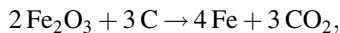

1

INTRODUCTION AND FORMS OF CORROSION

1.1 DEFINITION

The term “corrosion” has its origin in Latin. The Latin word *rodere* means “gnawing,” and *corrodere* means “gnawing to pieces.” In daily life, corrosion manifests itself in many forms, such as corroded automobiles, nails, pipes, pots, pans, and shovels. Corrosion is a costly materials science problem. Metallic corrosion has been a problem since common metals were first put to use.

Most metals occur in nature as compounds, such as oxides, sulfides, silicates, or carbonates. Very few metals occur in native form. The obvious reason is the thermodynamic stability of compounds as opposed to the metals. Extraction of a metal from ore is *reduction*. The reduction of iron oxide with carbon as a reducing agent gives rise to metallic iron



while the oxidation of metallic iron to produce the brown oxide known commonly as “rust” is corrosion. The extraction of iron from the oxide must be conducted with utmost careful control of the conditions so that the reverse reaction is prevented.

1.2 DEVELOPMENTS IN CORROSION SCIENCE

During the Gupta Dynasty (320–480 CE), the production of iron in India achieved a high degree of sophistication, as attested by the Dhar Pillar, a 7-tonne (7000 kg), one-piece iron column made in the fourth century CE. The existence of this pillar implies that the production of iron from oxide ore was a well-established process, and the personnel involved in the production of the iron pillar were aware of the reverse reaction involving the oxidation of iron to produce iron oxide (the familiar rusting of iron) and of the need to minimize the extent of this reverse reaction.

Copper nails coated with lead were used by the Greeks in the construction of lead-covered decks for ships (1). The Greeks probably realized that metallic couples of common metals are undesirable in seawater. Protection of iron by bitumen and tar was known and practiced by the Romans.

TABLE 1.1 Timeline of Developments in Corrosion Science

L.J. Thénard	1819	Enunciated electrochemical nature of corrosion
Sir H. Davy	1829	Principle of cathodic protection
A. de la Rive	1830	Established best quality of zinc for galvanic batteries
M. Faraday	1834–1840	Established relations between chemical action and generation of electric currents based on what were later called “Faraday’s laws”
S. Arrhenius	1901	Postulated the formation of microcells
W.R. Whitney	1903	Confirmed the theory of microcells
A.S. Cushman	1907	
W. Walker	1907	Established the role of oxygen in corrosion as a cathodic simulation
A. Cederholm	1908	
L. Bent, W. Tilden		
E. Heyn and O. Bauer	1908	Corrosion studies of iron and steel, both alone and in contact with other metals, leading to the concept that iron in contact with a nobler metal increased corrosion rate, while its contact with a base metal resulted in partial or complete protection
R. Corey	1939	Investigated attack of iron
T. Finnegan		
M. de Kay Thompson		
A. Thiel	1928	Investigated the attack of iron by dilute alkali with liberation of hydrogen
Luckmann		
W. Whitman, R. Russell	1924	Observed increased corrosion rate when a small anode is connected to a large cathode
U. Evans	1928	
G.V. Akimov	1935	

Robert Boyle (1627–1691) published two papers, “Of the Mechanical Origin of Corrosiveness” and “Of the Mechanical Origin of Corrodibility” in 1675 in London (2). At the turn of the nineteenth century (3, 4), the discovery of the galvanic cell and Davy’s theory on the close relationship between electricity and chemical changes (5) led to the understanding of some of the basic principles of corrosion.

Some of the developments in corrosion science are summarized in Table 1.1.

1.3 DEVELOPMENT OF SOME CORROSION-RELATED PHENOMENA

Some of the developments of corrosion-related phenomena are given in Table 1.2. The development of corrosion science in terms of published scientific literature through 1907–2007 is illustrated by the number of scientific papers given in Table 1.3.

Developments can be found in the scientific journals listed in Table 1.4. Some leading organizations championing corrosion science are detailed in Table 1.5.

TABLE 1.2 Development of Some Corrosion-Related Phenomena

J.S. MacArthur	1887	Process of cyanide dissolution of gold (gold is not soluble in hot acids)
P.F. Thompson	1947	Dissolution of gold in dilute cyanide solutions recognized as an electrochemical process
<i>Concept of Passivity</i>		
J. Keir	1790	Observed that iron in concentrated nitric acid altered its properties
C.F. Schönbein	1799–1868	Suggested the state of iron in concentrated nitric acid as passivity
W. Müller (K. Konopicky, W. Machu)	1927	Postulated the mathematical basis of the mechanism of anodic passivation
G.D. Bengough (J.M. Stuart, A.R. Lee, F. Wormwell)	1927	Systematic and carefully controlled experimental work on passivity
<i>Role of Oxygen</i>		
Marianini	1830	Indicated the electric currents were due to variations in oxygen concentration
Adie	1845	
Warburg	1889	
V.A. Kistiakowsky	1908	
	~1900	Hydrogen peroxide detected during the corrosion of metals
	~1905	The view that acids were required for corrosion to occur dispelled by observation of rusting of iron in water and oxygen
Aston	1916	Role of local differences in oxygen concentration in the process of rusting of iron
McKay	1922	Currents due to a single metal of varying concentrations of metal ion

(continued)

TABLE 1.2 (Continued)

U.R. Evans	1923	Differential aerations and their role in metallic corrosion
Evans and co-workers	1931–1934	Electric currents due to corrosion of metal in salt solutions were measured and a quantitative electrochemical basis of corrosion was propounded. The oxygen-rich region becomes cathodic and the metal is protected, while the lower oxygen region, being anodic, is attacked
<i>Inhibitors</i>		
Roman civilization	–	Protection of iron by bitumen, tar, extracts of glue, gelatin, and bran were used to inhibit corrosion of iron in acid
Marangoni, Stefanelli	1872	Distinction between inhibitive paints and mechanically excluding paints made, based on laboratory and field tests Development of paints containing zinc dust
Friend	1920	Colloidal solution of ferric hydroxide acts as an oxygen carrier, passing between ferrous and ferric states
Forrest, Roetheli, Brown	1930	Protective property of coating varied and depended on the rate of supply of oxygen to the surface
Herzog	1936	Postulated that iron, on long exposure to water, becomes covered by magnetite overlaid by ferric hydroxide. Magnetite layer acts as cathode and ferric hydroxide is converted to hydrated magnetite. Hydrated magnetite may lose water and reinforce the preexisting magnetite or absorb oxygen from air to give ferric hydroxide.
Chyzewski	1938	Classified inhibitors as cathodic and anodic inhibitors
V.S. Sastri	1988	Classification of corrosion inhibition mechanisms as interface inhibition, intraphase inhibition, interphase inhibition, and precipitation coating (<i>Corrosion</i> '88, paper no. 155)
V.S. Sastri	1990	Modern classification of inhibitors as hard, soft, and borderline inhibitors (30)
K. Jüttner, W.J. Lorenz, F. Mansfeld	1993	<i>Reviews on corrosion inhibitor science and technology</i> , 1993
V.S. Sastri, J.R. Perumareddi, M. Elboujdaini	1994	Novel theoretical method of selection of inhibitors (<i>Corrosion</i> , 50 , 432, 1994)

TABLE 1.2 (Continued)

V.S. Sastri, J.R. Perumareddi, M. Elboujdaini	2005	Sastri equation relating percent inhibition to the fractional electronic charge on the donor atom in the inhibitor (6)
V.S. Sastri, J.R. Perumareddi, M. Elboujdaini, M. Lashgari	2008	Application of ligand field theory in corrosion inhibition (<i>Corrosion</i> , 64 , 283, 2008)
V.S. Sastri, J.R. Perumareddi, M. Elboujdaini	2008	Photochemical corrosion inhibition (<i>Corrosion</i> , 64 , 657, 2008)
<i>Microbiological Corrosion</i>		
R.H. Gaines	1910	Sulfate-reducing bacteria in soils produce H ₂ S and cause corrosion
<i>Role of thermodynamics</i>		
–	–	Corrosion of metals obeys the laws of thermodynamics; was recognized in the early development of corrosion science
M. Pourbaix	1940	Pourbaix diagrams involving pH and potential give regions of corrosion, immunity, and passivity
<i>Kinetics</i>		
Evans, Hoar	1932	Quantitative correlation of corrosion rates with measured electrochemical reaction rates
F. Habashi	1965	Validity of single kinetic law irrespective of the metal, composition of the aqueous phase, and evolution of hydrogen when no insoluble products, scales, or films are formed

TABLE 1.3 Numbers of Corrosion Science Publications

Theme	1907	1950	2000	2007
Corrosion	35	922	10,985	15,903
Corrosion and protection	3	122	1,162	1,578
Corrosion inhibition	0	19	367	416

TABLE 1.4 Beginning Journal Years for Corrosion Developments

Title	Year
<i>Corrosion</i>	1945
<i>Corrosion Science</i>	1961
<i>British Corrosion Journal</i>	1965
<i>Werkstoffe und Korrosion</i>	1950
<i>Corrosion Prevention and Control</i>	1954
<i>Anti-corrosion Methods and Materials</i>	1962
<i>Materials Performance</i>	1962

TABLE 1.5 Organizations at Forefront of Corrosion Science Starting Year

American Society for Testing Materials (ASTM)	1898
American Society of Metals (ASM)	1913
Corrosion Division of the Electrochemical Society	1942
National Association of Corrosion Engineers	1943
Comité international de thermodynamique et cinétique électrochimique (CITCE)	1949
International Society of Electrochemistry (ISE)	1971
International Corrosion Council	1961
The Corrosion Group of the Society of Chemical Industry	1951
Belgium Centre for Corrosion Study (CEBELCOR)	1951
Commission of Electrochemistry	1952
National Corrosion Centre (Australia)	
Australian Corrosion Association	~1980
Chinese Society of Corrosion and Protection	~1980
National Association of Corrosion Engineers (in Canada)	—

Some of the research groups that became active in corrosion studies in the early stages are

Massachusetts Institute of Technology
 National Bureau of Standards
 Ohio State University
 University of Texas
 University of California, Los Angeles
 National Research Council Canada
 Cambridge University
 Technical University, Vienna

Some industrial laboratories, such as U.S. Steel, International Nickel Company, Aluminum Company of America, and DuPont, initiated their own research in corrosion.

The advances made in the scientific approach and the degree of maturity attained will be obvious from the following two abstracts of papers. The abstract of a paper published by A.S. Cushman (*American Society for Testing Materials* **8**, 605, 1908) noted that, “the inhibitive power of some pigments on iron and steel were tested by agitating in water with a current of air and the loss in weight due to rusting was determined.” It is instructive to compare this with a paper entitled “Selection of Corrosion Inhibitors.” Its abstract is given below:

Data on the inhibition of corrosion of iron by methyl pyridines in HCl, H₂SO₄, and H₂S solutions, by *para*-substituted anilines in HCl solutions and by *ortho*-substituted benzimidazoles in HCl solutions, and on the inhibition of corrosion of aluminum by methyl pyridines have been analyzed in terms of the Hammett equation and in terms of a new equation relating the degree of inhibition with the

fraction of the electronic charge due to the substituent in the inhibition molecule. The new relationship has been found to be useful in predicting new inhibitors offering a greater degree of inhibition than the currently known inhibitor systems. *Source:* (6).

The impact of corrosion is felt in three areas of concern—economics, safety, and environmental damage. Metallic corrosion, seemingly innocuous, affects many sectors of the national economy. The National Bureau of Standards (NBS) in collaboration with Battelle Columbus Laboratory (BCL) studied the costs of corrosion in the United States using the input/output model (7).

Elements of the costs of corrosion used in the model include those concerned with capital, design, and control, as well as associated costs. They are outlined next.

1.4 ECONOMICS OF CORROSION

Capital costs:

- Replacement of equipment and buildings
- Excess capacity
- Redundant equipment

Control costs:

- Maintenance and repair
- Corrosion control

Design costs:

- Materials of construction
- Corrosion allowance
- Special processing

Associated costs:

- Loss of product
- Technical support
- Insurance
- Parts and equipment inventory

The data resulting from the calculations using the I/O model are given in Table 1.6. Data for the year 2010 are estimates only.

The estimated costs of corrosion in Canada in 2010 along with the various sectors are given in Tables 1.7 and 1.8.

The cost of corrosion in other countries in the world is given in Table 1.9.

TABLE 1.6 Corrosion Costs in the United States (Billions of Dollars)

Industry		1975	1995	2010
All industries	Total	82.0	296	549
	Avoidable	33.0	104	194
Automotive	Total	31.4	94	167
	Avoidable	23.1	65	116
Aircraft	Total	3.0	13	25
	Avoidable	0.7	3	5.9
Others	Total	47.6	159	290
	Avoidable	9.3	36	70

TABLE 1.7 Corrosion Costs in Canada⁸

Sector	\$ Billion
Utilities	10.5
Transportation	7.3
Infrastructure	5.5
Government	5.1
Production and manufacturing	4.4
Total	32.8

TABLE 1.8 Total Corrosion Costs in Canada

	\$ Billion
Total direct cost of corrosion	32.8
Cost of corrosion (extrapolated to Canadian economy)	64.5
Estimated savings by corrosion control	19.5

TABLE 1.9 Corrosion Costs of Other Countries

Country	Year	Corrosion Costs (\$)	Percent of GNP	Avoidable Cost (\$)	Reference
United Kingdom	1969–1970	3.2 billion	3.5	0.73 billion	9
West Germany	1968–1969	1.5 billion	3.0	0.375 billion	10
Sweden	1964	58–77 million	–	15–19 million	11
Finland	1965	47–62 million	–	–	12
Russia	1969	6.7 billion	2.0	–	13
Australia	1973	470 million A\$	1.5	–	14
India	1960–1961	320 million	–	–	15
Japan	1976–1977	9.2 billion	1.8	–	16

TABLE 1.10 Some Nations' Efforts to Combat Corrosion

United Kingdom		
National Corrosion Service	1975	Educating engineering undergraduate students in corrosion awareness. Published 15 guides on corrosion and 6 booklets on "controlling corrosion" for distribution. Published directory of personnel involved in corrosion prevention
National Corrosion Coordination Centre		Carrying out multiclient 50/50 cost-shared research on high-temperature corrosion, metal finishing, microbial corrosion, and expert systems in corrosion engineering
United States	~1980	National Association of Corrosion Engineers in collaboration with the National Bureau of Standards developed corrosion data program
Australia	1982	National Corrosion Centre. Established nationwide referral service for corrosion problems
Peoples Republic of China	1980	Educating and training of personnel in corrosion. Organized 15 corrosion courses. Established 11 institutes offering courses in corrosion
Canada	1994	A proposal to establish a national corrosion secretariat (19) to educate industrial personnel, operate a referral service, assemble a directory of corrosion experts, initiate site visits, show videos on corrosion, and establish 50/50 cost-shared projects in corrosion was submitted in 1994

The high costs of corrosion have a significant effect on the national economy, and therefore it is necessary that corrosion personnel adopt corrosion control measures in order to avoid corrosion losses. A useful report entitled "Economics of Corrosion" (17) has been produced by the National Association of Corrosion Engineers (NACE) Task Group T-3C-1. The report deals with (i) economic techniques that can be used by personnel as a decision-making tool; (ii) facilitating communications between corrosion scientists and management; and (iii) justifying the investments in corrosion prevention measures to achieve significant long-term benefits.

In general, corrosion costs amount to about 2–4% of GNP, and about 25% of the costs are avoidable when corrosion control measures are adopted. The measures taken to combat corrosion in the United Kingdom, United States, Australia, China, and Canada have been discussed (18). Some efforts to combat corrosion worldwide are given in Table 1.10.

1.5 SAFETY AND ENVIRONMENTAL CONSIDERATIONS

One of the most important impacts of corrosion is safety. While safety should be uppermost in the minds of industrial personnel, accidents do occur, in spite of great precautions. So, corrosion not only is expensive but also poses risks to human life and

safety. An example, corrosion of iron hulls in ships and their resulting loss poses a threat to crew. Accidents are more likely to occur in chemical industries handling corrosive chemicals releasing cyclohexene (Flixborough, England) and hydrogen cyanide (Bhopal, India) than in those that do not. Fatal airline accidents, bridge collapse, bursting of gas pipelines, failure of steam pipes in nuclear power plants—all have caused loss of life.

Corrosion can also impact the environment. Corrosion-related failure of oil or gas pipelines or oil tanks can have severe detrimental effects on the environment in the form of water and air pollution, leading to the demise of aquatic life. Corrosion-related accidents can, in principle, destroy irreplaceable flora or fauna. Another aspect is the corrosion's effects on limited resources. Some decades ago, recycling was accorded scant attention. At present, it is widely practiced and recycling of metal products, paper, and plastics is commonplace, since recycling helps to conserve limited and finite resources. Corrosion prevention and protection arrests the degradation of metals and materials, and hence contributes in a significant way to the conservation of resources with minimum damage to the ecosystem.

1.6 FORMS OF CORROSION

Corrosion can be defined in general terms and of universal applicability or in specific terms depending upon the perspective from which it is defined. For instance, corrosion in aqueous media is defined as an electrochemical process. In more general terms, corrosion is defined as the degradation of material caused by an aggressive environment. The corrosive environment can be water, air, carbon dioxide, organic liquids, molten salts, or gaseous sulfur. Some less common corrosive environments are neutron beams, ultraviolet light, nuclear fission fragments, and gamma radiation.

Materials subject to corrosion include engineering materials, such as metals, plastics, rubber, and ionic and covalent solids; aggregates such as concrete, composite materials; and wood. The present discussion is concerned with metals, alloys, and aggregates. Corrosion can manifest in many forms, such as uniform or general corrosion, galvanic corrosion, crevice corrosion, pitting corrosion, intergranular corrosion, selective leaching, erosion corrosion, stress corrosion, corrosion fatigue, and fretting corrosion. The eight forms of corrosion defined by Fontana are general corrosion, pitting corrosion, intergranular corrosion, parting, galvanic corrosion, crevice corrosion, stress-corrosion cracking (SCC), and erosion corrosion.

Classification of the different forms of corrosion may be based on intrinsic and extrinsic modes. Intrinsic modes of corrosion independent of design are general corrosion, pitting, intergranular corrosion, parting, and stress-corrosion cracking. Extrinsic modes of corrosion affected by design are crevice or underdeposit corrosion, galvanic corrosion, erosion corrosion, fretting corrosion, and corrosion fatigue.

The forms of corrosion have been identified based on the apparent morphology of corrosion, the basic factor influencing the mechanism of corrosion in each form. Thus, the six forms of corrosion are as given in Table 1.11.

TABLE 1.11 Morphological Classification of Corrosion

1. General corrosion	Uniform, quasi-uniform, and nonuniform corrosion, galvanic corrosion
2. Localized corrosion	Pitting corrosion, crevice corrosion, filiform corrosion
3. Metallurgically influenced corrosion	Intergranular corrosion, sensitization, exfoliation, dealloying
4. Microbiological corrosion	
5. Mechanically assisted corrosion	Wear corrosion, erosion corrosion, corrosion fatigue
6. Environmentally induced cracking	Stress-corrosion cracking, hydrogen damage, embrittlement, hydrogen-induced cracking, high-temperature hydrogen attack, hot-cracking, hydride formation, liquid metal embrittlement, solid metal-induced embrittlement

1.6.1 General Corrosion

General corrosion can be even or uneven and is the most common form of corrosion. It is characterized by a chemical or electrochemical reaction that takes place on the exposed surface. The metal becomes thinner and eventually results in perforation and failure. General corrosion accounts for the greatest loss of metal on a tonnage basis. This mode of corrosion does not present a great threat from a technical standpoint since the life of the equipment can be estimated from the corrosion rates obtained from immersion of the sample material in the medium of interest. The corrosion rate data may then be used in the design of the equipment. General corrosion can be prevented or reduced by the proper choice of materials or by use of corrosion inhibitors or cathodic protection (Fig. 1.1).

1.6.2 Galvanic Corrosion

Galvanic corrosion occurs when a potential difference exists between two dissimilar metals immersed in a corrosive solution. The potential difference results in the flow of

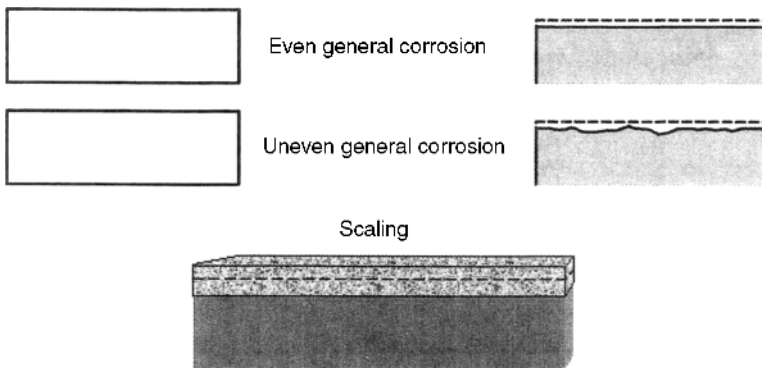


FIGURE 1.1 General corrosion and high-temperature scaling.

electrons between the metals. The less corrosion-resistant metal becomes the anode, and the more corrosion-resistant metal the cathode. Galvanic corrosion is generally more prominent at the junction of two dissimilar metals and the severity of attack decreases with increasing distance from the junction. The distance affected depends upon the conductivity of the solution. The cathode-to-anode ratio plays an important role in this form of corrosion. Severe galvanic corrosion occurs when a cathode of a large surface area and an anode of a small surface area are involved. Corrosion of leaded or nonleaded solders in copper pipes carrying drinking water is an example of this form of corrosion.

Some preventive measures to combat galvanic corrosion are (a) selection of metals that are close to each other in galvanic series; (b) maintenance of cathode/anode surface area ratio to the smallest possible minimum; (c) providing insulation between the two dissimilar metals; (d) use of coatings that are kept in good condition; (e) use of corrosion inhibitors to reduce the corrosivity of the medium; (f) avoiding threaded joints between the two dissimilar metals; (g) use of a suitable design such that replacement of anodic parts is easy; and (h) use of a third metal that is anodic to both the metals in galvanic contact. Galvanic corrosion of mild steel elbow fixed on copper pipe is illustrated in Fig. 1.2.

1.6.3 Crevice Corrosion

Crevice corrosion usually occurs within crevices and shielded areas on metal surfaces in contact with corrosive media. This type of corrosion is generally associated with small volumes of stagnant solution trapped in holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt and rivet heads. Crevice corrosion is also known as deposit or gasket corrosion. Some of the deposits that cause crevice corrosion are sand, dirt, corrosion products, and other solids. Contact between a metal and nonmetallic surface such as a gasket can result in crevice corrosion. Stainless steels in particular are prone to crevice corrosion. The mechanism of crevice corrosion consists of the oxidation of the metal and the reduction of oxygen, yielding hydroxyl ion. After some time, the oxygen in the crevice is consumed and converted into hydroxyl ion. The metal continues to be attacked and the excess positive charge is

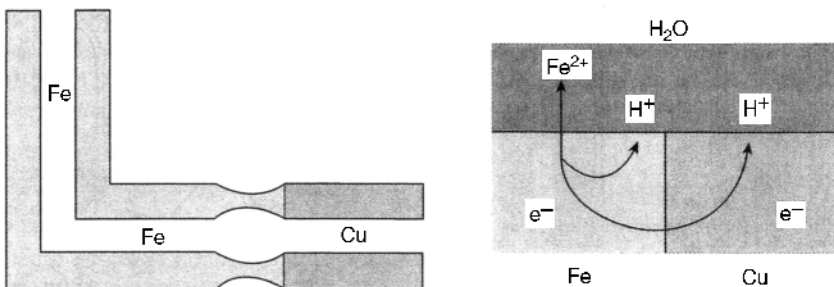


FIGURE 1.2 Galvanic corrosion of mild steel elbow connected to a copper pipe.

balanced by the migration of chloride anion from the bulk into the crevice. Thus, ferric or ferrous chloride builds up in the crevice. The ferric chloride can hydrolyze in the crevice and give rise to iron hydroxide and hydrochloric acid. The pH in the crevice can fall to 2 or 3 along with a high concentration of chloride.

Some preventive measures against crevice corrosion are (a) use of welded butt joints in place of riveted or bolted joints; (b) closure of crevices in lap joints by continuous welding; (c) caulking or soldering; (d) vessel design that allows complete drainage without stagnation; (e) removal of solid deposits; (f) use of nonabsorbent gaskets such as Teflon; and (g) flushing of the equipment with an inhibitor solution.

1.6.4 Pitting Corrosion

Pitting corrosion is a form of localized attack that results in localized penetration of the metal. This is one of the most destructive and insidious forms of corrosion. Pitting can cause equipment failure due to perforation, accompanied by a small percentage weight loss of the whole structure. Areas where a brass valve is incorporated into steel or galvanized pipeline are prone to pitting corrosion. The junction between the two areas is often pitted, and if the pipe is threaded, the thread in close contact with the brass valve pits rapidly, resulting in a leak. This occurs frequently in industry, homes, and farms. Pitting corrosion is difficult to measure in laboratory tests because of the varying number of pits and the depth under identical conditions. Pitting attack usually requires several months or a year to show up in service. Because of the localized and intense nature, pitting corrosion failures may occur suddenly. Pits usually grow in the gravitational direction. Most pits develop and grow downwards from horizontal surfaces. Pitting usually requires an extended initiation period on the order of months to years. Pitting can be considered a unique type of anodic reaction as well as an autocatalytic type of process. The metal in the pit dissolves along with the reduction of oxygen, as is the case with crevice corrosion. The rapid dissolution of metal in the pit results in a buildup of excessive positive charge in the pit followed by the migration of chloride ions into the pits to maintain the electroneutrality condition. Because of the high ionic potential of ferrous or ferric ion, hydrolysis of a ferric or ferrous ion results in lowering of the pH in the pit, which, together with the high chloride ion concentration in the pit, increases the corrosion rate.

The preventive measures cited for crevice corrosion also apply to pitting corrosion. The pitting corrosion resistance of some commonly used metals and alloys is in the order:

Titanium > Hastelloy C > Hastelloy F > Type 316 stainless steel > Type 304 stainless steel.

The addition of molybdenum to Type 304 stainless steel was found to improve the resistance of the steel to pitting corrosion. Localized corrosion morphologies are given in Fig. 1.3, which illustrates pitting and crevice corrosion.

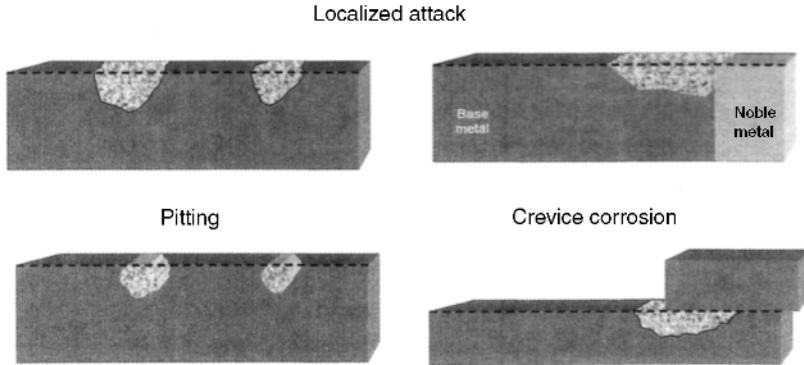


FIGURE 1.3 Forms of localized corrosion.

1.6.5 Dealloying or Selective Leaching

Selective leaching is the removal of an element from an alloy by corrosion. Selective removal of zinc from brass, known also as “dezincification,” is a prime example of this form of corrosion. Selective leaching has also been observed with other alloys in which iron, aluminum, cobalt, and chromium are removed selectively. Selective leaching of zinc from yellow brass containing 30% zinc and 70% copper is a common example. The removal of zinc can be uniform or localized. As a general rule, the uniform type of dezincification is observed in brasses containing high zinc in an acidic medium. A localized type of dezincification is commonly observed in low zinc brasses exposed to a neutral, alkaline, or mildly acidic medium.

The addition of small amounts of arsenic, antimony, phosphorus, or tin to 70/30 brass resulted in minimizing dezincification. The added minor elements minimize dezincification of brass by forming a protective film on the brass. Brasses suffer severe corrosion in aggressive environments and hence cupronickel alloys (70–90% Cu, 30–10% Ni) are used in place of brasses. Gray cast iron is known to exhibit selective leaching, giving the appearance of graphite. This type of attack is known as graphitic corrosion. Corrosion inhibitors have been used in the inhibition of dezincification of brasses. Uniform dealloying in admiralty brass is illustrated in Fig. 1.4.

1.6.6 Intergranular Corrosion

This form of corrosion consists of localized attack at—and adjacent to—grain boundaries, causing relatively little corrosion of grains, but resulting in disintegration of the alloy and loss of strength. The impurities at the grain boundaries, enrichment of one of the alloying elements, or depletion of one of the elements in the grain boundary areas causes intergranular corrosion. This form of corrosion has been observed in the case of failures of 18-8 stainless steels. The 18-8 stainless steels on heating to temperatures of 950–1450°F fail due to intergranular corrosion. It is surmised that depletion of chromium in the grain-boundary location of the steels results in

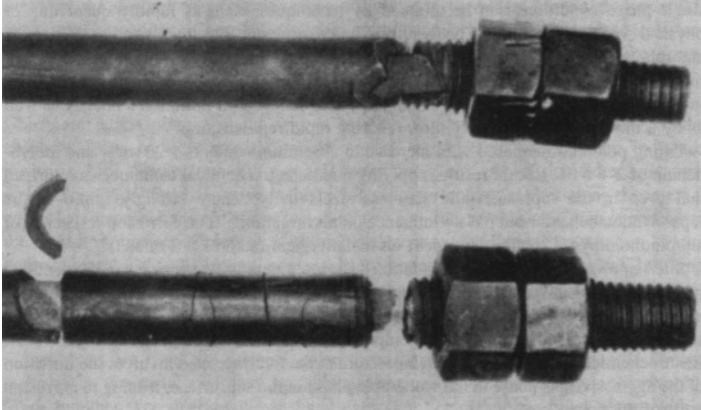


FIGURE 1.4 Dezincification of a bolt in brass.

intergranular corrosion. When the carbon content of the steels is 0.02% or higher, the chromium carbide (Cr_{23}C_6), being insoluble, precipitates out of the solid solution and results in depletion of chromium in areas adjacent to grain boundaries. The chromium carbide remains unattacked while the chromium-depleted areas near the grain boundary corrode. Intergranular corrosion of austenitic stainless steels can be controlled or minimized by quench annealing or by the addition of small amounts of niobium or tantalum, which form carbides readily, or by lowering the carbon content of the steel to less than 0.02%. By heating the steel to 1950–2050°F followed by water quenching, the chromium carbide dissolves, resulting in a more homogeneous alloy resistant to corrosion.

Mechanically assisted corrosion consists of (i) erosion corrosion, (ii) cavitation damage, (iii) fretting corrosion, and (iv) corrosion fatigue. These four forms of mechanically assisted corrosion are illustrated in Fig. 1.5. Erosion corrosion consists of the increase in attack of a metal due to the relative movement between a corrosive medium and the metal surface. The rapid movement or flow of the medium results in mechanical wear. The metal is removed from the surface in the form of dissolved ions or in the form of solid corrosion products, which are mechanically swept from a surface. Erosion corrosion of a metal appears in the form of grooves. Erosion corrosion is observed in piping systems such as bends, elbows, tees, valves, pumps, blowers, centrifuges, propellers, impellers, agitators, heaters and condensers, turbine blades, nozzles, wear plates, grinders, mills, and baffles. All types of equipment exposed to moving fluids are prone to erosion corrosion.

Some of the factors involved in erosion corrosion are (a) the nature of the surface films formed on the metal surface, (b) velocity of the moving fluid, (c) amount of turbulence in the liquid, (d) impingement, (e) the galvanic effect, (f) chemical composition, (g) hardness, (h) corrosion resistance, and (i) the metallurgical history of the metals and alloys.

In general, increased velocity results in increased erosion corrosion, and this effect is more pronounced beyond a critical velocity. The increase or decrease in erosion

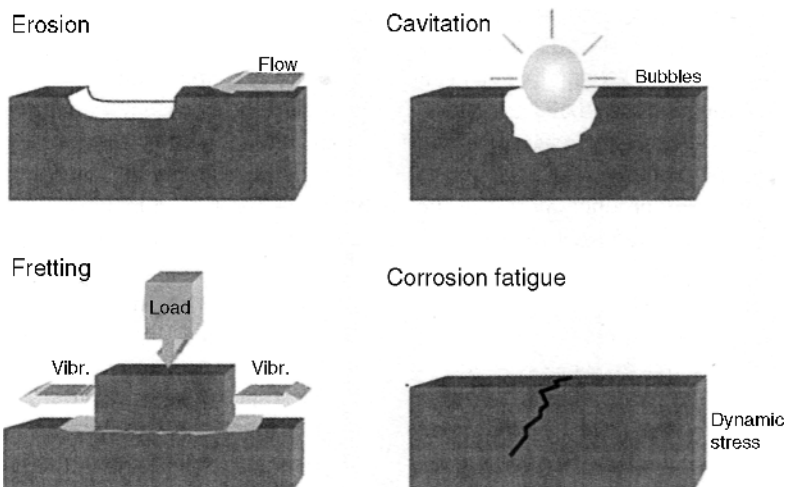


FIGURE 1.5 Forms of mechanically assisted corrosion.

corrosion with increase in flow of the medium depends upon the corrosion mechanisms involved. The increase in velocity increases the supply of oxygen, carbon dioxide, or hydrogen sulfide, resulting in greater attack of the metal. Unlike laminar flow, turbulence causes greater agitation of liquid at the metal surface, as well as more intimate contact between the metal and the environment. Turbulent flow occurs in the inlet ends of tubing in condensers and heat exchangers. Turbulence causes the erosion corrosion in impellers and propellers.

Failure due to impingement attack is a common failure mode where the aqueous medium is forced to change its direction, as it does in bends, tees, cyclones, and inlet pipes in tanks. Galvanic corrosion can accentuate erosion corrosion in a synergistic manner. At high velocities, the erosion-corrosion attack on steel coupled to copper or nickel becomes significant and can be attributed to the galvanic effect.

Stainless steels form passive oxide film and, as a result, offer resistance to corrosion. A hard, dense, and adherent film gives good protection from erosion corrosion, since the film cannot be displaced by mechanical forces. Titanium has probably the best resistance to erosion corrosion due to the titanium oxide film formed on the surface.

A noble metal has inherent corrosion resistance and, as a result, gives better performance when all other conditions are the same. An example of this is the better performance of 80/20 Ni/Cr alloy than 80/20 Fe/Cr alloy, because nickel has better resistance to corrosion than iron. The addition of a third metal such as iron to cupronickel improves the resistance to erosion corrosion in seawater. The addition of up to 13% chromium to steel and iron alloys results in increase in resistance to erosion corrosion in acid mine waters.

Some of the measures for prevention of erosion-corrosion damage are proper selection of materials with good resistance to erosion corrosion, proper design, coatings, cathodic protection, and reduction in the degree of the aggressive nature of



FIGURE 1.6 Erosion-corroded pump propeller.

the environment. The most economical solution is the selection of a suitable alloy with high resistance to erosion corrosion. Increasing pipe diameter reduces the flow velocity, giving rise to laminar flow, and streamlining bends reduces the impingement effects. Filtration of solids in the medium and lowering the temperature of the environment are useful in reducing erosion-corrosion damage. Hard facings and repair of damaged areas by welding as well as use of zinc plugs in pumps are some of the ways of combating erosion corrosion. The erosion-corrosion damage of a pump propeller in copper/tin/zinc alloy in the form of grooves, gullies, rounded holes, and valleys is shown in Fig. 1.6.

1.6.7 Cavitation Damage

Cavitation damage is a special form of erosion corrosion caused by the formation of vapor bubbles and their collapse in the liquid near a metal surface. This form of damage occurs in hydraulic turbines, pump impellers, and other surfaces that are in contact with high-velocity liquid flow along with high pressures. The formation and collapse of water vapor bubbles can produce shock waves with pressures as high as $60,000 \text{ lb/in}^2$, which can cause plastic deformation of metals.

Cavitation damage resembles pitting corrosion, except that the pitted areas are closely spaced, resulting in a very rough surface. Cavitation damage can be reduced by selection of more corrosion-resistant metals or alloys, choosing a design to minimize hydrodynamic pressure drops, or using pump impellers with a smooth finish and cathodic protection. Cavitation erosion damage of a cylinder liner of a diesel engine is shown in Fig. 1.7.

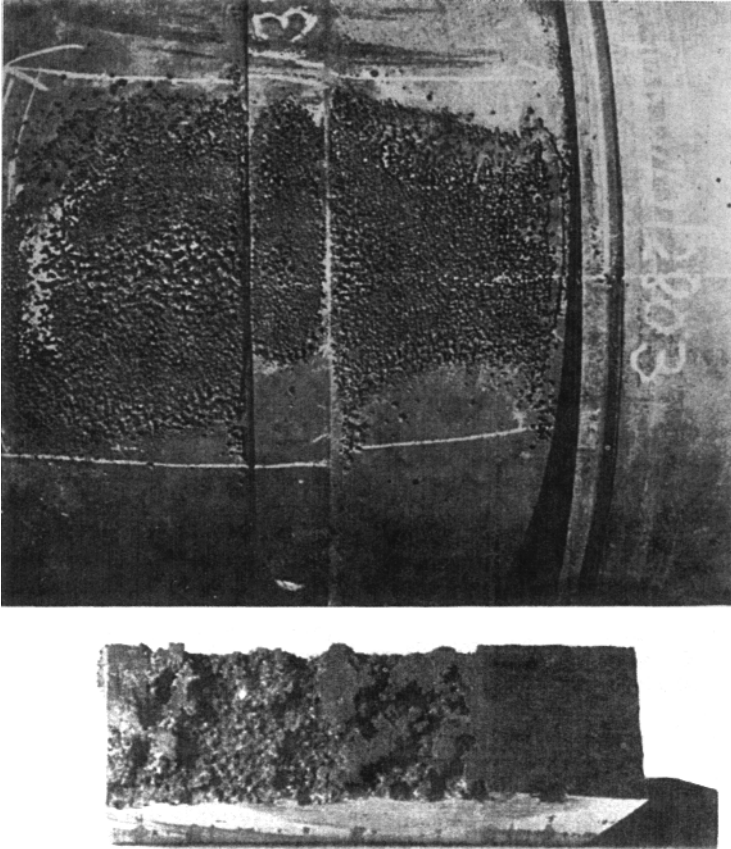


FIGURE 1.7 Cavitation damage in cylinder liner of a diesel engine.

1.6.8 Fretting Corrosion

Fretting corrosion is a combination of wear and corrosion in which material is removed from contacting surfaces when the motion between the surfaces is limited to very small amplitude oscillations. The oscillatory motion between the contacting surfaces in the tangential direction results in fretting corrosion. Oxidation is the primary factor in the fretting process. In oxidizing systems, fine metal particles removed by adhesive wear are oxidized and trapped between the fretting surfaces. The oxides act like an abrasive and increase the rate of removal of the material.

Some samples of vulnerable components are shrink-fits, bolted parts, and spines. The contacts between hubs, shrink- and press-fits and bearing houses on loaded rotating shafts or axles and many parts of vibrating machinery are prone to fretting corrosion. Fretting corrosion can destroy electrical contacts between gold and copper parts in electronic equipment. Fretting is also encountered in a stainless steel spacer used to mount a control rudder on the space shuttle. Fretting corrosion also occurs in

bolted fish plates used in railway tracks and in loosening of wheels and turbines from the attached shafts.

Fretting corrosion may be controlled by using low viscosity, high tenacity oils and greases and phosphate coatings in conjunction with lubricants. Increasing the hardness of one or both the parts in contact, increasing the surface hardness by shot-peening or cold-working, use of lead coatings, use of gaskets, increasing the relative motion between the parts, use of laminated plastic on gold plate, and cast iron-on-cast iron with phosphate coating or rubber cement coating are some methods useful in combating fretting corrosion damage.

1.6.9 Corrosion Fatigue

Corrosion fatigue consists of cracking of materials under the combined action of fluctuating or cyclic stress and a corrosive environment. While purely mechanical fatigue failure occurs above a critical cyclic stress value known as the fatigue limit, corrosion fatigue can occur at stresses lower than the fatigue limit. The damage due to corrosion fatigue is usually greater than the sum of the damage due to corrosion and fatigue acting separately. The fracture tension as a function of the number of cycles in purely mechanical fatigue and in corrosion fatigue is illustrated in Fig. 1.8.

Corrosion fatigue differs from stress-corrosion cracking in the sense that it occurs in most of the aqueous media. The mechanism consists of exposure of oxide-free, cold-worked metal by extrusion of slip bands in grains of the metal surface. These parts of the metal become anodic and result in grooves, which develop into transcrystalline cracks.

Corrosion fatigue is affected by oxygen content, pH, temperature, and the composition of the solution. Iron, steel, stainless steels, and aluminum bronzes have good resistance to corrosion fatigue in water. On the other hand, aluminum bronzes and austenitic stainless steels have only 70–80% of normal fatigue resistance in seawater. High-chromium alloys have only 20–40% of fatigue resistance in seawater.

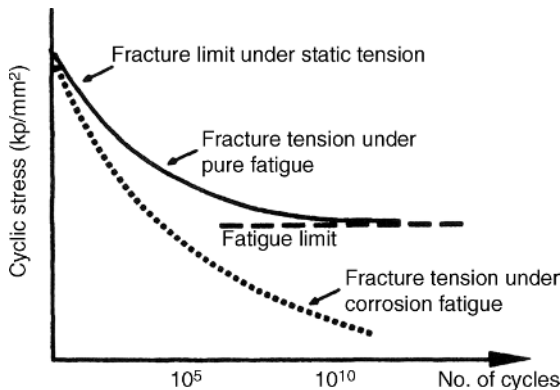


FIGURE 1.8 Fracture tension as a function of cycles in mechanical fatigue and corrosion fatigue.

Corrosion fatigue is generally defined in terms of the alloy and the environment. Corrosion fatigue may be eliminated or minimized by changes in design of the equipment, or by heat treatment to relieve stress or shot-peening of the metal surface to induce compressive stresses. Corrosion fatigue may also be minimized by the use of corrosion inhibitors and also by the use of electrodeposited zinc, chromium, nickel, copper, and nitride coatings. A typical corrosion fatigue crack through a sample of mild steel exposed to flue gas condensate is shown in Fig. 1.9.

1.6.10 Stress-Corrosion Cracking

Stress-corrosion cracking involves cracking of susceptible material caused by the simultaneous presence of tensile stress and a specific corrosive environment as shown in Fig. 1.10. During SCC the metal may be virtually unattacked over most of the surface, but fine cracks progress through the metal. Stress-corrosion cracking has serious consequences, because it can occur at stresses within the range of typical design stress. The important factors that influence this mode of damage are temperature, composition of the solution and the metal or alloy, stress, and the structure of the metal. Two typical examples of stress-corrosion cracking are the seasonal cracking of brass and the caustic embrittlement of steel. Seasonal cracking of brass cartridge cases

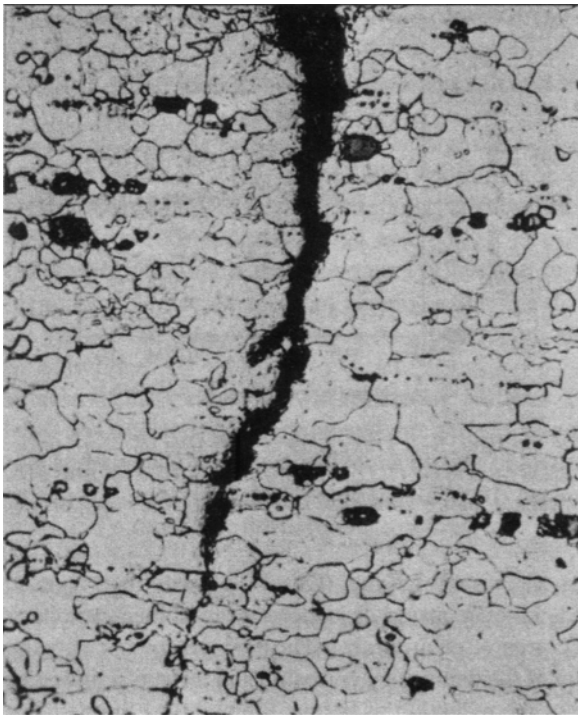


FIGURE 1.9 Corrosion fatigue crack in mild steel sheet exposed to flue gas condensate.

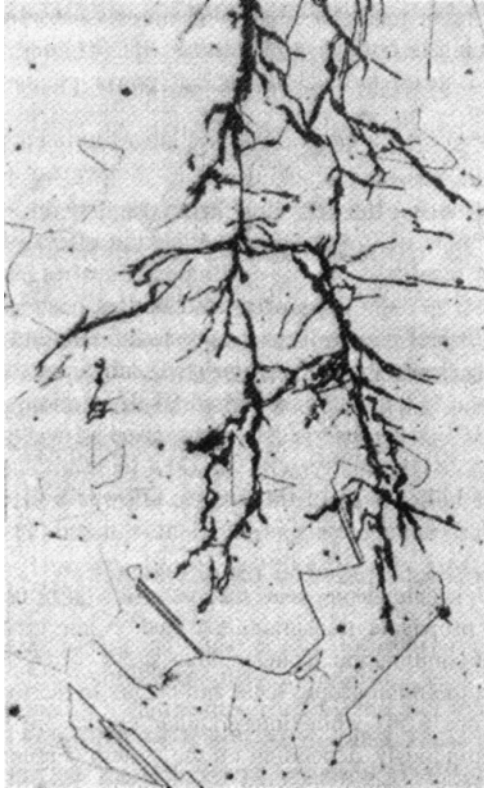


FIGURE 1.10 Transgranular stress-corrosion cracking in 304 steel.

develop cracks during heavy rainfall, coupled with hot temperatures in the tropics. Carbon steels subjected to stress close to the elastic limit and exposed to hot concentrated alkali solutions or nitrate solutions are susceptible to stress-corrosion cracking.

Stress-corrosion cracks appear like brittle mechanical fracture, although the cracks are due to corrosion. Intergranular SCC occurs along grain boundaries, and transgranular cracking occurs without preference to grain boundaries. Transgranular stress-corrosion crack propagation is generally discontinuous on the microscopic scale and occurs by periodic jumps on the order of micrometer (Fig. 1.10), while intergranular cracks propagate continuously or discontinuously, depending on the system (Fig. 1.11). Both types of cracking have been observed in high-nickel alloys, iron/chromium alloys, and brasses. In general, cracking occurs perpendicular to the applied stress. The type of crack, either single or branching, depends upon the structure and composition of the metal and the composition of the environment. For a given metal or alloy and a particular environment, a threshold stress can be defined, above which cracking occurs. The source of the stress can be applied, residual, thermal, welding, or corrosion products in constricted regions.

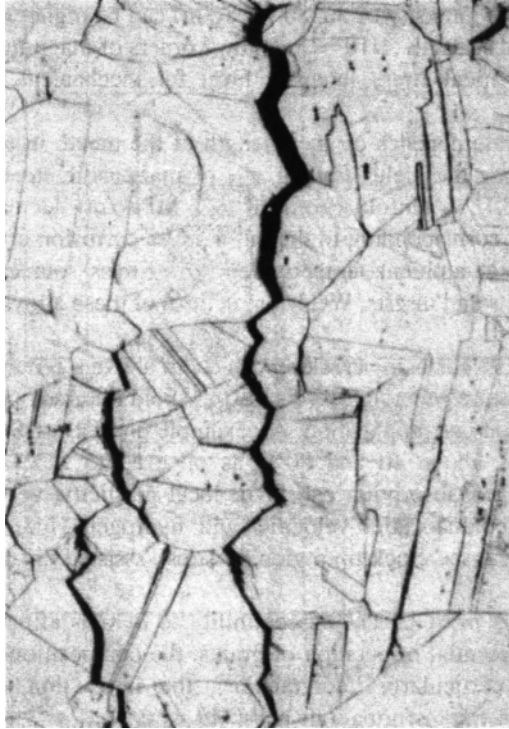


FIGURE 1.11 Intergranular stress-corrosion cracking in brass.

The time required for cracking is of importance. As the stress-corrosion cracks penetrate the metal, the cross-sectional area decreases, and the cracking failure occurs due to mechanical action. The cracking tendencies of the alloys can be defined only by carrying out long-term tests. Stress-corrosion cracking has been observed in the case of aluminum alloys in seawater or chloride solutions, copper alloys in ammoniac solutions, magnesium alloys in chloride dichromate, nickel in sodium hydroxide solutions, stainless steels in chloride solutions, and titanium alloys in seawater and fuming nitric acid solutions. Stress-corrosion cracking is influenced by metallurgical factors such as the chemical composition of the alloys, preferential orientation of the grains, composition and distribution of precipitates, degree of progress of phase transformation, and dislocations.

The precise mechanism of stress-corrosion cracking is not well known in spite of the large amount of work done on the subject. The main reason for this is the complex interplay of metal, tensile stress, and the corrosive environment. Corrosion plays an important role in the initiation of cracks. Any discontinuity like pits on the surface of the metal increases the stress. Stress concentration at the tip of the notch increases considerably as the radius of the notch decreases and cracks initiate at the base of the pit. The combined action of corrosion and stress in crack propagation was established by the observation that cathodic protection arrested crack propagation.

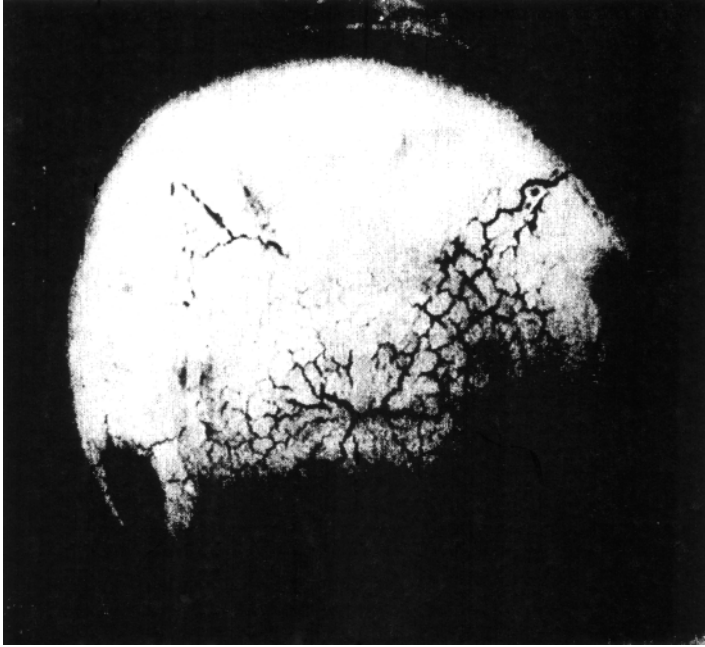


FIGURE 1.12 Stress corrosion of type 304 autoclave.

The methods used for the mitigation of SCC tend to be general because the exact mechanism of this form of degradation is not well understood. Annealing the alloy lowers the residual stress and hence lowers the propensity to stress-corrosion cracking. Carbon steels and austenitic steels can be annealed at 1100–1200°F and 1500–1700°F respectively, thereby lowering the tendency of the steels to suffer cracking. The corrosive environment can be made less aggressive by degasification or demineralization. Material selection such as substituting type 304 stainless steel by a more corrosion-resistant alloy such as Inconel can be done to mitigate the corrosive attack. Cathodic protection of the structure and addition of corrosion inhibitors to make the environment less corrosive are some methods to combat stress-corrosion cracking failures.

Stress-corrosion cracking damage of a type 304 stainless steel autoclave used under vapor condensation conditions in aqueous chloride solutions is depicted in Fig. 1.12.

1.7 CORROSION INHIBITION

In general, any corrosion retardation process can be considered corrosion inhibition. Corrosion inhibition has been achieved by the addition of a chemical compound that inhibits the oxidation of the metal. The chemical inhibitor added to the system may be in the form of a liquid or vapor or both.

TABLE 1.12 Number of Abstracts as a Function of Time

Year	Corrosion	Passivity	Corrosion Inhibitors
1908	22	2	1
1912	61	5	10
1957	>800	38	280
1994	>2,000	>100	>400
2007	15,903	–	416

The two steps involved in the action of the corrosion inhibitor are the transport of the inhibitor to the metal surface followed by the interaction of the inhibitor with the metal surface. The interaction of a corrosion inhibitor with a metal surface is similar to the interaction of a drug molecule with human physiology in that both involve transport of the moiety to the active site followed by the interaction with the site.

In early times, protection of iron by bitumen and tar was practiced by the Romans. At the turn of the nineteenth century, some of the fundamentals of the corrosion phenomena were understood (3, 4) soon after the discovery of the galvanic cell and the relationship between electricity and chemical changes (20). The basic electrochemical theory of corrosion accepted today is due to Wollaston (21). The use of corrosion inhibitors for the protection of metals can be traced to the last half of the nineteenth century. Marangoni and Stefanelli (22) used extracts of glue, gelatin, and bran to inhibit the corrosion of iron in acids. This and subsequent discoveries of effective inhibitors for metals were the result of empirical studies. The first patent given to Baldwin (British Patent 2327) consisted of the use of molasses and vegetable oils for pickling sheet steel in acids.

The progressive increase in the number of abstracts dealing with corrosion and corrosion inhibition is clear evidence of the increased activity in corrosion and corrosion inhibition studies (Table 1.12).

In early studies, the effect of inhibitors was tested by the determination of loss in weight of samples agitated in solutions containing inhibitors compared to solutions devoid of inhibitors. In earlier times, the selection of inhibitors was done on a trial and error basis. Intensive fundamental studies on corrosion inhibitors and the factors influencing their effectiveness have been in progress over the last 50 years. The advent of modern surface analytical techniques has made it possible to study the nature and composition of corrosion inhibitor films on metal surfaces. It is instructive to compare two abstracts of the work that appeared in 1908 and 1987. The abstract of the 1908 patent (22) reads

The Coslett Rust Preventing Process involving the immersion of clean steel in a boiling iron phosphate solution for 3 to 4 hours followed by drying at 100°C.

The abstract of the 1987 paper (23) states

Corrosion inhibition is a complex phenomenon and depends on the formation of protective layers on the metal surface. Of the many factors that affect the protective nature of the surface layers, the incorporation of the inhibitor in the surface layer is the most important. The manner in which the inhibitor is incorporated in the surface layer leads to three types of inhibition; namely, interface inhibition, interphase inhibition, and precipitation coating.

Determining the composition of the surface layers of metals is facilitated by modern surface analytical techniques, such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), reflectance spectroscopy (RS), and electron microprobe analysis (EMPA). The roles of these modern surface analytical techniques are discussed with respect to elucidating the interfacial inhibition of copper by mercaptobenzothiazole, interphase inhibition of mild steel AISI 1010 by oxyanions such as chromate, molybdate, and tungstate, and precipitation coating of AISI 1010 steel by oxalate in acid mine water.

Two recent papers (24, 25) with the titles “Selection of corrosion inhibitors based on structural features” and “Selection of inhibitors based on theoretical considerations” provide evidence for the advances that took place in the past 25 years.

The scientific basis of corrosion inhibition may well have begun with the recognition of the phenomenon of the adsorption of the inhibitor on a metal surface (26). Further *ortho*-substituted organic bases, such as *ortho*-toluidine, were found to be more effective corrosion inhibitors than the *meta*- and *para*-toluidines in oil field corrosion (27). The effect of the structure of organic bases such as polyethylene imines on corrosion inhibition was studied by varying the methylene rings and their influence on the CNC bond angles, which in turn affected the availability of the electron pair and hence the extent of corrosion inhibition.

The ready availability and capability of modern scientific instrumentation to study solid–liquid interfaces *in situ*, to analyze various species in solution, to monitor fast electrochemical reactions, and to determine inhibitor film composition and structure helped in the development of mechanistic models of corrosion inhibition such as the corrosion inhibition of copper by benzotriazole in a hydrochloric acid medium (28).

Hackerman proposed the type of bonding and the effect of the structure of the metal–inhibitor adsorbate on the strength and stability of the bond lead to the concept of a two-dimensional quasi-compound (29). The surface film retards either the anodic or the cathodic reaction, or both. The surface film may also impede the transfer of reactant on the product or influence the rate constant. The net effect is corrosion inhibition, although different principles are involved in the various processes.

Corrosion inhibitors that retard the cathodic reaction are known as cathodic inhibitors. Similarly, the inhibitors that retard the anodic reaction are known as anodic inhibitors. Some compounds that influence both the cathodic and the anodic reactions are known as mixed inhibitors. Corrosion inhibitors have also been classified as organic and inorganic inhibitors. Based upon the hard and soft acid and base principle (HSAB), the inhibitors have been termed as hard, soft, and

borderline inhibitors (30). These concepts will be discussed in detail in the appropriate section.

In spite of the considerable progress made in the chemistry of inhibitors, the problem of inhibition in a corrosion system presents the same challenges today as it did in the past. The transport of the corrosion inhibitor from bulk solution to the surface of the metal and the active inhibitor species that is available to interact with the metal are the fundamental factors governing corrosion inhibition. Other equally important factors are the flow rate, temperature, solubility, inhibitor stability, surface adherence properties, and changes in corroding conditions that govern the effectiveness of corrosion inhibitors. Factors such as pit, temperature, flow rate of bulk fluid, and metal interface are of importance (31). Readily available modern computerized electrochemical and surface analytical instrumentation enables the understanding of the corrosion inhibition process to some extent. It is necessary to follow the corrosion inhibition process *in situ* by a combination of electrochemical and surface analytical probes to arrive at the actual mechanism of corrosion inhibition.

It is now useful to turn to the science of inorganic inhibitors and their action in the protection of metals from corrosion. The science of inorganic corrosion inhibitors has not reached the same level of advancement as that of organic inhibitors. The most common inhibitors, such as chromates used for corrosion inhibition of iron and its alloys in aqueous media of wide pH range and arsenates in neutral pH aqueous media, are considered unacceptable for use from an environmental point of view and are banned by governmental agencies. In most of the applications, environment-friendly, otherwise known as green inhibitors, such as molybdates and tungstates, have replaced chromates.

Other common inhibitors such as borates, carbonates, silicates, and phosphates continue to find applications. Some of the inorganic inhibitors, such as borates, offer corrosion protection by increasing the pH of the system while others such as phosphates form insoluble compounds on the metal surface to be protected. The mechanism of corrosion protection by oxyanions such as chromates, molybdates, and tungstates of mild steel AISI 1010 was studied by detailed electrochemical polarization along with a combination of surface analytical techniques such as X-ray photoelectron spectroscopy, auger electron spectroscopy, and electron microprobe analysis (32). These studies enabled the determination of the nature, composition, and thickness of the inhibitor films on the surface of the steel sample, which in turn threw light on the mechanism of corrosion inhibition.

The vast literature that is available on corrosion inhibitors and their use in different systems poses a daunting task in the selection and use of an inhibitor in a particular situation. The selection of inhibitors has been made on an empirical basis. The selection of corrosion inhibitors based on structural features (24) and theoretical considerations (25) are two significant approaches. With the advent of electronic computers, the selection of inhibitors can be done by using expert systems (33). In the normal course, the selection of an inhibitor from the literature is a time-consuming task, since the literature on the available inhibitors is vast and the choice depends on the metal to be protected, as well as the type of corrosive environment and the operating conditions.

With widespread access to computers, the expert's knowledge is stored and can be recalled easily and rapidly at will. The required information can be accessed in a number of ways, such as the database and the expert system. In the database system, data are stored in a structural manner and the user must have available all the important information about his or her system so as to be able to move logically through the database to extract the required data. When the expert system is used, the user is taken through the model by a series of questions from the model; the answers to the questions allow the appropriate advice to be given to the user.

Both the use of database and expert systems can result in the same conclusions, although the method of using each is different. The user must know important parameters of his system while using the database, while the expert system will elicit the required information by itself. Both the database and expert system have their own useful features. The scientist who wants to find an inhibitor for a particular application might not like the verbosity of the expert system, while an inexperienced user might find the database system unfriendly to use and also find the information possibly misleading.

In conclusion, it can be stated that the field of corrosion inhibitors is old and has developed into a mature science as a result of advances made in electrochemical and surface analytical aspects. It is interesting to note that inhibitors such as glue, gelatin, bran, and vegetable oils were used in corrosion inhibition of iron in acids during the nineteenth century. Incidentally, these inhibitors are nontoxic and can be considered environmentally acceptable green inhibitors. No consideration of environmental compatibility was shown with respect to the use of inhibitors until the period 1970–1980. The success achieved in the future will depend upon a balanced approach based on basic science, practice, and environmental considerations.

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