

# CORROSION ENGINEERING HANDBOOK

EDITED BY

Philip A. Schweitzer, P.E.

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*Consultant  
Fallston, Maryland*

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# CORROSION TECHNOLOGY

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3. *Corrosion Resistance of Elastomers*, Philip A. Schweitzer
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7. *Corrosion of Ceramics*, Ronald A. McCauley
8. *Corrosion Mechanisms in Theory and Practice*, edited by P. Marcus and J. Oudar
9. *Corrosion Resistance of Stainless Steels*, C. P. Dillon
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# Preface

Corrosion is both costly and dangerous. Billions of dollars are spent annually for the replacement of corroded structures, machinery, and components, including metal roofing, condenser tubes, pipelines, and many other items. In addition to replacement costs are those associated with preventive maintenance to prevent corrosion, inspections, and the upkeep of cathodically protected structures and pipelines. Indirect costs of corrosion result from shutdown, loss of efficiency, and product contamination or loss.

While the actual replacement cost of an item may not be high, the loss of production resulting from the need to shut down an operation to permit the replacement may amount to hundreds of dollars per hour. When a tank or pipeline develops a leak, product is lost. If the leak goes undetected for a period of time, the value of the lost product could be considerable. In addition, contamination can result from the leaking material, requiring cleanup, and this can be quite expensive. When corrosion takes place corrosion products build up, resulting in reduced flow in pipelines and reduced efficiency of heat transfer in heat exchangers. Both conditions increase operating costs. Corrosion products may also be detrimental to the quality of the product being handled, making it necessary to discard valuable materials.

Premature failure of bridges or structures due to corrosion can also result

in human injury or even loss of life. Failures of operating equipment resulting from corrosion can have the same disastrous results.

When all of these factors are considered it becomes obvious why the potential problem of corrosion should be considered during the early design stages of any project and why it is necessary to constantly monitor the integrity of structures, bridges, machinery, and equipment to prevent premature failures.

In order to cope with the potential problems of corrosion it is necessary to understand

1. Mechanisms of corrosion
2. Corrosion resistant properties of various materials
3. Proper fabrication and installation techniques
4. Methods to prevent or control corrosion
5. Corrosion testing techniques
6. Corrosion monitoring techniques

It is the intention of this book to provide a source of information on these six items for designers, engineers, and maintenance and operating personnel. This knowledge is essential when dealing with the problems of corrosion.

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# 1

## Fundamentals of Metallic Corrosion

**Paul K. Whitcraft**

*Rolled Alloys, Inc.  
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Corrosion is all around us. It shows itself in rust-stained structures that are falling down with age. It shows itself in the beautiful green patina associated with copper sculptures and roofs. Corrosion processes cost billions of dollars each year in maintenance and repair. Corrosion is relentless and patient, and inevitable. But in some ways corrosion is also predictable and useful. The use of controlled corrosion processes is routinely selected as the most cost-effective solution to catastrophic corrosion. Galvanized steel construction materials have served well since their invention in the early 1800s. The standard lead-zinc storage batteries in most of our automobiles are in effect controlled and reversible corrosion cells.

Corrosion is the degradation of a material's properties or mass over time due to environmental effects. It is the natural tendency of a material's compositional elements to return to their most thermodynamically stable state. For most metallic materials this means the formation of oxides or sulfides, or other basic metallic compounds generally considered to be ores. Fortunately, the rate at which most of these processes progress is slow enough to provide useful building materials. Only inert atmospheres and vacuums can be considered free of corrosion for most metallic materials.

These corrosion processes, as with all of the physical world, follow the basic laws of thermodynamics. Corrosion is an electrochemical process. Under controlled conditions it can be measured, repeated, and predicted. Since it is governed by reactions on an atomic level, however, corrosion processes can act on isolated regions, uniform surface areas, or result in subsurface microscopic damage. Complicate these forms of corrosion with further subdivisions, add just basic environmental variables such as pH, temperature, and stress, and the predictability of corrosion begins to suffer rapidly. Figure 1 illustrates the basics of this complexity.

SOILS		A Q U E O U S	L I Q U I D S	G A S E S	O B X E Y A G R E I N N G	DRY    STEAM	
BIOLOGICAL						SPECIES	NO <sub>x</sub>
WET STEAM							SO <sub>x</sub>
SEAWATER	WATERS						CO <sub>x</sub>
BRACKISH							O <sub>2</sub> , AIR
FRESH						VOC's	
HIGH PURITY	CHEMICALS					PROCESS	INDUSTRIAL HEATING
ACIDS					POWER GENERATION		
ALKALIES					AEROSPACE		
HALOGENS					COMBUSTION		
ORGANIC	PROCESS				SPECIES	SULFUR	
INORGANIC						CARBON	
FOOD/MEDICAL						HYDROGEN	
CPI						H <sub>2</sub> S	
PULP/PAPER	PROCESS				SPECIES	NH <sub>3</sub> , NITROGEN	
POLLUTION CONTROL						HALOGENS	
INDUSTRIAL						INDUSTRIAL HEATING	
MOLTEN    SALTS		W F A R T E E R			PROCESS	METAL TREATING	
LIQUID    METALS						CHEMICAL PROCESS	
INORGANIC    CHEMICALS						OTHER	
ORGANIC    CHEMICALS		E E			INERT    GASES		
OTHER		R			VACUUM		

Figure 1    Corrosion environments.

## I. FORMS OF CORROSION

The effect of corrosion on a metallic surface can take many forms. Identifying these forms can assist in understanding the corrosion process and offer insight into its control.

### A. Uniform Corrosion

The simplest form of corrosion is “uniform” or “general” corrosion. Uniform corrosion is an even rate of metal loss over the exposed surface. It is one of the most easily measured and predictable forms of corrosion. Many references exist which report average or typical rates of corrosion for various metals in common media.

Since the corrosion is so uniform, corrosion rates for materials are often expressed in terms of metal thickness loss per unit of time. One common expression is “mils per year” or, sometimes, millimeters per year. Because of its predictability, low rates of corrosion are often tolerated and catastrophic failures are rare if planned inspection and monitoring is implemented. For most chemical process and structures, general corrosion rates of less than 3 mils per year (mpy) are considered acceptable. Rates between 2 and 20 mpy are routinely considered useful engineering materials for the given environment. In severe environments, materials exhibiting high general corrosion rates of between 20 and 50 mpy might be economically justifiable. Materials which exhibit rates of general corrosion beyond this are usually unacceptable. It should be remembered that not only does the metal loss need to be considered, but where that metal is going must also be considered. Contamination of product, even at low concentrations, can be more costly than the replacement of the corroded component.

Uniform corrosion is generally thought of in terms of metal loss due to chemical attack or dissolution of the metallic component into metallic ions. In high-temperature situations, uniform metal loss is more commonly preceded by its combination with another element rather than its oxidation to a metallic ion. Combination with oxygen to form metallic oxides, or scale, results in the loss of the material in its useful engineering form, which ultimately flakes off to return to nature.

### B. Galvanic Corrosion

When two different metallic materials are electrically connected and placed in a conductive solution, an electrical potential will exist. This potential difference will provide a stronger driving force for the dissolution of the less noble (more

**Table 1** Galvanic Series of Metals and Alloys  
in Flowing Seawater

Least noble	Magnesium	
	Beryllium	
	Aluminum	
	Cadmium	
	Low alloy steel	
	Aluminum bronze	←
	Yellow brass	
	Copper	
	Admiralty brass	
	Martensitic stainless steel	—
	90-10 copper nickel	
	Ferritic stainless steel	—
	70-30 copper nickel	
	Nickel-chromium alloy 600	
	Nickel alloy 200	
	Austenitic stainless steel	—
	Titanium	
	Superaustenitic stainless steels	
	Platinum	
Most noble	Graphite	

When  
active

electrically negative) material. It will also reduce the tendency for the more noble material to dissolve.

While the relative differences in potential will change from one environment to another, they remain fundamentally the same since the potential is related to the energy required to oxidize them to metal ions in the given environment. The significance of this becomes more apparent when a variety of materials are listed in order of their electrical potential in a familiar environment such as that shown in Table 1. Notice that the precious metals of gold and platinum are at the high potential (more noble or cathodic) end of the series, while zinc and magnesium are at the low potential (less noble or anodic) end.

The practical implications of this concept constantly surround us. It is this principle that forms the scientific basis for using a material such as zinc to “sacrificially” protect a stainless steel drive shaft on a pleasure boat. It supplies the logic for the use of galvanized steel. Galvanic corrosion is often experienced by owners of older homes where more modern copper water tubing is connected to the older existing carbon steel water lines.

### C. Erosion Corrosion

An increased rate of corrosion attack which is attributable to the movement of a corrodent over a surface is recognized as erosion corrosion. The movement of the corrodent can be associated with mechanical wear. The increase in localized corrosion due to the erosion process is usually related to the removal or damage of the protective surface film. The mechanism is usually identified by localized corrosion which exhibits a pattern that follows the flow of the corrodent.

Fretting corrosion is a specialized form of erosion corrosion where two metal surfaces are in contact and experience very slight relative motion causing damage to one or both surfaces. Again, in the presence of a corrodent, the movement causes mechanical damage of the protective film leading to localized corrosion. The corrosion usually takes the form of pitting-type attack.

A second subset of erosion corrosion is the case of cavitation. A type of corrosion familiar to pump impellers, this form of attack is caused by the formation and collapse of tiny vapor bubbles near a metallic surface in the presence of a corrodent. The protective surface film is again damaged, in this case by the high pressures caused by the collapse of the bubbles.

### D. Pitting Corrosion

Pitting corrosion is in itself a corrosion mechanism, but it is also a form of corrosion often associated with other types of corrosion mechanisms. It is characterized by a highly localized loss of metal. In the extreme case, it appears as a deep, tiny hole in an otherwise unaffected surface. Figure 2 illustrates the nature of pitting and other forms of corrosion.

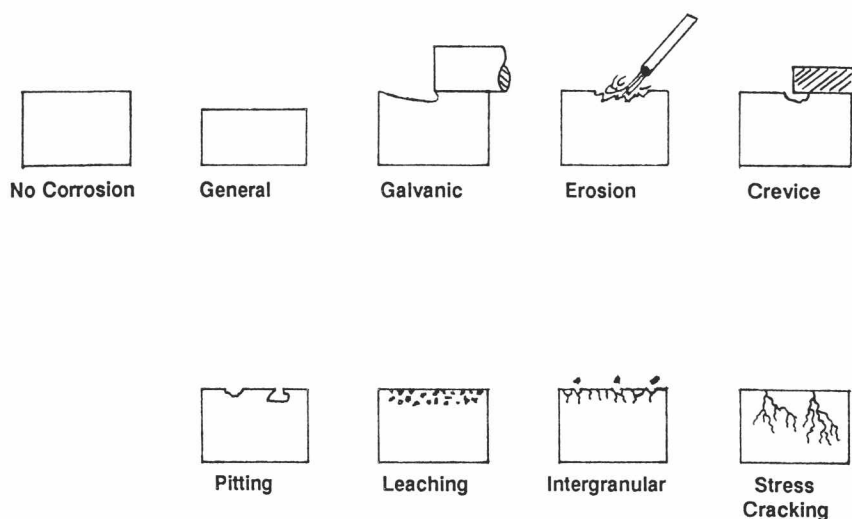
The initiation of a pit is associated with the breakdown of the protective film on the metal surface. In cases where pit depths increase rapidly, the environment is usually such that no repair or repassivation of the protective layer can be accomplished. For other instances where many shallow pits form, the environment is usually one where repassivation of the damaged film can be made but initiation of new sites is occurring on a regular basis.

The localized nature of pitting attack can be associated with component geometry, the mechanics of the corrosion process, or with imperfections in the material itself. The growth of pits, once initiated, is closely related to another corrosion mechanism, i.e., crevice corrosion.

### E. Crevice Corrosion

Crevice corrosion occurs in some environments because the nature of the environment within the crevice will become more aggressive with time. Movement





**Figure 2** Forms of corrosion.

of the corrodent within a crevice is slow or nonexistent. Over time, small changes due to minor localized corrosion may become magnified because they are not constantly being replenished or minimized by the bulk solution.

As a result of a slow initial rate of corrosion the pH of the crevice environment may become more acidic or detrimental ion species may concentrate. As a result of the low flow condition the crevice region may become depleted of oxygen or preclude the replacement of reacted inhibitors.

### F. Selective Leaching

Selective leaching is the process whereby a specific element is removed from an alloy due to an electrochemical interaction with the environment. Dezincification of brass alloys is the most familiar example of this type of corrosion. It occurs most commonly when exposed to soft waters and can be accelerated by high carbon dioxide concentrations and the presence of chloride ions.

The result of this corrosion is that of leaving a porous and usually brittle shadow of the original component. Other alloy systems are susceptible to this form of corrosion. Examples include the selective loss of aluminum in aluminum-copper alloys and the loss of iron in cast iron-carbon steels.

### G. Intergranular Corrosion

As the name suggests, this particular corrosion mechanism attacks those sites where individual grains within a metallic material touch each other. These