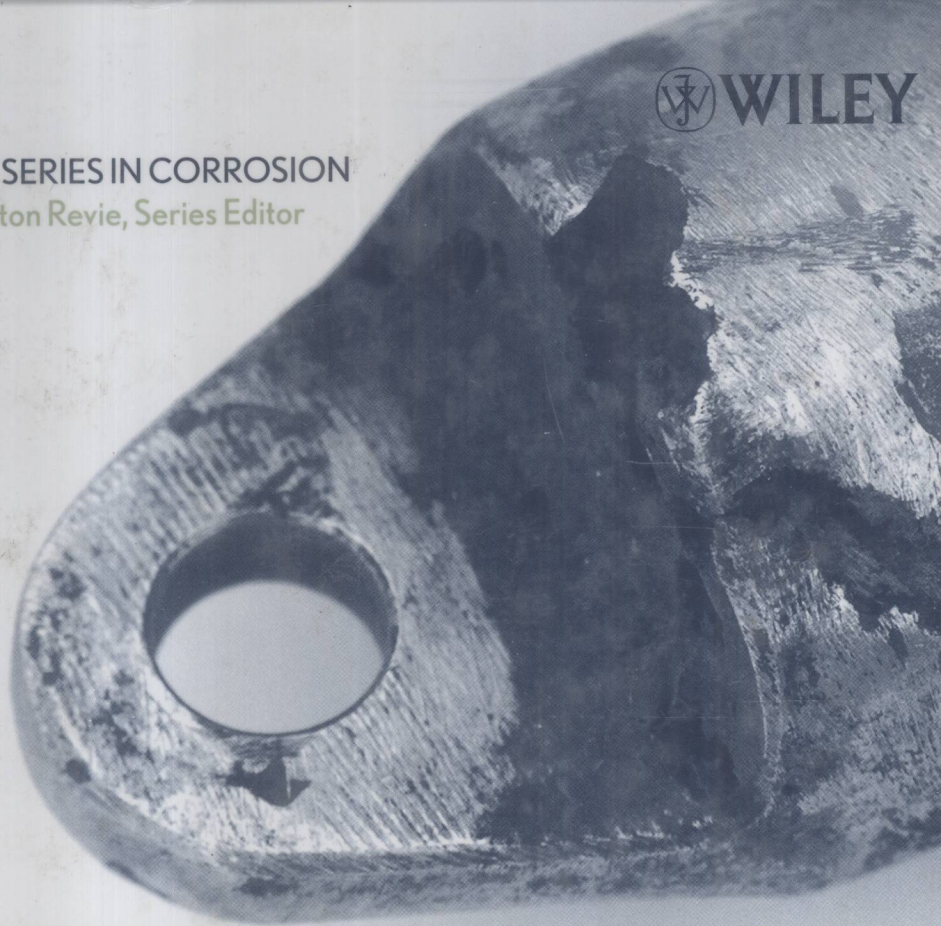


 WILEY

WILEY SERIES IN CORROSION

R. Winston Revie, Series Editor



CORROSION INSPECTION AND MONITORING



PIERRE R. ROBERGE

TG172
R638

Corrosion Inspection and Monitoring

Pierre R. Roberge

*Royal Military College of Canada
Ontario, Canada*



E2008001813

WILEY-INTERSCIENCE
A John Wiley & Sons, Inc., Publication

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey.

Published simultaneously in Canada.

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Wiley Bicentennial Logo: Richard J. Pacifico

Library of Congress Cataloging-in-Publication Data:

Roberge, Pierre R.

Corrosion inspection and monitoring / Pierre R. Roberge.

p. cm.

Includes index.

ISBN: 978-0-471-74248-7 (cloth)

1. Corrosion and anti-corrosives. 2. Corrosion and anti-corrosives—Testing. I. Title.

TA462.R528 2007

620.1'1223—dc22

2006023012

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

Corrosion Inspection and Monitoring

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Preface

Corrosion is a form of damage that has accompanied mankind since the very introduction of metals thousands of years ago. Corrosion is often insidious and hidden until striking at the worst moment of a system operation. While there are many ways to try and prevent such damage, the optimum control method relies on an early diagnosis of the problems. However, in many cases such a task is far from trivial. Consider, for example, the oil and gas systems deployed in the most remote areas, often at depths never exploited before, or the transmission pipelines traversing the harshest environments on the planet. The inspectability of these systems is very limited and extremely costly.

While there is an abundance of publications and reference documents on all aspects of corrosion science and engineering, the coverage on how the problems are prevented by inspection and monitoring is very limited. This is a poor reflection of the many advances in the tools and strategies that have been developed in many countries and organizations in recent years to improve the management of increasingly complex systems. After reviewing the principles of corrosion management as they have evolved in many industries since the introduction of risk-based thinking in the 1970's, the present book corrects this situation by bringing together descriptions of the most modern techniques developed to inspect and monitor corrosion susceptible systems.

In the first chapter the readers are introduced to the general nature of corrosion and to the complex factors that control such a universal foe. The impact of corrosion on the economy and safe operation of systems in various operational environments is also briefly introduced as a reminder that corrosion losses are a real impediment to economic growth.

The second chapter establishes the basis for assessing corrosion flaws by putting in perspective the relations between defects, faults, failures, and their consequences. The concepts of probability of failure (POF) and probability of detection (POD) are also introduced. The classic corrosion taxonomy detailing the forms of corrosion is then covered with a special focus on the detectability of the various types of corrosion damage encountered in practice.

Corrosion inspection and monitoring are maintenance tasks that should be designed to provide information for the general management and operation of systems. Chapter three reviews the maintenance strategies as they are evolving from corrective to predictive in a world increasingly focused on risk based assessments. The concepts of life cycle assessment and asset management are discussed in relation to inspection strategies and key performance indicators. The principles of risk based inspection and various risk assessment methodologies (HAZOP, FMECA, FTA, and ETA) are explained and illustrated with industrial

examples. Some general guidance in carrying out failure analysis is also provided since such process can generate very valuable information for subsequent inspection tasks. The chapter concludes by describing how various industries and organizations have established very useful roadmaps for carrying out the most complex inspection and monitoring schedules.

The role of corrosion monitoring and considerations for establishing a corrosion monitoring program are discussed at the onset of chapter four. This introduction is then followed by discussions on generic aspects of probe design and selection, location of monitoring hardware, and other important points that need to be envisaged when embarking on a corrosion monitoring program. The main sections of chapter four then present a series of technical descriptions detailing important features of intrusive and non-intrusive methods that can produce direct measurement of corrosion rates or that can provide an indirect way of monitoring corrosion by following a variable or a feature related to the corrosion degradation of a system. Chapter four also includes discussions on three additional areas of corrosion management: effects and monitoring of microbiologically induced corrosion (MIC), the monitoring of cathodic protection (CP) systems, and monitoring of atmospheric corrosion.

In many areas of modern engineering, non-destructive evaluation (NDE) techniques have provided valuable and often critical information for the safe operation of the most complex systems. Such usefulness has recently been greatly enhanced by the tremendous advances in computer and communication tools. Chapter five first provides a discussion on the purpose and other aspects specific to NDE: defect response variance, validation of inspection tools, and data representation. Following this general introduction, detailed descriptions of the main NDE inspection techniques and their many variants are presented: visual, ultrasonic, radiographic, electromagnetic, and thermographic inspection.

It is sincerely hoped that the readers will enjoy this timely reference text as much as I have enjoyed writing it.

PIERRE R. ROBERGE

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Chapter 1

Corrosion and Its Cost In a Modern World

- 1.1. Corrosion, Why Bother?
- 1.2. Nature Of Corrosion
- 1.3. Corrosion Factors
 - 1.3.1. Environment Factor
 - 1.3.1.1. Local Cells
 - 1.3.1.2. Presence of Microbes
 - 1.3.1.3. Flow Effect
 - 1.3.2. Temperature Factor
 - 1.3.3. Stress Factor
 - 1.3.4. Material Factor
- 1.4. Strategic Impact and Cost of Corrosion Damage
- References

1.1. CORROSION, WHY BOTHER?

In a modern business environment, successful enterprises cannot tolerate major corrosion failures, especially those involving personal injuries, fatalities, unscheduled shutdowns and environmental contamination. For this reason considerable efforts are generally expended in corrosion control at the design stage and in the operational phase.

Corrosion can lead to failures in plant infrastructure and machines that are usually costly to repair, costly in terms of lost or contaminated product, in terms of environmental damage, and possibly costly in terms of human safety. Decisions regarding the future integrity of a structure or its components depend on an accurate assessment of the conditions affecting its corrosion and rate of deterioration. With this information an informed decision can be made as to the type, cost and urgency of possible remedial measures.

Required levels of maintenance can vary greatly depending on the severity of the operating environments. While some of the infrastructure equipment might

only require regular repainting and occasional inspection of electrical and plumbing lines, some chemical processing plants, power generation plants, aircraft and marine equipment, are operated with extensive maintenance schedules.

Even the best of designs cannot be expected to anticipate all conditions that may arise during the life of a system. Corrosion inspection and monitoring are used to determine the condition of a system and to determine how well corrosion control and maintenance programs are performing. Traditional corrosion inspection practices typically require planned periodic shutdowns or service interruptions to allow the inspection process. These scheduled interruptions may be costly in terms of productivity losses, restart energy, equipment availability, and material costs. However, accidental interruptions or shutdowns are potentially much more disruptive and expensive.

1.2. NATURE OF CORROSION

The degradation of materials generally occurs via three well-known avenues: corrosion, fracture, and wear. Corrosion is traditionally related to chemical processes that break chemical bonds while fracture is related to mechanical processes that break bonds and wear to relative motion that break bonds. These are, to some extent, separate considerations, but they are also interconnected. Chemical environments accelerate fracture, chemical environments accelerate wear and vice versa as wear products produce deposits that accelerate corrosion, and fracture processes can permit one component to contaminate another (1).

Humans have most likely been trying to understand and control metallic corrosion for as long as they have been using objects made of metals. The most important periods of prerecorded history are named for the metals that were used for tools and weapons, for example, Iron Age, Bronze Age. However, these metals are unstable in ordinary aqueous environments.

The driving force that causes metals to corrode is a natural consequence of their temporary existence in metallic form. To reach this metallic state from their occurrence in Nature in the form of various chemical compounds (ores), it is necessary for them to the energy that is later returned through the corrosion process. The amount of energy required and stored varies between metals. It is relatively high for metals, such as magnesium, aluminum, and iron, and relatively low for metals, such as copper, silver, and gold. Table 1.1 lists a few metals in order of diminishing amounts of energy required to convert them from their oxides to metal.

A typical metallic cycle is illustrated by iron. The most common iron ore, hematite, is an oxide of iron (Fe_2O_3). The most common product of the corrosion of iron, rust, has a similar chemical composition. The energy required to convert iron ore to metallic iron is returned when the iron corrodes to form the original compound. Only the rate at which these energy changes occur may be different.

In contact with the environment, corrosion is a primary route by which metals deteriorate. Most metals corrode on contact with water or moisture, acids, bases, salts, oils, aggressive metal polishes, and other solid and liquid chemicals.

Table 1.1. Positions of Some Metals in the Order of Energy Required to Convert Their Oxides to Produce 1 kg of Metal

	Metal	Oxide	Energy, MJ kg ⁻¹
Highest energy	Li	Li ₂ O	40.94
	Al	Al ₂ O ₃	29.44
	Mg	MgO	23.52
	Ti	TiO ₂	18.66
	Cr	Cr ₂ O ₃	10.24
	Na	Na ₂ O	8.32
	Fe	Fe ₂ O ₃	6.71
	Zn	ZnO	4.93
	K	K ₂ O	4.17
	Ni	NiO	3.65
	Cu	Cu ₂ O	1.18
	Pb	PbO	0.92
	Pt	PtO ₂	0.44
	Ag	Ag ₂ O	0.06
Lowest energy	Au	Au ₂ O ₃	-0.18

Metals will also corrode when exposed to gaseous materials, such as acid vapors, formaldehyde gas, ammonia gas, and sulfur-containing gases.

The fundamental nature of a corrosion process is usually electrochemical in nature, having the essential features of a battery. When metal atoms are exposed to an environment containing water molecules they can give up electrons, becoming themselves positively charged ions provided an electrical circuit can be completed.

Corrosion damage can be concentrated locally to form a pit or, sometimes, a crack, or it can extend across a wide area to produce general wastage. Localized corrosion that leads to pitting may provide sites for fatigue initiation and, additionally, corrosive agents, such as seawater, may lead to greatly enhanced growth of fatigue cracks. Pitting corrosion also occurs much faster in areas where microstructural changes have occurred due to welding operations.

1.3. CORROSION FACTORS

Considering the many complex forms and mechanisms of corrosion damage, the limitations of individual plant inspection and monitoring techniques are considerable. The large number of variables involved also implies that no single method can be expected to satisfy all possible conditions and environments. Destruction

by corrosion takes many forms (see Chapter 2), and depends on the complex interaction of a multitude of factors described in the following sections.

1.3.1. Environment Factor

The environments to which materials are exposed dominate considerations in predicting and assuring their reliable performance, but environments are difficult to define and their broad and uncertain variability decreases their predictability. Environments of concern are local environments on the surface of a metal, and their characters are often quite different from bulk environments. The differences between the bulk and local chemistries are produced, for example, by heat transfer, evaporation, flow, and electrochemical cells. Environments may also vary greatly between systems.

1.3.1.1. Local Cells

Local cells can be produced by differences among small nearby areas on the metal surface. Local cells may result from differences in the metal or the environment. The differences may sometimes be simply in the thickness of a surface film at adjacent sites on a metallic surface. These differences in the environment are a driving force that can trigger the onset of a localized corrosion problem. Corrosion under insulation (CUI), for example, is a particularly severe form of localized corrosion that has been plaguing chemical process industries since the energy crisis of the 1970s forced plant designers to include much more insulation in their designs (2).

Intruding water is the key problem in CUI. Water entering an insulation material and diffusing inward will eventually reach a region of dryout at the hot pipe or equipment wall. Next to this dryout region is a zone in which the pores of the insulation are filled with a saturated salt solution. When a shutdown or process change occurs and the metal–wall temperature falls, the zone of saturated salt solution moves into the metal wall.

Upon reheating, the wall will temporarily be in contact with the saturated solution and stress-corrosion cracking (SCC) may begin. Corrosion may attack the jacketing, the insulation hardware, or the underlying piping or equipment. These drying–wetting cycles in CUI associated problems are strong accelerators of corrosion damage since they provoke the formation of an increasingly aggressive chemistry that may lead to the worst corrosion problems possible, (e.g., SCC), and premature catastrophic equipment failures.

Another important characteristic of aqueous or humid environments is the redox potential that is both a function of the chemistry of species present and the geometric conditions that can affect the potential and pH. In aqueous environments, this includes oxygen as it increases the redox potential or an oxygen scavenger, (e.g., erythorbic acid, sulfite, bisulfite, or hydrazine), as it decreases the potential. The electrochemical potential produces a powerful effect on chemical reactions and is the product not only of environmental chemistry, but of

separated electrochemical cells, especially where the relative areas of anodes and cathodes are different.

1.3.1.2. Presence of Microbes

Microbes are present almost everywhere in soils, freshwater, seawater, and air. However, the mere detection of microorganisms in an environment does not necessarily indicate a corrosion problem. What is important is the number of microorganisms of the specifically corrosive types. In unaerated (anaerobic) soils, the corrosion attack is attributed to the influence of the sulfate-reducing bacteria (SRB). The mechanism is believed to involve both direct attack of the steel by hydrogen sulfide and cathodic depolarization aided by the presence of bacteria. Even in aerated (aerobic) soils, there are sufficiently large variations in aeration that the action of SRB cannot be neglected. For example, within active corrosion pits, the oxygen content becomes exceedingly low.

Microbiologically influenced corrosion (MIC) is responsible for the degradation of a wide range of materials. A useful representation of materials degradation by microbes has been made in the form of a pipe cross-section (Fig. 1.1) (3). Most metals and their alloys, (e.g. stainless steels, aluminum and copper alloys, polymers, ceramic materials, and concrete) can be attacked by microorganisms. The synergistic effect of different microbes and degradation mechanisms should be noted in Fig. 1.1.

The muddy bottom of any relatively stagnant body of water with a high biological oxygen demand often supports massive growth of SRB, and may waterlog soils. Any metallic installations buried or immersed in such environments can be expected to suffer badly from microbiological corrosion. The most serious economic problem is to pipelines, although sheet piles, ship hulls, and piers are frequently attacked. In some instances, cast iron pipes of 6.3 mm thickness have perforated within the first year of operation under such conditions, while perforation in 3 years is common.

1.3.1.3. Flow Effect

The destruction of a protective film on a metallic surface exposed to high flow rates can have a major impact on the acceleration of corrosion damage. Carbon steel pipe carrying water, for example, is usually protected by a film of rust that slows down the rate of mass transfer of dissolved oxygen to the pipe wall. The resulting corrosion rates are typically $<1 \text{ mm year}^{-1}$. The removal of the film by flowing sand slurry has been shown to raise corrosion rates 10-fold to $\sim 10 \text{ mm year}^{-1}$ (4). Figure 1.2 illustrates the various states of an oxide surface film behavior as liquid velocity or surface shear stresses are increased (5, 6).

Change in the corrosion and erosion mechanisms associated with flow accelerated corrosion (FAC) are summarized in Figs. 1.3 and 1.4. In stagnant water (origin of the plot in Fig. 1.2), the corrosion rate is low and decreases parabolically with time due to the formation and growth of a corrosion protective film at

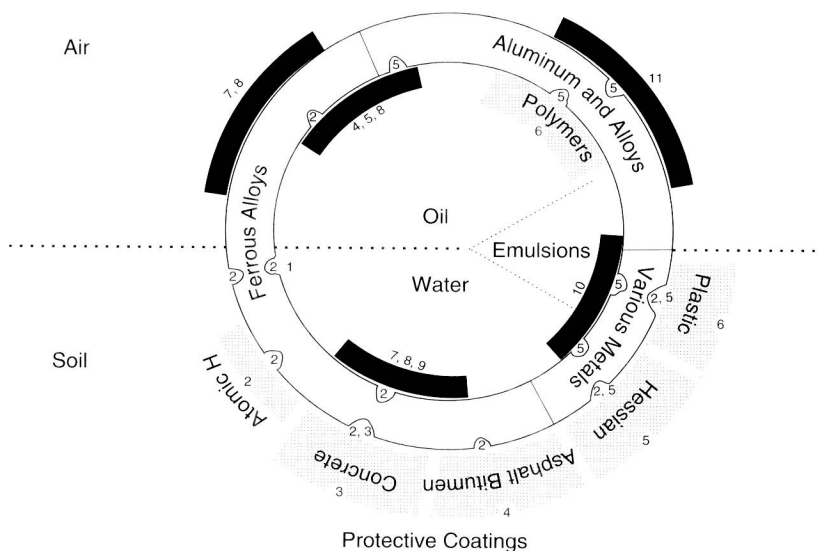


Fig. 1.1. Schematic illustration of the principal methods of microbial degradation of metallic alloys and protective coatings. 1. Tubercle leading to differential aeration corrosion cell and providing environment for "2". 2. Anaerobic sulfate reducing bacteria (SRB). 3. Sulfur-oxidizing bacteria, producing sulfates and sulfuric acid. 4. Hydrocarbon utilizers, breaking down aliphatic and bitumen coatings and allowing access of "2" to underlying metallic structure. 5. Various microbes producing organic acids as end-products of growth, attacking mainly non-ferrous metals–alloys and coatings. 6. Bacteria and molds breaking down polymers. 7. Algae-forming slimes on above-ground damp surfaces. 8. Slime-forming molds and bacteria (which may produce organic acids or utilize hydrocarbons), providing differential aeration cells and growth conditions for "2". 9. Mud on river bottoms, and so on providing matrix for heavy growth of microbes (including anaerobic conditions for "2"). 10. Sludge (inorganic debris, scale, corrosion products, etc.) providing matrix for heavy growth and differential aeration cells, and organic debris providing nutrients for growth. 11. Debris (mainly organic) on metal above ground, providing growth conditions for organic acid-producing microbes.

the surface (curve *a* in Fig. 1.3). At low flow velocities for which laminar and turbulent flow conditions coexist (parts A and B of Fig. 1.2), corrosion stems from a flow-accelerated process. The protective film that forms on the surface by corrosion is dissolved by the flowing water. It is generally accepted that the phenomenon is a steady-state process. It exhibits linear corrosion kinetics (curve *b* in Fig. 1.3), that is, the dissolved layer at the oxide–water interface is replaced by a new layer of the same thickness.

1.3.2. Temperature Factor

Metals as many other materials may be greatly affected by increasing the service temperature close to or above their stability limit. What is called high-temperature

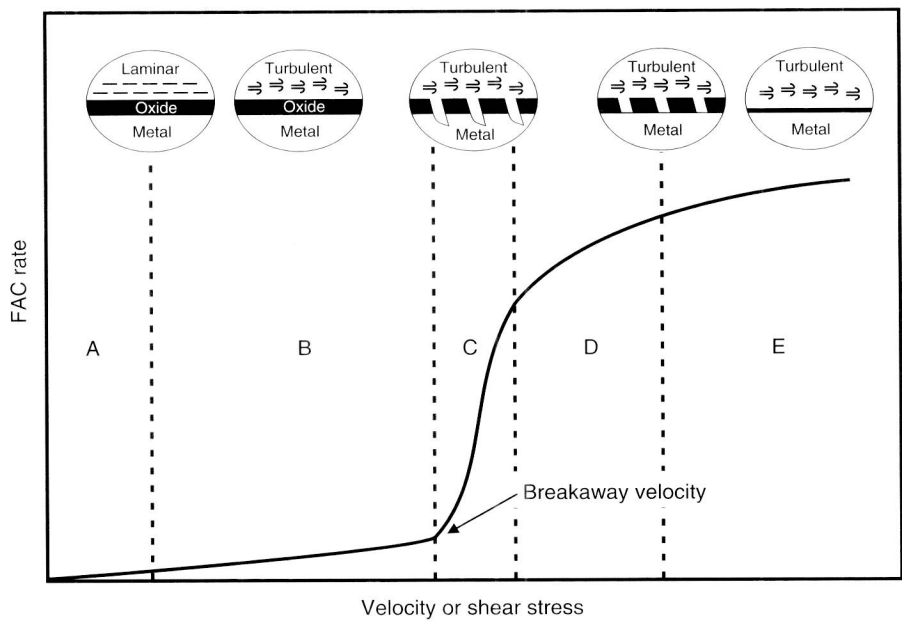


Fig. 1.2. Changes in the corrosion and erosion mechanisms as a function of liquid velocity (5).

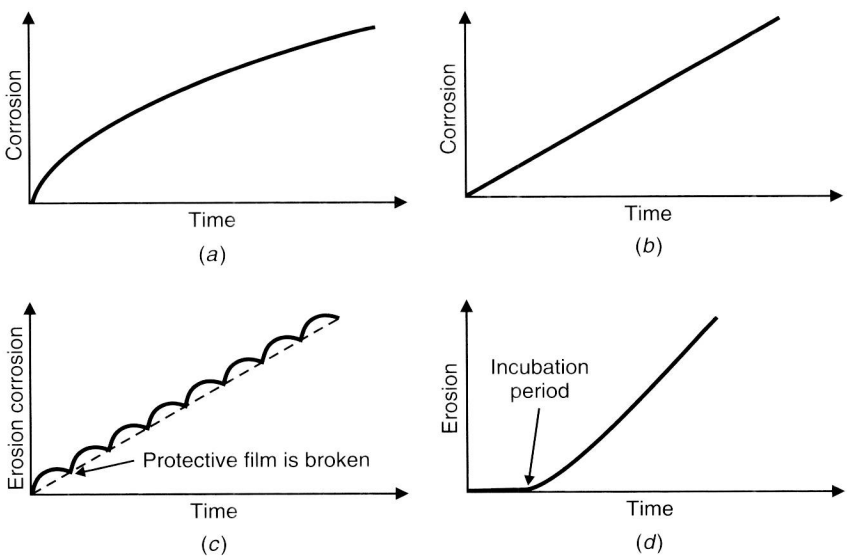


Fig. 1.3. Various time-dependent corrosion–erosion behaviors and processes: (a) corrosion follows a parabolic time law, (b) FAC follows a linear time law, (c) erosion and corrosion follows a quasilinear time law with repeated breaks in the protective surface film, and (d) erosion linear time dependency after an initial incubation period (5).

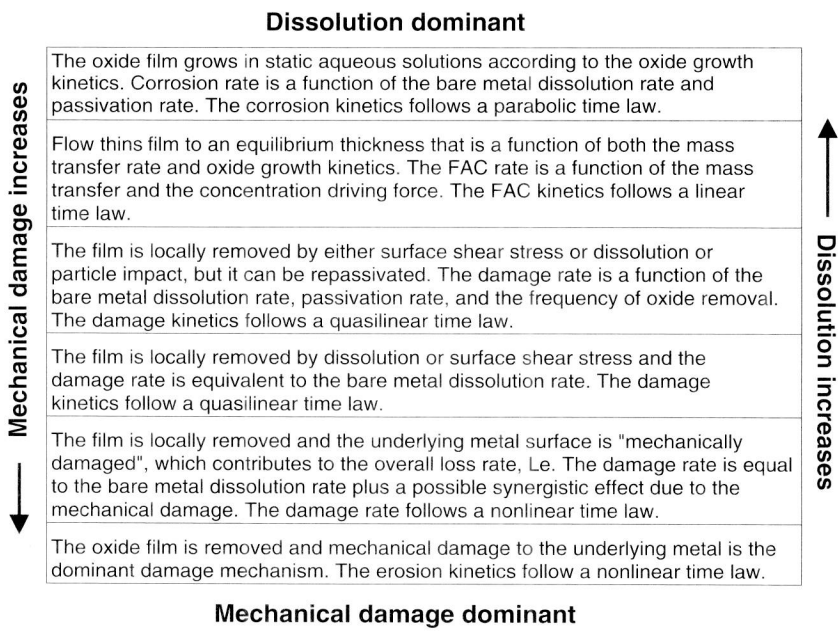
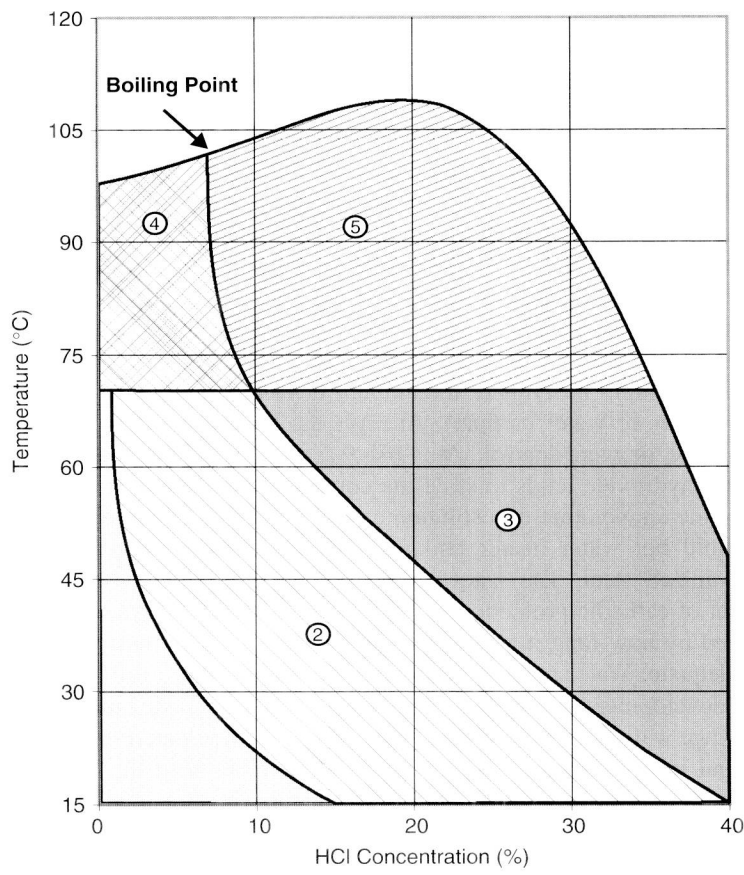


Fig. 1.4. Summary of damage mechanisms experienced with FAC (5).

corrosion is a form of corrosion that does not require the presence of a liquid electrolyte. Sometimes, this type of damage is called “dry corrosion” or “scaling”. This important and complex subject is a field of its own and is not considered here.

In aqueous environments, temperature affects reaction rates, surface temperatures, heat flux and associated surface concentrations, and temperature gradient chemical transfer. In most chemical reactions, an increase in temperature is accompanied by an increase in reaction rate. A rough rule-of-thumb suggests that the reaction rate doubles for each 10° Celsius (°C) rise in temperature. Although there are numerous exceptions to this “rule”, it is important to take into consideration the influence of temperature when analyzing why materials fail, and in designing to prevent corrosion.

In chemical industries that handle very corrosive products, the choice of vessel materials depends on a multitude of factors that include service temperature. Figure 1.5 illustrates the influence of temperature and composition on the corrosion behavior of materials exposed to hydrochloric acid solutions. The iso-corrosion chart shown in Fig. 1.5 is drawn for a corrosion rate of 0.5 mm/year or less. The upper (high-temperature) boundary of each area represents a corrosion rate of 0.5 mm year⁻¹. The materials listed in each area are metals having a corrosion rate of 0.5 mm/year or less under the indicated conditions of temperature and acid concentration. The boiling point curve for atmospheric pressure



Materials in shaded zones have reported corrosion rates of $< 0.5\text{mm year}^{-1}$

Zone1	Zone 2	Zone 3	Zone 4	Zone 5
20Cr 30Ni ^a	Zirconium	62Ni 28Mo ^e	66Ni 32Cu ^{b, f}	62Ni 28Mo ^e
66Ni 32Cu ^b	62Ni 32Cu	Molybdenum	62Ni 28Mo ^e	Platinum
62Ni 28Mo	Molybdenum	Platinum	Platinum	Silver
Copper ^b	Platinum	Silver	Silver	Tantalum
Nickel	Silicon bronze ^b	Tantalum		Zirconium
Platinum	Silicon cast iron ^c	Zirconium		
Silicon bronze ^b	Silver			
Silicon cast iron ^c	Tantalum			
Silver	Zirconium			
Tantalum				
Titanium ^d				
Tungsten				
Zirconium				
Tantalum				
Tungsten				

^a $< 2\%$ at 25°C
^b No air
^c No FeCl_3
^d $< 10\%$ at 25°C
^e No chlorine
^f $< 0.05\%$ concentration

Fig. 1.5. Corrosion rate map of metallic materials in hydrochloric acid (7).