
 - relationship of inspection problem to causes of, 201.01, **7**
 - summary of causes of, 201.02, **7**
- Dew point of water, 202.022, **10**
- Dezincification, 202.066, **38**
- Distillation equipment:
 - hydrogen chloride corrosion of, 202.022, **9**
 - hydrogen sulfide corrosion of, 202.023b, **13**; 202.023c, **15**
- Distortion of equipment, 201.02, **8**
- Ductile irons, Appendix I, **65**
- Earthquakes, 208, **56**
- Eddy currents, 203.022, **43**
- Elastic properties of metals and alloys, 204.011, **43**
- Electrolyte, 202.067, **38**
- Embrittlement:
 - high temperature, 204.022g, **50**
 - hydrogen, 202.023b, **14**; 204.035, **52**
 - sulfur, 202.055, **34**
- Environmental corrosion, 202.04, **27**
 - cooling water, 202.042d, **30**
 - under fireproofing, 202.042a, **29**
 - galvanic, 202.041, **28**
 - beneath insulation, 202.042a, **29**
 - pipelines, 202.042b, **29**
 - rate of, 202.041, **28**
 - refinery atmospheres, 202.041, **27**
 - specific problems of, 202.042, **28**
 - structures, 202.042c, **30**
- Equipment, faulty, 210, **60**
 - evidences of, 210.03, **63**
 - improper selection, 210.02, **61**
 - errors, 210.021, **61**
 - low-cost materials, 210.023, **61**
 - new processes, 210.022, **61**
- Equipment sections, and corrosive compounds affecting, 202.021, **9**
- Erosion, 203, **40**
 - cavitation, 203.022, **43**
 - effects of, 201.02, **7**
 - solids in flowing fluids, 203.021, **40**
- Excessive pressures, 206, **53**
 - causes of, 206.02, **53**
 - blocking against pressure source, 206.022, **53**
 - heat in excess of normal operation, 206.021, **53**
 - hydraulic hammer, 206.024, **53**
 - resonant vibration, 206.024, **53**
 - thermal expansion of trapped liquid, 206.023, **53**
 - vents, inadequate or defective, 206.025, **53**
 - definition of, 206.01, **53**
 - effects of, 201.02, **8**; 206.03, **53**
- Exchanger, preheat, corrosion of, 202.021, 202.022, **9**
- "Eyebrow" graphite formation, 204.022c, **47**
- Failure of parts, 201.02, **7**
- Fatigue, thermal, 201.02, **8**
- Fatigue failures, 201.02, **7**
- Ferrite, 204.022d, **47**; Appendix I, **64**
- Ferritic steels, 202.024b, **18**; Appendix I, **64**
- Ferrous alloys, Appendix I, **64**
- Fireproofing, atmospheric corrosion under, 202.042a, **29**
- Flowing fluids, solids in, 203.021, **40**
- Fluidized-solids principle, 203.021, **40**
- Fretting corrosion, definition of, 202.032c, **24**
- Fungi, 202.069, **39**
- Furnace, preheat, corrosion of, 202.021, **9**
- Furnace, vacuum, corrosion of, 202.021, **9**
- Furnace tubes, hydrogen sulfide corrosion of, 202.023c, **15**
- Galvanic corrosion, 202.041, **28**; 202.067, **38**
 - galvanic series (Table 1), 202.067, **38**
 - rules to prevent trouble from, 202.067, **39**
- Gas-handling and stabilization units, hydrogen sulfide corrosion of, 202.023c, **17**
- Gases, corrosive, infiltration of, 202.056, **34**
- General, 201, **7**
- Grain growth, 204.022a, **45**
- Graphitic corrosion of cast iron, 202.063, **35**
- Graphitization, 202.056, **34**; 202.063, **35**; 204.022c, **46**
- Ground movement, 208, **56**
- Growth of cast irons, 202.056, **34**
- Guniting fireproofing, 207.01, **55**
- Hardening, 204.022d, **47**
- Hastelloy B, 202.032a, **23**
- Hastelloy C, 202.032a, **24**
- Hastelloy D, 202.032c, **25**
- Heat, excess, as cause of excessive pressure, 206.021, **53**
- Heating elements, high-silicon cast iron, 202.032c, **25**
- High temperature, 204, **43**
 - corrosion at, 202.05, **31**
 - hydrogen sulfide, 202.023c, **14**; 202.055, **33**
 - oxygen, 202.052, **31**
 - steam, 202.053, **32**
 - sulfur dioxide, 202.055, **33**
 - vanadium oxide, 202.054, **33**
 - effects of, 201.02, **8**; 204, **43**
 - gases, corrosive, effect on cast iron at, 202.056, **34**
 - hydrogen sulfide, 202.023c, **14**

- hydrogen sulfide corrosion in presence of hydrogen, 202.023d, 17
- metallurgical chemical changes, 204.03, 50
- carburization, 204.032, 50
 - decarburization, 204.034, 51
 - hydrogen attack, 204.035, 51
 - metal dusting, 204.033, 50
- metallurgical structural changes, 204.02, 45
- carbide precipitation, 204.022e, 48
 - embrittlement, 204.022g, 50
 - grain growth, 204.022a, 45
 - graphitization, 204.022c, 46
 - hardening, 204.022d, 47
 - incipient melting, 204.022b, 46
 - sensitization, 204.022e, 48
 - sigma phase, 204.022f, 49
- organic acids, 202.026, 21
- strength, 204.01, 43
- creep, 204.012, 43
 - properties, 204.014, 44
 - stress rupture, 204.013, 43
- Humidity, 202.041, 28
- Hydraulic hammer, 206.024, 53
- Hydrochloric acid, 202.022, 9
- corrosion of iron by, 202.022, 12
 - corrosion rates, 202.024a, 18
 - in crude oil distillation process, 202.022, 12
- Hydrofluoric acid, 202.032a, 23
- Hydrogen, high-temperature hydrogen sulfide in presence of, 202.023d, 17
- Hydrogen attack, 204.035, 51
- Hydrogen blistering, 202.023b, 14
- Hydrogen chloride, 202.022, 9
- chemicals to control corrosion by, 202.022, 12
 - cyclic reaction of, 202.022, 12
 - formation of, 202.022, 9
 - locations where it causes corrosion, 202.022, 9
 - in preheating exchangers, 202.022, 9
 - production of, 202.022, 9
 - rate of corrosion caused by, 202.022, 10
 - reduction of, 202.022, 12
 - when corrosive, 202.022, 9
- Hydrogen disease, 204.035, 52
- Hydrogen embrittlement, 202.023b, 14
- Hydrogen fluoride, 202.032, 22
- Hydrogen-hydrogen sulfide corrosion, 202.065, 37
- Hydrogen plant corrosion, 202.024b, 18
- Hydrogen sulfide, 202.021, 8; 202.023, 13
- catalytic cracking units, corrosion by, 202.023c, 15
 - coking processes, corrosion by, 202.023c, 17
 - crude oil distillation units, corrosion by, 202.023b, 13; 202.023c, 15
 - formation of, 202.023a, 13
 - gas-handling and stabilization units, corrosion by, 202.023c, 17
 - general, 202.021, 8; 202.023a, 13
 - high-temperature corrosion by, 202.023c, 14; 202.023d, 17; 202.055, 33
 - hydrogen blistering and embrittlement caused by, 202.023b, 14
 - stress corrosion cracking caused by, 202.064, 36
 - sulfur corrosion at low and intermediate temperatures, 202.023b, 13
 - thermal cracking units, corrosion by, 202.023c, 15
- Hydrolysis, 202.022, 9
- Impingement, angle of, 203.021, 41
- Incipient melting, 204.022b, 46
- Infiltration of corrosive gases, 202.056, 34
- Inhibitors, 202.022, 11; 202.042d, 30; 202.071, 40
- Injection of chemicals, 202.022, 12
- Inspection problems, relationship to causes of deterioration, 201.01, 7
- Insulation, atmospheric corrosion under, 202.042a, 29
- Intercrystalline dezincification, 202.066, 38
- Intergranular corrosion, 202.024b, 18; 202.062, 35; 204.022e, 48
- Iron, ferrous alloys and cast, Appendix I, 64
- gases, hot corrosive, effect on, 202.056, 34
 - graphitic corrosion of, 202.063, 35
- Iron, corrosion of, 202.022, 12
- Iron, galvanized, 202.041, 28
- Iron alloys:
- steam temperature for corrosion of, 202.053, 33
 - temperature, metal, for low oxidation of, 202.052, 32
- Iron chloride, 202.022, 12
- Iron sulfide, 202.022, 12
- Isomerization units, aluminum chloride corrosion of, 202.039, 27
- Layer-type dezincification, 202.066, 38
- Linings, erosion protection by, 203.021, 40
- Localized graphitization, 204.022c, 46
- Low-temperature corrosion, 202.022, 9
- Luder's lines, 204.022c, 47
- Machinery parts, failures in, 201.02, 7
- Macroorganisms, 202.069, 39
- Marine organisms, 202.069, 39
- Martensite, 202.024b, 18; 204.022d, 47
- Material, faulty, 210, 60
- evidences of, 210.03, 63
 - improper selection, 210.02, 61
 - errors, 210.021, 61
 - low-cost materials, 210.023, 61
 - new processes, 210.022, 61
- Materials, corrosive, added to process, 202.03, 22
- aluminum chloride, 202.039, 27
 - ammonia, 202.037, 27
 - caustic, 202.035, 26
 - chlorine, 202.038, 27
 - hydrogen fluoride, 202.032, 22
 - mercury, 202.036, 27
 - phenol, 202.033, 25
 - phosphoric acid, 202.034, 26
 - sodium hydroxide, 202.035, 26
 - sulfuric acid, 202.032, 22
- Mechanical damage, 209, 56
- causes of, 209.03, 58
 - examples of, 209.02, 56
 - sources of, 209.01, 56
- Mercaptans, 202.021, 8; 202.023, 13
- Mercury:
- corrosion by, 202.036, 27
 - stress corrosion caused by, 202.064, 37
- Metal dusting, 204.033, 50
- Metals, *see* Alloys
- Metal temperatures for low oxidation rates, 202.052, 32
- Metal thickness, losses in, 201.02, 7
- Metallurgical chemical changes, 204.03, 50
- carburization, 204.032, 50
 - decarburization, 204.034, 51
 - hydrogen attack, 204.035, 51
 - metal dusting, 204.033, 50
- Metallurgical structural changes, 204.02, 45
- carbide precipitation, 204.022e, 48
 - embrittlement, 204.022g, 50
 - grain growth, 204.022a, 45
 - graphitization, 204.022c, 46
 - hardening, 204.022d, 47
 - incipient melting, 204.022b, 46
 - sensitization, 204.022e, 48
 - sigma phase, 204.022f, 49
- Metals, nonferrous, Appendix I, 65
- Metals and alloys, common refinery, Appendix I, 64
- Metals and alloys, galvanic series of refinery, 202.067, 38
- Methane reaction, 204.035, 51
- Microorganisms, 202.069, 39
- Molecular hydrogen, 202.023b, 14
- Monel, 202.022, 11; 202.024b, 18; 202.032a, 23
- Naphthenic acids, corrosion by, 202.026, 21
- Neutralization, 202.072, 40
- Neutralized salts, 202.021, 9
- Neutralizers:
- anhydrous and aqueous ammonia, 202.022, 12
 - for cooling water, 202.042d, 30
 - as corrosives, 202.072, 40

- Nickel and nickel alloys, Appendix I, 65
 hydrogen sulfide corrosion of, 202.055, 34
 steam, at high temperature, effect on, 202.053, 33
 stress corrosion cracking of, 202.064, 37
 sulfur dioxide corrosion of, 202.055, 34
 temperature, metal, for low oxidation of, 202.052, 32
- Nitrogen compounds, 202.021, 8; 202.027, 21
- Nonferrous metals and alloys, Appendix I, 65
- Notch toughness, 205.01, 52
- Oil-hardened steels, 204.022d, 47
- Olefin-extraction units, sulfuric acid corrosion of, 202.032b, 24
- Organic acids, 202.021, 8; 202.026, 21
- Organisms, corrosion influenced by, 202.069, 39
- Overhead systems:
 corrosion by hydrogen sulfide and hydrogen chloride, 202.023b, 13
 corrosion rates, 202.022, 10
- Overloading, 207, 54
 causes of, 207.01, 54
 definition of, 207.01, 54
 evidences of, 207.02, 56
- Oxidation rates, metal temperatures for low, 202.052, 32
- Oxygen:
 atmospheric corrosion requires, 202.041, 28
 at high temperatures, 202.052, 31
 hydrogen sulfide corrosion requiring, 202.023b, 13
- Oxygen, dissolved, and water, 202.021, 8; 202.025, 19
- pH values, 202.022, 10; 202.024a, 18; 202.064, 37
- Phenol (carbolic acid), 202.033, 25
- Phosphoric acid, 202.034, 26
- Pipe for conveying hot concentrated sulfuric acid, 202.032c, 25
- Pipelines:
 atmospheric corrosion of, 202.042b, 29
 biological corrosion of, 202.069, 40
- Pit-type corrosion of tanks, 202.025, 20
- Plastic properties of metals and alloys, 204.011, 43
- Plug-type dezincification, 202.066, 38
- Polymerization units, phosphoric acid corrosion of, 202.034, 26
- Polythionic acid corrosion, 202.065, 37
- Preheat exchanger, corrosion of, 202.021, 202.022, 9
- Preheat furnace, corrosion of, 202.021, 9
- Pressures, excessive, 206, 53
 causes of, 206.02, 53
 blocking against pressure source, 206.022, 53
 heat in excess of normal operation, 206.021, 53
 hydraulic hammer or resonant vibration, 206.024, 53
 thermal expansion of trapped liquid, 206.023, 53
 vents, inadequate or defective, 206.025, 53
 definition of, 206.01, 53
 effects of, 201.02, 8; 206.03, 53
- Properties for high-temperature strength, 204.014, 44
- Quenching, 204.022d, 47
- Random graphitization, 204.022c, 46
- Reboilers, 202.023c, 17
- Reciprocating parts, stress reversals in, 201.02, 7
- Reference to:
 API publications, 204.013, 44; 204.035, 51; 205.01, 52
 standards (ASTM and ASME), 204.014, 44
- References, 65
- Refinery atmospheres, 202.041, 27
- Reflux pumps, hydrogen chloride corrosion of, 202.022, 11
- Resonant vibration, 206.024, 53
- Safety factor in structural design, 207.01, 54; 210.02, 61
- Salts:
 in crude oil, 202.022, 9
 corrosion by, 202.022, 12
 neutralized, 202.021, 9
- Scaling, 202.053, 33
- Sea water, analysis of, 202.022, 9
- Sensitization, 202.065, 37; 204.022e, 48
- Sensitized stainless steels, 202.024b, 19
- Settling of crude oil, 202.022, 12
- Sigma phase, 204.022f, 49
- Slime, 202.069, 39
- Sodium carbonate, hydrogen chloride neutralizer, 202.022, 12
- Sodium hydroxide:
 corrosion by, 202.035, 26
 embrittlement by, 202.064, 36
 hydrogen chloride neutralizer, 202.022, 12
- Sodium hypochlorite, 202.038, 27
- Solids concentration in relation to rate of erosion, 203.021, 41
- Solids in flowing fluids, 203.021, 40
- Sour crudes, definition of, 202.022, 12
- Stabilized steels, 204.022e, 49
- Stainless steels, corrosion resistance of, 202.024b, 18
- Steam, high-temperature, 202.053, 32
- Steam-condensate corrosion by carbon dioxide, 202.024a, 18
- Steels, *see* Alloys; Metals
- Storage tanks, *see* Tanks
- Strength:
 creep, 204.012, 43
 stress rupture, 204.013, 43
 temperature effects on, 204.01, 43
- Stress corrosion cracking, 202.022, 12; 202.024b, 18; 202.064, 35
- Stress relieving, 204.022d, 48
- Stress reversals, effects of, 201.02, 7
- Stress rupture, 204.013, 43
- Structural changes, metallurgical, 204.02, 45
 carbide precipitation, 204.022e, 48
 embrittlement, 204.022g, 50
 grain growth, 204.022a, 45
 graphitization, 204.022c, 46
 hardening, 204.022d, 47
 incipient melting, 204.022b, 46
 sensitization, 204.022e, 48
 sigma phase, 204.022f, 49
- Structures, atmospheric corrosion of, 202.042c, 30
- Subnormal temperature effects, 205, 52
 brittle fracture, 205.01, 52
- "Sugaring," 204.022e, 49
- Sulfur:
 high-temperature corrosion by, 202.055, 34
 low-temperature corrosion by, 202.023b, 13
- Sulphur compounds, organic, 202.021, 8; 202.023, 13
- Sulfur content, total, corrosion measured as function of, 202.023, 13
- Sulfur dioxide, corrosion by, at high temperatures, 202.055, 33
- Sulfuric acid, 202.032, 22
 acid-concentration facilities for, 202.032c, 24
 alkylation units, corrosion by, 202.032a, 22
 olefin-extraction units, 202.032b, 24
- Sweet crudes, definition of, 202.022, 12
- Tanks:
 corrosion of, 202.021, 9; 202.023b, 13; 202.025, 19; 205.01, 52
 moisture and oxygen in, 202.025, 19
- Tantalum, 202.032c, 24
- Temperature:
 distortion caused by changes in, 201.02, 8
 erosion increases with, 203.021, 41
 metal temperatures for low oxidation rates, 202.052, 32
 subnormal and ambient, 205, 52
 sulfur corrosion at low and intermediate temperatures, 202.023b, 13
see also High temperature
- Thermal cracking units, hydrogen sulfide corrosion of, 202.023c, 15
- Thermal expansion, 206.023, 53; 207.01, 55
- Thermal fatigue, 201.02, 8
- Towers, corrosion of, 202.021, 9; 202.022, 11; 202.023c, 15
- Transition temperature, 205.01, 52
- Vacuum furnace, corrosion of, 202.021, 9
- Vanadium oxide, corrosion by, 202.054, 33
- Velocity:
 erosion rate in relation to, 203.021, 41
 high fluid velocities, 203.022, 43
- Vents, inadequate or defective, 206.025, 53
- Vibration loads, 207.01, 55

Water:

atmospheric corrosion requires, 202.041, **28**
dezincification requires, 202.066, **38**
hydrogen chloride corrosion requires, 202.022, **9**
Water, cooling, corrosion resulting from, 202.042*d*, **30**
Water and dissolved oxygen, 202.021, **8**; 202.025, **19**

Water condensation, 202.022, **10**

Water dew point, 202.022, **10**

Water-hardened steels, 204.022*d*, **47**

Wind damage, 209, **56**

causes of, 209.03, **58**

examples of, 209.02, **56**