A Guide to Safe Material and Chemical Handling

Nicholas P. Cheremisinoff
Anton Davletshin

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A Guide to Safe Material and Chemical Handling

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Anton Davletshin
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Though the world has seen a great deal of change in industry and science over the last two decades, the growth of new technologies, and the rise of new industries, the most important information for engineers has not changed. There is still an intense need for an easy reference for anyone working with materials and chemicals. That is one of the aims of this volume.

There is a second, equally important, reason for this work, namely, to offer a useful contribution to the industrial health and safety literature, for which there is also still an intense, or growing, need. Even with all we have learned, there are still explosions, chemical spills, and other incidents that could have been avoided by following basic standards. Our hope, with this volume, is to prevent such accidents by providing the engineer with the information necessary for a safer, incident-free environment.

This volume is intended as a general reference of useful information for engineers, technologists and students. It is a compilation of general data that have been collected over the years and serves as a quick reference for information that can be consulted for general properties values of materials, chemicals and safety measures when handling industrial chemicals.

The volume provides short discussions that are introductory notes and then provides data in the form of tables. There are five chapters that cover the subjects of corrosion, material properties and selection information, properties of various liquids, gases and fuels, properties of hydrocarbons and fuel properties, guidelines on fire protection, and chemical safety data.

To get maximum use of the volume the user should first refer to the List of Tables at the beginning of the volume to find the topical areas of interest.

The authors wish to thank Scrivener Publishing for the fine production of this volume.

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Anton Davletshin
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Corrosion

1.1 General Information

Corrosion occurs in various forms and is promoted by a variety of causes, all related to process operating conditions to which equipment and support structures are subjected. It is a continuous problem that can lead to contaminated process streams. This subsequently leads to poor product quality and unscheduled equipment shutdowns, the consequence of which is reduced production, high maintenance costs, and equipment replacement costs. Minimizing corrosion is a key consideration for the designer and can be accomplished in two ways: (1) proper material selection for apparatus, and (2) preventive maintenance practices. Both of these approaches must be examined.

1.2 Types of Corrosion

Corrosion is characterized by the controlling chemical-physical reaction that promotes each type. Each of the major types is described below.

**Uniform corrosion** is the deterioration of a metal surface that occurs uniformly across the material. It occurs primarily when the surface is in contact with an aqueous environment, which results in a chemical reaction between the metal and the service environment. Since this form of corrosion results in a relatively uniform degradation of apparatus material, it can be accounted for most readily at the time the equipment is designed, either by proper material selection, special coatings or linings, or increased wall thicknesses.

**Galvanic corrosion** results when two dissimilar metals are in contact, thus forming a path for the transfer of electrons. The contact may be in the form of a direct connection (e.g., a steel union joining two lengths of copper piping), or the dissimilar metals may be immersed in an electrically conducting medium (e.g., an electrolytic solution). One metal acts as an anode and consequently suffers more corrosion than the other metal, which acts as the cathode.
The driving force for this type of corrosion is the electrochemical potential existing between two metals. This potential difference represents an approximate indication of the rate at which corrosion will take place; that is, corrosion rates will be faster in service environments where electrochemical potential differences between dissimilar metals are high.

**Therogalvanic corrosion** is promoted by an electrical potential caused by temperature gradients and can occur on the same material. The region of the metal higher in temperature acts as an anode and thus undergoes a high rate of corrosion. The cooler region of the metal serves as the cathode; hence, large temperature gradients on process equipment surfaces exposed to service environments will undergo rapid deterioration.

**Erosion corrosion** occurs in an environment where there is flow of the corrosive medium over the apparatus surface. This type of corrosion greatly accelerates when the flowing medium contains solid particles. The corrosion rate increases with velocity. Erosion corrosion generally manifests as a localized problem due to mal-distributions of flow in the apparatus. Corroded regions are often clean, due to the abrasive action of moving particulates, and occur in patterns or waves in the direction of flow.

**Concentration cell corrosion** occurs in an environment in which an electrochemical cell is affected by a difference in concentrations in the aqueous medium. The most common form is crevice corrosion. If an oxygen concentration gradient exists, usually at gaskets and lap joints, crevice corrosion often occurs. Larger concentration gradients cause increased corrosion due to the larger electrical potentials present.

**Cavitation corrosion** occurs when a surface is exposed to pressure changes and high-velocity flows. Under pressure conditions, bubbles form on the surface. Implosion of the bubbles causes large enough pressure changes to flake off microscopic portion of the metal from the surface. The resulting surface roughness promotes further bubble formation, thus increasing the rate of corrosion.

**Fretting corrosion** occurs where there is friction, generally caused by vibrations, between two metal surfaces. The debris formed by fretting corrosion accelerates the initial damage done by contact welding. Vibrations cause contact welds to break with subsequent surface deterioration. Debris formed acts to accelerate this form of corrosion by serving as an abrasive. Fretting corrosion is especially prevalent in areas where motion between surfaces is not foreseen.
If allowances for vibration are not made during design, fretting corrosion may be a strong candidate.

**Pitting corrosion** is a form of localized corrosion in which large pits are formed in the surface of a metal usually in contact with an aqueous solution. The pits can penetrate the metal completely. The overall appearance of the surface involved does not change considerably; hence, the actual damage is not readily apparent. Once a pit forms, it acts as a local anode. Conditions such as debris and concentration gradients in the pit further accelerate degradation. There are several possible mechanisms for the onset of pitting corrosion. Slight damage or imperfections in the metal surface, such as a scratch or local molecular dislocation, may provide the environment necessary for the beginning of a pit.

**Exfoliation corrosion** is especially prevalent in aluminum alloys. The grain structure of the metal determines whether exfoliation corrosion will occur. In this form of corrosion, degradation propagates below the surface of the metal. Corrosion products in layers below the metal surface cause flaking of the metal.

**Selective leaching** occurs when a particular constituent of an alloy is removed. Selective leaching occurs in aqueous environments, particularly acidic solutions. Graphitization and dezincification are two common forms of selective leaching. Dezincification is the selective removal of zinc from alloys containing zinc, particularly brass. The mechanism of dezincification of brass involves dissolving the brass with subsequent plating back of copper while zinc remains in solution. Graphitization is the selective leaching of iron or steel from gray cast irons.

**Intergranular corrosion** occurs selectively along the grain boundaries of a metal. This is an electrochemical corrosion in which potential differences between grain boundaries and the grain become the driving force. Even with relatively pure metals of only one phase, sufficient impurities can exist along grain boundaries to allow for intergranular corrosion. Intergranular corrosion is generally not visible until the metal is in advanced stages of deterioration. These advanced stages appear as rough surfaces with loose debris, or dislodged grains. Welding can cause local crystal graphic changes which favor intergranular corrosion. It is especially prevalent near welds.

**Stress corrosion cracking** is an especially dangerous form of corrosion. It occurs when a metal under a constant stress (external, residual or internal) is exposed to a particular corrosive environment. The effects of a particular corrosive environment vary for
different metals. For example, Inconel-600 exhibits stress corrosion cracking in high-purity water with only a few parts per million of contaminants at about 300°C. The stress necessary for this type of corrosion to occur is generally of the residual or internal type. Most external stresses are not sufficient to induce stress corrosion cracking. Extensive cold working and the presence of a rivet are common stress providers. Corrosion products also can build up to provide stress sufficient to cause stress corrosion cracking. The damage done by stress corrosion cracking is not obvious until the metal fails. This aspect of stress corrosion cracking makes it especially dangerous.

Corrosion fatigue is caused by the joint action of cyclically applied stresses (fatigue) and a corrosive medium, generally aqueous. Metals will fail due to cyclic application of stress. The presence of an aqueous corrosive environment causes such failure more rapidly. The frequency of the applied stress affects the rate of degradation in corrosion fatigue. Ordinary fatigue is generally not frequency dependent. Low-frequency applied stresses cause more rapid corrosion rates. Intuitively, low frequencies cause extended contact time between cracks and the corrosive medium. Generally, the cracks formed are transgranular.

Hydrogen blistering is caused by bubbling of a metal surface due to absorbed hydrogen. Monatomic hydrogen can diffuse through metals, whereas diatomic hydrogen cannot. Ionic hydrogen generated by chemical processes, such as electrolysis or corrosion, can form monatomic hydrogen at a metal surface. This hydrogen can diffuse through the metal and combine on the far side of the metal forming diatomic hydrogen. The diffusion hydrogen also can combine in voids in the metal. Pressure within the void increases until the void actually grows visibly apparent as a blister and ultimately ruptures, leading to mechanical failure.

Hydrogen embrittlement is due to the reaction of diffused hydrogen with a metal. Different metals undergo specific reactions, but the result is the same. Reaction with hydrogen produces a metal that is lower in strength and more brittle.

Decarburization results from hydrogen absorption from gas streams at elevated temperatures. In addition to hydrogen blistering, hydrogen can remove carbon from alloys. The particular mechanism depends to a large extent on the properties of other gases present. Removal of carbon causes the metal to lose strength and fail.
Grooving is a type of corrosion particular to environmental conditions where metals are exposed to acid-condensed phases. For example, high concentrations of carbonates in the feed to a boiler can produce steam in the condenser to form acidic condensates. This type of corrosion manifests as grooves along the surface following the general flow of the condensate.

Biological corrosion involves all corrosion mechanisms in which some living organism is involved. Any organism, from bacteria and fungi to mussels, which can attach themselves to a metal surface, can cause corrosion. Biological processes may cause corrosion by producing corrosive agents, such as acids. Concentration gradients also can be caused by localized colonies of organisms. Some organisms remove protective films from metals, either directly or indirectly, leaving the actual metal surface vulnerable to corrosion. By selective removal of products of corrosion, biological organisms also can cause accelerated corrosion reactions. Some bacteria also directly remove certain metals (e.g., iron, copper or aluminum). Microorganisms also may promote galvanic corrosion by removing hydrogen from the surface of a metal, causing potential irregularities between different parts of metal.

Stray current corrosion is an electrolytic degradation of a metal caused by unintentional electrical currents. Bad grounds are the most prevalent causes. The corrosion is actually a typical electrolysis reaction.

Gaseous corrosion is a general form of corrosion whereby a metal is exposed to a gas, usually at elevated temperatures. Direct oxidation of a metal in air is the most common cause. Cast iron growth is a specific form of gaseous corrosion in which corrosion products accumulate onto the metal surface, particularly at grain boundaries, to the extent that they cause visible thickening of the metal. The entire metal thickness may succumb to this before loss of strength causes failure.

Tuberculation occurs in aqueous solutions. Mounds form over metal surfaces providing for concentration differences, favorable environments for biological growth, and an increase in acidity leading to hydrogen formation.

Deposit attack occurs when there is non-uniform deposition of a film on a metal surface. The most common form appears as unequal scale deposits in an aqueous environment. Unequal film provides for concentration cells, which degrade the metal by galvanic means.
Impingement is corrosion caused by aerated water streams, constricting metal surfaces. It is similar to erosion corrosion in which air bubbles take the place of particles. The pits formed by impingement attack have a characteristic tear drop shape.

Liquid metal corrosion occurs when a metal is in contact with a liquid metal. The main type of corrosion with highly pure liquid metals is simple solution. The solubility of the solid metal in the liquid metal controls the rate of damage. If a temperature gradient exists, a much more damaging form of corrosion takes place. Metal dissolves from the higher temperature zone and crystallizes in the colder zone. Transfer of solids to liquid metal is greatly accelerated by thermal gradients. If two dissimilar metals are in contact with the same liquid metal, the more soluble metal exhibits serious corrosion. The more soluble metal dissolves along with alloys from the less soluble metal. Metal in solutions may move by gross movement of the liquid metal or by diffusion. Depending on the system, small amounts of impurities may cause corrosive chemical reactions.

High-temperature corrosion is induced by accelerated reaction rates inherent in any temperature reaction. Layers of different types of corrosion on one metal surface is one phenomenon that occurs frequently in heavy oil-firing boilers.

Causes of corrosion are the subject of extensive investigation by industry. Almost any type of corrosion can manifest itself under widely differing operating conditions. Also, different types of corrosion can occur simultaneously. It is not uncommon to see crack growth from stress corrosion to be accelerated by crevice corrosion, for example.

1.3 Materials Evaluation and Selection

Materials evaluation and selection are fundamental considerations. When done properly, and in a systematic manner, considerable time and cost can be saved in design work, and design errors can be avoided. The design or specification of any equipment must be unified and result in a safe functional system. Materials used for each apparatus should form a well coordinated and integrated entity, which should not only meet the requirements of the apparatus’ functional utility, but also those of safety and product purity.

Materials evaluation should be based only on actual data obtained at conditions as close as possible to intended operating environments.
Prediction of a material's performance is most accurate when standard corrosion testing is done in the actual service environment. Often it is extremely difficult in laboratory testing to expose a material to all of the impurities that the apparatus actually will contact. In addition, not all operating characteristics are readily simulated in laboratory testing. Nevertheless, there are standard laboratory practices that enable engineering estimates of the corrosion resistance of materials to be evaluated.

Environmental composition is one of the most critical factors to consider. It is necessary to simulate as closely as possible all constituents of the service environment in their proper concentrations. Sufficient amounts of corrosive media, as well as contact time, must be provided for test samples to obtain information representative of material properties degradation. If an insufficient volume of corrosive media is exposed to the construction material, corrosion will subside prematurely.

The American Society for Testing Materials (ASTM) recommends 250 ml of solution for every square inch of area of test metal. Exposure time is also critical. Often it is desirable to extrapolate results from short time tests to long service periods. Typically, corrosion is more intense in its early stages before protective coatings of corrosion products build up. Results obtained from short-term tests tend to overestimate corrosion rates, which often results in an overly conservative design.

Immersion into the corrosive medium is important. Corrosion can proceed at different rates, depending on whether the metal is completely immersed in the corrosive medium, partially immersed or alternately immersed and withdrawn. Immersion should be reproduced as closely as possible since there are no general guidelines on how this affects corrosion rates.

Oxygen concentration is an especially important parameter to metals exposed to aqueous environments. Temperature and temperature gradients should also be reproduced as closely as possible. Concentration gradients and mixing conditions should be reproduced as closely as possible, and careful attention should be given to any movement of the corrosive medium.

The condition of the test metal is important. Clean metal samples with uniform finishes are preferred. The accelerating effects of surface defects lead to deceptive results in samples. The ratio of the area of a defect to the total surface area of the metal is much higher in a sample than in any metal in service. This is an indication
of the inaccuracy of tests made on metals with improper finishes. The sample metal should have the same type of heat treatment as the metal to be used in service. Different heat treatments have different effects on corrosion. Heat treatment may improve or reduce the corrosion resistance of a metal in an unpredictable manner. For the purpose of selectivity, a metal stress corrosion test may be performed. General trends of the performance of a material can be obtained from such tests; however, it is difficult to reproduce the stress that actually will occur during service.

For galvanic corrosion tests, it is important to maintain the same ratio of anode to cathode in the test sample as in the service environment. Evaluation of the extent of corrosion is no trivial matter. The first step in evaluating degradation is the cleaning of the metal. Any cleaning process involves removal of some of the substrate. In cases in which corrosion products are strongly bound to the metal surface, removal causes inaccurate assessment of degradation due to surface loss from the cleaning process. Unfortunately, corrosion assessments involving weight gain measurements are of little value. It is rare for all of the corrosion products to adhere to a metal. Corrosion products that flake off cause large errors in weight gain assessment schemes.

The most common method of assessing corrosion extent involves determining the weight loss after careful cleaning. Weight loss is generally considered a linear loss by conversion. Sometimes direct measurement of the sample thickness is made. Typical destructive testing methods are used to evaluate loss of mechanical strength. Aside from inherent loss of strength due to loss of cross section, changes brought about by corrosion may cause loss of mechanical strength. Standard tests for tensile strength, fatigue, and impact resistance should be run on test materials.

There are several schemes for nondestructive evaluation. Changes in electrical resistance can be used to follow corrosion. Radiographic techniques involving X-rays and gamma rays have been applied. Transmitted radiation and back-scattered radiation have been used.

Radiation transmission methods, in which thickness is determined by (measured as) the shadow cast from a radioactive source, are limited to pieces of equipment small enough to be illuminated by small radioactive sources. There are several schemes for highlighting cracks. If the metal is appropriate, magnetic particles can be used to accentuate cracks. Magnetic particles will congregate along
cracks too small to be seen normally. An alternate method involves a dye. A dye can be used that will soak into cracks preferentially.

Because of the multitude of engineering materials and the profusion of material-oriented literature, it is not possible to describe specific engineering practices in detail in a single chapter. However, we can outline general criteria for parallel evaluation of various materials that can assist in proper selection. The following is a list of general guidelines that can assist in material selection:

1. Select materials based on their functional suitability to the service environment. Materials selected must be capable of maintaining their function safely and for the expected life of the equipment and at reasonable cost.

2. When designing apparatus with several materials, consider all materials as an integrated entity. More highly resistant materials should be selected for the critical components and for cases in which relatively high fabrication costs are anticipated. Often, a compromise must be made between mechanically advantageous properties and corrosion resistance.

3. Thorough assessment of the service environment and a review of options for corrosion control must be made. In severe, humid environments it is sometimes more economical to use a relatively cheap structural material and apply additional protection, rather than use costly corrosion-resistant ones. In relatively dry environments, many materials can be used without special protection, even when pollutants are present.

4. The use of fully corrosion-resistant materials is not always the best choice. One must optimize the relation between capital investment and cost of subsequent maintenance over the entire estimated life of the equipment.

5. Consideration should be given to special treatments that can improve corrosion resistance (e.g., special welding methods, blast peening, stress relieving, metallizing, sealing of welds). Also, consideration should be given to fabrication methods that minimize corrosion.

6. Alloys or tempers chosen should be free of susceptibility to corrosion and should meet strength and fabrication requirements. Often a weaker alloy must be
selected over one that cannot be reliably heat-treated and whose resistance to a particular corrosion is low.

7. If, after fabrication, heat treatment is not possible, materials and fabrication methods must have optimum corrosion resistance in their as-fabricated form. Materials that are susceptible to stress corrosion cracking should not be employed in environments conducive to failure. Stress relieving alone does not always provide a reliable solution.

8. Materials with short life expectancies should not be combined with those of long life in irreparable assemblies.

9. For apparatuses for which heat transfer is important, materials prone to scaling or fouling should not be used.

10. For service environments in which erosion is anticipated, the wall thickness of the apparatus should be increased. This thickness allowance should secure that various types of corrosion or erosion do not reduce the apparatus wall thickness below that required for mechanical stability of the operation. Where thickness allowance cannot be provided, a proportionally more resistant material should be selected.

11. Nonmetallic materials should have the following desirable characteristics: low moisture absorption, resistance to microorganisms, stability through temperature range, resistance to flame and arc, freedom from out-gassing, resistance to weathering, and compatibility with other materials.

12. Fragile or brittle materials whose design does not provide any special protection should not be employed under corrosion-prone conditions.

Thorough knowledge of both engineering requirements and corrosion control technology is required in the proper design of equipment. Only after a systematic comparison of the various properties, characteristics, and fabrication methods of different materials can a logical selection be made for a particular design. Design limitations or restrictions for materials might include:

- size and thickness
- velocity
CORROSION

- temperature
- composition of constituents
- bimetallic attachment
- geometric form
- static and cyclic loading
- surface configuration and texture
- special protection methods and techniques
- maintainability
- compatibility with adjacent materials

1.4 Corrosion Data

Table 1.1 provides data on zinc and steel panels exposed to varying environmental conditions over 2 year exposure periods. Table 1.2 provides corrosion data for different materials exposed to various industrial chemicals.

Table 1.1 Corrosion rates of zinc and steel panels

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<th>No.</th>
<th>Location</th>
<th>Normal Wells, NWT, Canada</th>
<th>Phoenix, AZ</th>
<th>Saskatoon, Sask., Canada</th>
<th>Vancouver Island, BC, Canada</th>
<th>Detroit, Mi</th>
<th>Fort Amidor, Panama C.Z.</th>
<th>Morenci, MI</th>
<th>Ottawa, Out., Canada</th>
<th>Potter County, PA</th>
<th>Waterbury, CT</th>
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*Environment codes: R = Rustic, M = Marine, U = Urban, I = Industrial.
Table 1.1 (cont.) Corrosion rates of zinc and steel panels

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<thead>
<tr>
<th>No.</th>
<th>Location</th>
<th>Steel</th>
<th>Zinc</th>
<th>Environment</th>
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<td>0.030</td>
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<tr>
<td>14</td>
<td>Halifax, NS, Canada</td>
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<td>Durham, NH</td>
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<tr>
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