Practical Self-Study Guide to
CORROSION
CONTROL

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Click Table of Contents

Click Subject Index

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PREFACE

This self-study guidebook is designed for the person who faces corrosion problems related to metals but who has no formal training in the subject. Rather than learning by making mistakes that may even escalate the problem, the reader will be able to identify the type of corrosion and be guided to the best ways to solve, or at least cope with, the situation.

Most successful corrosion engineers today have developed their skill under the guidance of a mentor who acquired knowledge through years of experience. This book cannot replace experience but it will provide the reader with a better understanding of basic principles of corrosion and corrosion protection so that both old and new problems can be dealt with.

This is a non-mathematical approach, assuming no knowledge of basic science. The bare minimum of chemistry and metallurgy needed to understand corrosion is provided here. To make sure the reader has grasped the main points, each chapter is followed by multiple-choice questions - over 175 in all. Terms that might be unclear are defined at the end of each chapter and are also listed in the index for quick reference. There are more than 450 terms that might be encountered in a wide range of industries.

The author holds B.S. and M.S. degrees in chemistry, a Ph.D. in metallurgy, plus electronics training in the U.S. Army Signal Corps school. He has had ten years industrial experience in metallurgy and chemistry and thirty years experience making corrosion understandable to students, both undergraduates and professionals. He is a registered professional engineer, consulting in corrosion and metal failures.

Corrosion can be successfully controlled.

Samuel A. Bradford

TABLE OF CONTENTS

Chapter

1

WHY CONTROL CORROSION?

Corrosion of metals is a natural process. For the most part, corrosion is quiet, gradual, and unspectacular, unlike other forces of nature such as earthquakes and tornadoes. These natural, dramatic processes we can do very little about except to watch for them, but corrosion can be prevented or at least controlled so that the metals can perform their required tasks.

The Cost of Corrosion

Reliability and Cost

Estimates of the cost of corrosion have been made by several nations (Great Britain, United States, Australia, and others) and all have reached similar conclusions. The direct costs–replacement and costs of corrosion protection–come to roughly 4% of a developed nation's gross national product (GNP) value, which for the United States means about $270 billion annually lost to corrosion. To put that in more comprehendible numbers, the cost is over $1000 per person each year.

Indirect costs, such as costs of shutdowns, loss or contamination of products, loss of efficiency, and the costs of over-design, are much more difficult to estimate but they are believed to be at least as great as the direct costs.

Example: Speaking of downtime, Moroccan sugar beet plants probably hold the world record. They get about three months effective production per year; the rest of the year is spent on maintenance. Maximum sugar extraction is made under slightly acidic conditions (pH 5-5.5), but poor control allows acidity to increase until the steel equipment corrodes at over one millimetre per month.

Most corrosion costs are unpreventable. Metals must sometimes be used in corrosive environments such as acids, so the choice comes down to paying extra for very expensive materials, for inhibitor chemicals, for electrical protection, etc., or simply replacing the metal as it corrodes. But the best or most economical choice is often not made. It is estimated that of that $1000 per year that corrosion costs you, approximately one-fourth to one-third is entirely unnecessary. Knowledge of corrosion's causes, proper design, good materials selection, and all the other ways of controlling corrosion could make a considerable difference.

Safety

Thirty percent of all aircraft accidents are caused by corrosion combined with tensile stresses. Some of the accidents are minor but others result in loss of human life. Airlines inspect their planes constantly for corrosion but still have as many corrosion-related problems as they had 25 years ago.

In Seoul, South Korea, October 1994, a bridge carrying rush hour traffic collapsed into the San River, killing 32 people. Rusted extension hinges broke under the heavy load. The inspectors who had certified the bridge as safe evidently thought that rust couldn't hurt anybody.

Example: Pulp and paper mills must fight corrosion constantly because the solutions they use are extremely corrosive. Still, the industry averages about one major explosion a year in North America.

Corrosion can even be an indirect cause of disaster. In Guadalajara, Mexico in April 1991, sewer explosions killed over 200 people and injured 1500. A corroding pipeline had allowed gasoline to leak into the sewer system.

Failure to inspect thoroughly for corrosion and to combat it when it is detected can lead to tragic consequences.

Energy and Material Savings

Heat exchangers lose efficiency if accumulated rust reduces heat transfer. Clogging of pipes lowers pumping capacity. Corrosion of automobile piston rings reduces engine power. All are common examples of energy wasted by corrosion that perhaps could have been prevented.

On a larger scale, British Gas reports a leakage rate of 1% of throughput, principally in the cast iron mains of their distribution systems. Actually they are bragging, since many municipal gas companies in North America lose considerably more than 1%–a deplorable waste of our natural resources. Russian pipelines supply about one-third of western Europe's natural gas but need about $3 billion for the first stage of repairs. No estimate has been given for the total cost.

In July 1995 a spillway gate buckled on the Folsom Dam in northern California, spilling about 400,000 acre-feet (half a billion cubic metres) of water into the American River. Inspectors had recommended in 1988, 1991, and 1994 that the gates be painted and the bolts checked, but maintenance items such as this were low on the priority list. To put it in perspective, a safety engineer for the Bureau of Reclamation explained, "There is rust on every dam in the world." So evidently in his view, corrosion is not a sign of danger.

Good corrosion control obviously could save a lot of metal. It is estimated that 40% of our steel production is used just to replace metal lost to corrosion. And while steel is largely recycled, our high-grade ore deposits are gradually reduced while the need for metals increases. Recycling saves energy but energy costs are still high. For aluminum, its replacement requires approximately six times the energy consumption needed for the same weight of steel.

While most steel today is made from scrap, and aluminum and copper are recycled to a lesser extent, most of the rarer engineering metals are not recycled to any great degree. These metals are becoming more important as technology improves, but they also are becoming scarcer.

Environmental Protection

To replace a ton of steel lost to corrosion, production from iron ore releases about three-eighths of a ton of CO_2 into the atmosphere. By remelting scrap, "only" about one-eighth of a ton of CO_2 is released. Carbon dioxide (CO_2) is believed by many experts to be largely responsible for global warming. While the steel must be replaced if we are to maintain our present standard of living, at least 25% of that steel didn't need to corrode in the first place if careful corrosion control had been implemented.

Oil pipelines have the potential for severe environmental damage. A burst line a few years ago in the Russian Arctic spilled about three times as much oil as the Exxon Valdez did in 1989. The arctic environment will take centuries to repair itself. Closer to home, a completely unnecessary pipeline rupture in southern Missouri spilled 800,000 gallons (3 million litres) of crude oil in 1989.

Leaking underground storage tanks contribute to groundwater contamination. In a Canadian government study, an estimated 40,000 fuel tanks are leaking or have leaked in Canada. Multiply that by about ten to get an idea of the extent of the problem in the United States.

What You Need to Know

Background

This handbook assumes that you, like most people, are a bit vague about science and engineering. You may have had a chemistry course once upon a time but about all you remember are a few funny incidents in the lab. Math may not have been your strong point, but you can handle a simple calculator. And metallurgy? No way.

A lot of fine corrosion engineers have learned from years of experience with practically no knowledge of any of these subjects, but it has taken many years. This book is a shortcut that will enable you to understand a corrosion problem that perhaps no one has ever faced before and let you come up with a practical way to solve it. And with this one book you will have a better background than most workers in the field today, believe it or not.

The chemistry and physics you will need are given in the next chapter, the metallurgy in Chapter 3. These chapters introduce you to the basic concepts but also to the basic terms that you will run into. On any new job, one of the first things you must do is to learn new terminology. Once you learn the names of everything, it all begins to make sense. Every chapter has a *Definition of New Terms* section that makes this a lot easier.

Corrosion

Metals corrode for different reasons, each with its own mechanism. Chapter 4 describes the common way, uniform attack, while Chapters 5 and 6 explain the causes of the much more serious localized corrosion. Corrosion combined with mechanical stress, Chapter 7, creates sudden catastrophic failures with even different mechanisms. Three chapters (8-10) describe corrosion problems in various common environments, while Chapters 11 and 12 go into methods of testing and analyzing corrosion failures.

While this treatment won't make you a specialist in any one area, it will give you all the fundamentals you need to understand any problem.

Corrosion Control

Knowing what the corrosion problem is, you then can plan to control it. Careful materials selection and a good design can avoid the most serious corrosion problems, while other methods are available to reduce or stop all corrosion where the situation demands it.

A final chapter on the economics of corrosion can assist you in selling corrosion control to a skeptical management, always most concerned with "the bottom line." After all, corrosion control is not applied for appearance's sake, nor is it to make everything scientifically neat. It is a practical necessity.

Mathematics

Mark Twain once wrote a novel with no weather in it. He explained that he didn't do weather very well, so he simply added an appendix that quoted some great examples from authors who could describe weather dramatically, and he invited the reader to throw these into the story wherever they seemed appropriate.

This handbook has almost no math in it beyond multiplication and division, with two minor exceptions. One is logarithms, which virtually no modern engineer understands anyway, since calculators and computers became popular. Logarithms are simply a different way of expressing numbers, just as 1,000,000 and 10^6 are different ways of expressing a million. The logarithm or log of a million is 6, that exponent of 10. If you punch 6 on your calculator and then INV log the answer is 1,000,000. Similarly, 0.00l and 10^{-3} are the same number and log 0.001 = -3.

But what's the point? Logarithms allow very small numbers and very large numbers to be shown precisely on the same graph without using miles of graph paper. Furthermore, chemical processes such as corrosion often have rates that plot as curves on ordinary graph paper (Figure 1.1a) but plot as straight lines on log-log paper (Figure 1.1b). Straight lines are much easier to extrapolate beyond the known data points if you have to try to see into the future.

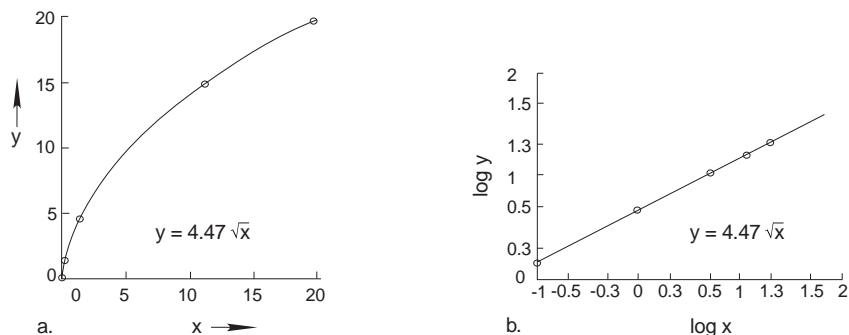Figure 1.1 Comparison of linear and logarithmic graphs of the same data.
(a) Linear plot; (b) log/log plot.

Also, reactions often change rates with temperature in a semilogarithmic manner (Figure 1.2). The resulting straight line of a semilog graph also gives information about the mechanisms involved.
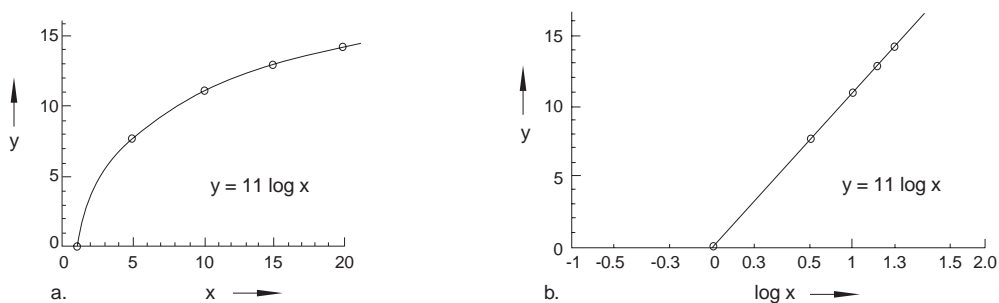

Figure 1.2 Comparison of linear and semilogarithmic graphs of the same data.
(a) Linear plot; (b) semilogarithmic plot.

One other thing: on graphs it is often necessary to find the slope of a line or a curve at some point. For a straight line, just pick off any two points on the line and calculate the slope: slope = y/x, illustrated in Figure 1.3a. For slopes along a curve, where the slope keeps changing, pick off a point you are interested in, draw a straight line tangent to the curve at that point (as in Figure 1.3c) and find the slope of the tangent.
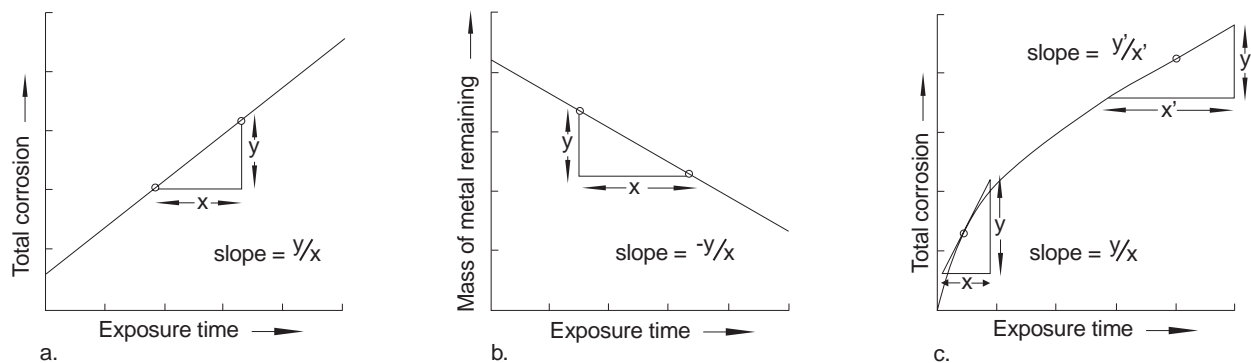

Figure 1.3 Determining slopes of graphs. (a) Straight line with constant positive slope; (b) straight line with negative slope; (c) curve with changing slope.

One other point. This handbook uses SI (Système International) units along with the common English units. Spellings (metre, litre, and the like) are correct for the SI system which strives to be truly international. Sometimes this makes things clearer. We use meters to measure things such as flow rates, while a metre is strictly a measure of length. Virtually the entire world, except the United States, uses the SI system, and even corrosion engineers in the U.S. often use it. You say SI units don't mean anything to you? Got any idea how much an acre-foot of water is?

SI units and conversions from English units are given in detail in Appendix A.

If a group of experienced corrosion engineers was asked to give the one most important piece of advice to a newcomer to the field, they would cry with one voice, "Keep good records!" What material was used for that tank? What is its corrosion rate? When was it lasted inspected? What repairs have been made on it? And so on. The point is: corrosion never gives up. Long after you are gone, corrosion will still be working, and someone else will have taken up the fight.

After that, experienced corrosion people might add, "Always consider the worst possible thing that could happen in each situation, and plan accordingly." That can save you a lot of sleepless nights.

Definition of New Terms

Downtime: time in which equipment is stopped for repair or maintenance.
Heat exchanger: device to conserve and transfer heat energy from one fluid to another.
Localized corrosion: corrosion concentrated primarily at one or only a few places on a metal surface.
log: abbreviation for logarithm.
Logarithm: the exponent to which 10 must be raised to equal a given number. For example $\log 1000 = \log(10^3) = 3$.
Log/log graph: two-dimensional graph where both vertical and horizontal axes are given on a logarithmic scale.
Semilog graph: a graph with one axis having a linear scale, as a ruler has, while the other axis has a logarithmic scale.

SI units: the international system of units using kilogram, metre, and second as the basic measurements of mass, length, and time.
Slope: the steepness of a line or curve at some point.
Tangent: a straight line that touches a curve at only one point.
Uniform corrosion: corrosion that occurs fairly evenly all over a metal's surface.

Questions

1. The annual direct cost of corrosion for each person is around:
   a. $10
   b. $100
   c. $1,000
   d. $10,000
   e. more than $10,000

2. Good corrosion control could save annually:
   a. about $250 to $400 per person.
   b. all of the direct costs of corrosion.
   c. all of the indirect costs of corrosion.
   d. nothing more than is saved at present.
   e. some of the direct and indirect costs.

3. For North American steel production, the percent of the production that is needed to replace corroded and scrapped steel is:
   a. negligible.
   b. 10%
   c. 20%
   d. 30%
   e. 40%

4. Underground gasoline storage tanks:
   a. can and do corrode.
   b. contaminate groundwater when they leak.
   c. create a serious safety hazard if they leak.
   d. don't corrode because gasoline doesn't attack steel.
   e. invariably corrode.

5. Most people working in corrosion control today have:
   a. a college degree in chemistry or chemical engineering.
   b. a college degree in corrosion engineering.
   c. a college degree in metallurgical engineering.
   d. learned mostly from their work experience.
   e. little knowledge of corrosion or its control.

6. The single most important task for a corrosion engineer is to:
   a. anticipate the wishes of his or her supervisor.
   b. keep good records.
   c. keep production going.
   d. know the condition of the equipment at all times.
   e. not use cheap material.

Chapter

2

BASIC CHEMISTRY AND PHYSICS

Some readers will find the information in this chapter so elementary that they will be tempted to skip over it. That's fine–except for the last section on electrochemical cells. Read it and reread it if necessary. Corrosion in aqueous (water) environments is electrochemical; thus, electrochemical concepts and terminology appear frequently in discussions of corrosion problems and ways of solving these problems.

Corrosion is the result of chemical reaction between a metal and its environment. The metal atoms break their bonds with one another, leave the metal surface, and go into the environment, which is usually some sort of liquid. The metal does not undergo simply a physical change, such as in wear where particles of metal rub off, or as in melting where bonding between atoms is greatly reduced although the atoms themselves remain unchanged. The chemical reaction of corrosion changes the very structure of the metal atoms.

Physical changes, although not themselves a chemical reaction, can greatly magnify a corrosion problem. For example, corrosive wear, where the two processes combine, is much more serious than corrosion and wear occurring separately. Physical changes can even start a corrosion process, such as with condensation of water vapor on a metal surface that can rust steel overnight. Above the dew point the metal might not show any visible corrosion for months.

With corrosion, the chemical reaction changes the electronic structure of each metal atom involved.

Atoms and Molecules

The Atom

An atom is the smallest particle of an element that will still have any of the properties of that element. Each atom consists of a nucleus containing positively charged protons along with neutral neutrons, surrounded by negatively charged electrons orbiting the nucleus. The number of electrons equals the number of protons to give a zero net charge to the atom. About 90 different elements occur in nature, varying from the smallest, hydrogen, with one proton and one electron, on up to neptunium with 93 protons, 144 neutrons, and 93 electrons.

In Table 2.1 the atomic numbers of elements are given. These are the numbers of protons in the nucleus of the atoms, and also the number of electrons in the neutral atom. The atomic masses of the elements are based (approximately) on the mass of a proton or a neutron equaling one atomic mass unit (a.m.u.). The mass of the electrons in the atom is so small as to be practically negligible. You may notice that the atomic masses in many cases are not whole numbers; this is the result of naturally occurring elements having isotopes–atoms with more or fewer neutrons than other atoms of the same element.

In a chemical reaction such as corrosion, only the electrons in the outermost orbits are affected. These electrons are called the *valence* electrons. The inner orbits are filled up with electrons to make a very stable, low-energy configuration that is not going to change. The nucleus, too, is extremely stable and remains unaffected by chemical reaction.

Table 2.1 Physical Properties of Selected Elements.

Elements	Symbol	Atomic Number	Atomic Mass, amu	Density g/cm^3, 20°C	Melting Point,°C	Usual Valences
Aluminum	Al	13	26.98	2.70	660	+3
Argon	Ar	18	39.95	1.66×10^{-3}	-189	0
Barium	Ba	56	137.33	3.51	725	+2
Beryllium	Be	4	9.01	1.85	1278	+2
Boron	B	5	10.81	2.37	2079	+3
Bromine	Br	35	79.90	3.12	-7	-1
Cadmium	Cd	48	112.41	8.64	321	+2
Calcium	Ca	20	40.08	1.55	839	+2
Carbon[1]	C	6	12.01	2.25	3550	+4
Cerium	Ce	58	140.12	6.77	798	+3
Chlorine	Cl	17	35.45	2.95×10^{-3}	-101	-1
Chromium	Cr	24	52.00	7.20	1857	+3
Cobalt	Co	27	58.93	8.90	1495	+2
Columbium	Cb	(see Niobium)				
Copper	Cu	29	63.55	8.92	1083	+1,+2
Fluorine	F	9	19.00	1.58×10^{-3}	-220	-1
Germanium	Ge	32	72.61	5.32	937	+4
Gold	Au	79	196.97	19.31	1064	+3
Helium	He	2	4.00	1.66×10^{-4}	-272	0
Hydrogen	H	1	1.008	8.38×10^{-5}	-259	+1
Iodine	I	53	126.90	4.93	114	-1
Iron	Fe	26	55.85	7.86	1535	+2,+3
Lead	Pb	82	207.21	11.34	327	+2
Lithium	Li	3	6.94	0.53	180	+1
Magnesium	Mg	12	24.31	1.74	649	+2
Manganese	Mn	25	54.94	7.44	1244	+2
Mercury	Hg	80	200.59	13.59	-39	+2
Molybdenum	Mo	42	95.94	10.22	2617	+4,+6
Nickel	Ni	28	58.69	8.90	1453	+2
Niobium	Nb	41	92.91	8.57	2468	+5
Nitrogen	N	7	14.01	1.16×10^{-3}	-210	-3,+5
Oxygen	O	8	16.00	1.33×10^{-3}	-218	-2
Phosphorus[2]	P	15	30.97	1.82	44	+5
Platinum	Pt	78	195.08	21.45	1772	+2
Potassium	K	19	39.10	0.86	63	+1
Silicon	Si	14	28.09	2.33	1410	+4
Silver	Ag	47	107.87	10.50	962	+1
Sodium	Na	11	22.99	0.97	98	+1
Strontium	Sr	38	87.62	2.54	769	+2

Elements	Symbol	Atomic Number	Atomic Mass, amu	Density g/cm^3, 20°C	Melting Point,°C	Usual Valences
Sulfur[3]	S	16	32.07	2.07	113	-2,+6
Tin	Sn	50	118.71	7.28	232	+4
Titanium	Ti	22	47.88	4.54	1668	+4
Tungsten	W	74	183.85	19.35	3410	+4,+6
Uranium	U	92	238.03	19.05	1132	+4
Vanadium	V	23	50.94	5.96	1890	+4
Zinc	Zn	30	65.39	7.14	420	+2
Zirconium	Zr	40	91.22	6.49	1852	+4

[1]Graphite, sublimes rather than melts

[2]White phosphorus

[3]Yellow sulfur

Ions

A chemical reaction lowers the energies of the reactants by transferring their valence electrons, from atoms that have only a few to atoms which need only a few to fill up their outer orbit. This transfer creates ions (electrically charged atoms). Ions which have lost electrons then have more protons in the nucleus than electrons surrounding the nucleus and thus become positively charged, counted as one positive charge for each electron lost. Ions that receive one or more extra electrons end up with one or more negative charges. The charges, positive or negative, are called valences because they have occurred in the valence (outermost) electron orbits of the atoms. Valences of common elements are given in Table 2.1. For example, aluminum corrodes when its surface atoms leave their three valence electrons and become Al^{3+} ions which go into solution or form a compound.

A few elements, the inert gases, have a valence of 0 because they have only filled orbits and therefore are quite unreactive, neither gaining nor losing valence electrons. Several metals have more than one valence. In a mild chemical reaction only the very highest energy electrons will be released. Under more severe conditions, electrons with slightly lower energy may also be pulled off from partially filled inner orbits. Iron, for example, usually corrodes by giving up its two valence electrons, for a valence of +2, but under highly oxidizing conditions one additional electron can also be removed, producing a valence of +3.

Nonmetals have valence orbits nearly filled with electrons so their energies can be lowered by completely filling their valence level. For example, chlorine needs only one more electron to completely fill its valence orbit. If chlorine gas reacts with aluminum metal, three chlorine atoms can react with each aluminum atom (which tends to give up three electrons) and a white aluminum chloride corrosion product forms on the aluminum surface. The energies of the chlorine and the aluminum can be lowered to a more stable level by reacting with each other, so the reaction is spontaneous.

In addition to single atoms that gain or lose electrons to form negative or positive ions, respectively, certain groups of atoms also bond together, with an excess or deficiency of electrons. Common examples of these *radicals* are given in Table 2.2.

Table 2.2 Common Ionic Radicals.

Name	Symbol	Name	Symbol
acetate	$C_2H_3O_2^-$	nitrate	NO_3^-
bicarbonate	HCO_3^-	nitrite	NO_2^-
carbonate	CO_3^{2-}	perchlorate	ClO_4^-
chlorate	ClO_3^-	phosphate	PO_4^{3-}
chromate	CrO_4^{2-}	silicate	SiO_x^{n-}
cyanide	CN^-	sulfate	SO_4^{2-}
hydroxide	OH^-	sulfite	SO_3^{2-}
		ammonium	NH_4^+

Molecules

A molecule is a group of atoms bonded strongly together to give properties different from its component atoms. A water molecule, H_2O, has entirely different properties than its components, hydrogen and oxygen. An oxygen gas molecule, O_2, has properties entirely different from atomic oxygen, O.

If the atoms in a molecule are not all the same, and if they are combined in definite proportions, the molecule is a *compound*. Consequently, H_2O is a compound but O_2 is not.

Solid salts and corrosion products such as metal oxides are usually crystalline with a three-dimensional repeating pattern of ions or atoms, with no separate molecules. Nevertheless, crystalline compounds are considered to be made up of molecules because the different atoms exist in a fixed ratio. Thus, people refer to table salt, NaCl, "molecules" even though no separate NaCl units exist.

Organic compounds are those containing carbon and hydrogen atoms, such as methane gas, CH_4, or ethyl alcohol, C_2H_5OH. The carbon atoms are usually bonded to each other in a chain, ring, or network with side groups of hydrogen and other atoms. Most plastics are huge organic molecules with carbon chains being several hundred to many thousands of carbon atoms in length.

Bonding of Atoms

Covalent bonds are primarily responsible for holding molecules together. Each bond is a shared pair of valence electrons with each of the two bonded atoms contributing an electron. Water thus has oxygen bonded to two hydrogens as shown in Figure 2.1. Covalent bonds do not form randomly; they place themselves at definite angles around each atom. Occasionally in a water molecule, a hydrogen nucleus (proton) will become separated from its electrons and move around as a hydrogen ion H^+, leaving an OH^- ion behind. Charged ions create an electric current as they move but because so few ions are normally present in pure water, water is a very poor conductor of electricity under the voltages produced in chemical reactions–on the order of one volt in corrosion processes.

Covalent bonds hold the atoms together within organic molecules, sometimes with double covalent bonds (two shared pairs of electrons), and occasionally even with triple covalent bonds. An example of a triple bond is found in the acetylene gas molecule, often written $H-C\equiv C-H$, where the lines indicate covalent bonds (electron pairs).
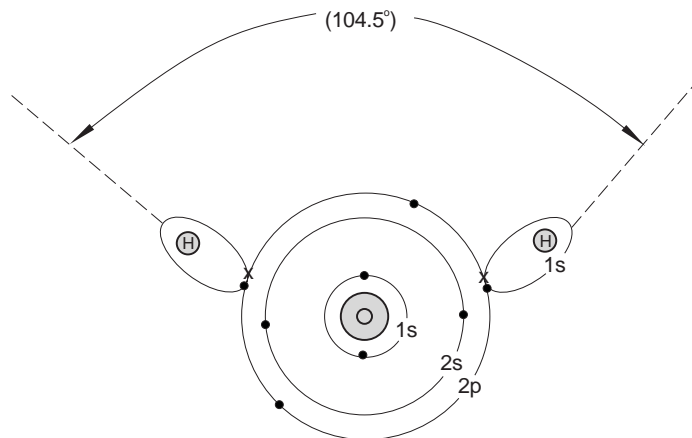
Figure 2.1 Schematic diagram of water molecule, H$_2$O, showing covalent bonds between oxygen and hydrogen atoms. Black dots symbolize oxygen's electrons, x indicates hydrogen's single electron.

Ionic bonds usually bond inorganic compounds such as salts and corrosion products. The bond strength lies in the attraction between positive and negative ions. Radical ions such as sulfate, SO_4^{2-}, are bonded primarily with covalent bonds within the radical and with ionic bonds to surrounding positive ions. Ionic bonding is nondirectional; positive ions cluster around negative ions and vice versa, using whatever pattern provides the most intimate contact along with the required charge balance.

Question: What kind of bonds are present in soda ash used for water softening? Its proper chemical name is sodium carbonate, Na_2CO_3.

Answer: The sodium is going to bond ionically as Na^+ ions (see Table 2.1) to the carbonate radical. Within the carbonate the bonding is covalent: This bonding leaves two oxygens with an extra electron each, giving the carbonate radical ion a valence of -2 (Table 2.2).

$$O = C \diagdown_{O^-}^{O^-}$$

Metallic bonding, the third type of strong atomic bonding, occurs in metals. The metal atoms pool all of their valence electrons to form an electron cloud surrounding the atoms. The attractive forces between the positive nuclei and the negative cloud pull the atoms as close together as possible. As with ionic bonds, metallic bonds are nondirectional, bringing the atoms together into a close-packed, or nearly close-packed, crystal.

Chemical Reactions

Corrosion processes are chemical reactions where atoms or molecules rearrange themselves in a different bonding pattern to produce new molecules. The chemical equation for the reaction ignores the physical situation unless the process occurs only under certain specific conditions, such as at a special temperature or with a catalyst. An example of an important unstated physical situation would be mud splashed on a car so that the steel rusted under the painted finish. The dirt didn't take part in the chemical reaction directly, and so is not shown in the chemical equation, but that dirt held moisture against the steel and was indirectly responsible for the rusting.

Even more importantly, the equation for a chemical reaction does not show how fast the process occurs. The automobile body may take three months to show any sign of rust but chemical reactions in other situations occur in an instant, as explosions. Regardless, we need a clear way to describe what is happening in corrosion so that some way can be found to reduce or stop it.

Chemical Equations

Chemical symbols given in Table 2.1 are used to indicate reactants and products. By convention, reactants are shown on the left side of the equation and an arrow points to the products on the right. Occasionally the arrow is replaced by an equals sign, indicating an equilibrium has occurred, with the reaction running both ways; that is, products are forming reactants again as fast as reactants form products. Corrosion reactions, however, seldom reach an equilibrium–the metal just keeps on forming more corrosion products.

For example: $Fe + \frac{1}{2}O_2 + H_2O \rightarrow Fe(OH)_2\downarrow$

says that one iron atom reacts with half a molecule of oxygen gas and one molecule of water to form one molecule of iron II hydroxide, also called ferrous hydroxide. The iron II designation is to show that the iron has a valence of +2, rather than iron's other common valence, +3, ferric ion. The downward arrow by the $Fe(OH)_2$ indicates that this solid precipitates, settling out of solution rather than floating around as ions. An arrow pointing upward beside a product shows a gas escaping. Both of these arrows indicate that the reaction goes to completion, with no chance that the products could turn around and form reactants again.

Now you might argue that there is no such thing as half a molecule of oxygen–an atom of oxygen is not bonded the same way a molecule is. Correct! The $\frac{1}{2}$ was put in merely to "balance" the reaction as if it were an algebraic equation. The right-hand side of the reaction shows one iron, two oxygens, and two hydrogens, so the left-hand side must show the same. It is perfectly correct to double the equation to eliminate the $\frac{1}{2}$:

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2 \downarrow$$
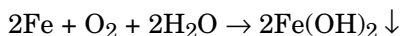
But that's not really quite right either. If a piece of iron rusts, billions of its surface atoms are reacting simultaneously, not just two of them. Thus we need the concept of the "mole."

The Mole

The mole, as now defined, is Avogadro's number (6.02×10^{23}) of particles. This strange number was chosen to make calculations easier! Iron corroding to form iron ions:

$$Fe \rightarrow Fe^{2+} + 2e^-$$
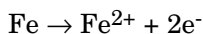
can be read to mean one iron atom ionizes; that is, 55.85 atomic mass units (a.m.u.) react. But the equation can also mean that 55.85 grams of iron–one mole–will ionize, and when it ionizes, it releases two moles of valence electrons ($2 \times 6.02 \times 10^{23}$ of them). Avogadro's number is simply the number of a.m.u.'s in a gram.

Question: For the reaction $Fe + \frac{1}{2}O_2 + H_2O \rightarrow Fe(OH)_2\downarrow$, what mass of ferrous hydroxide is produced by one mole of iron?

Answer: One mole of iron produces one mole of $Fe(OH)_2$

molecular weight of $Fe(OH)_2$ = atomic wts. of 1Fe + 2O + 2H = $55.85 + 2 \times 15.999 + 2 \times 1.008 = 89.864$ a.m.u. (atomic weights from Table 2.1). Therefore, one mole of $Fe(OH)_2$ has a mass of 89.864 g.

Question: Suppose only 5 g of iron corrodes by this reaction. How much $Fe(OH)_2$ forms?

Answer: 5 g is 5/55.85 of a mole of iron, or 8.95×10^{-2} mole.

8.95×10^{-2} mole of iron forms 8.95×10^{-2} mole of $Fe(OH)_2$

$8.95 \times 10^{-2} \times 89.864$ g/mole $Fe(OH)_2$ = 8.05 g $Fe(OH)_2$

Question: How much oxygen reacts when 5 g of iron corrodes?

Answer: 8.95×10^{-2} mole of iron reacts with half that many moles of O_2:

$\frac{1}{2} \times 8.95 \times 10^{-2} = 4.48 \times 10^{-2}$ mole O_2

4.48×10^{-2} mole $O_2 = 4.48 \times 10^{-2}(2 \times 15.999$ g/mol$) = 1.432$ g O_2

Question: What volume of O_2 gas would that be?

Answer: At standard temperature and pressure (273K, 1 atm), one mole of any gas has a volume of 22.4 L–worth remembering. Therefore, 22.4 L/mol $\times 4.48 \times 10^{-2}$ mol $O_2 = 1.003$ L O_2. Or, in practical terms, it takes over a gallon of air to completely corrode a piece of iron about the size of the eraser on the end of your pencil. (Air is approximately 21 vol.% O_2.)

Chemical reactions that are read as moles reacting and moles of product indicate amounts that are much closer to reality–amounts that can be weighed, amounts that can be visualized. Incidentally, the abbreviation of mole is mol (some improvement, huh?).

Molarity

The concentration of a solution in moles per litre is commonly called molarity, with the symbol M. Therefore, if hydrochloric acid (HCl) is 2.5 M, it contains 2.5 moles of HCl in a litre of solution. 2.5 moles of HCl is 2.5 x 36.5 g/mol, or 91.3 g of HCl.

Redox Reactions

Reduction-oxidation (redox) reactions are those involving electron exchange between reactants. An atom or ion loses one or more electrons to gain in positive valence–a process termed *oxidation*, while another atom or ion receives these electrons and is reduced in valence–termed *reduction*. For example, aluminum metal is corroded rapidly by hydrochloric acid, producing hydrogen gas:

$$Al + 3HCl \rightarrow AlCl_3 + \frac{3}{2}H_2\uparrow$$
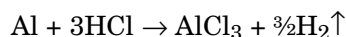
Originally, the aluminum metal atom has its valence electrons while hydrogen has given its valence electron to chlorine, producing H^+ and Cl^- in the solution. In the reaction, aluminum donates its three valence electrons to three hydrogen ions so that it becomes an ion Al^{3+}. Pairs of H atoms unite with a covalent bond to form the hydrogen molecule, H_2, a gas that bubbles off. Left behind in the water are the Al^{3+} and Cl^- ions which would form the salt $AlCl_3$ if dried.

This chemical reaction occurs spontaneously. Aluminum requires so much electrical power in its production that the metal has been called "solid energy." This energy is released by the corrosion

process. In general, corrosion reactions are nearly all spontaneous, taking high-energy metals and converting them to lower-energy products. In corrosion, the metal is "oxidized" while some other species (hydrogen, in the reaction above) is "reduced."

The ordinary chemical reaction written above gives only reactants and products. It not only fails to mention the very important water in the acid but also omits the essential electron transfer, which can be shown by dividing the reaction into an oxidation and a reduction step:

oxidation: $Al \rightarrow Al^{3+} + 3e^-$
reduction: $\underline{3H^+ + 3e^- \rightarrow \frac{3}{2} H_2 \uparrow}$
sum: $Al + 3H^+ \rightarrow Al^{3+} + \frac{3}{2} H_2 \uparrow$
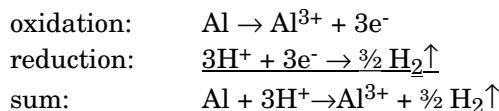
This sum leaves out the Cl^- and the H_2O which were neither oxidized nor reduced, but which could be added to both left and right sides of the equation. The separate oxidation and reduction steps are commonly called *half-cell reactions* and will be discussed in detail in the section on electrochemical cells.

Acids, Bases, and Solutions

Acids

Common acids produce hydrogen ions in solution and neutralize bases to form water. Acids have a sharp, biting taste–vinegar, for example. Vinegar is a dilute solution of acetic acid, $HC_2H_3O_2$, which will ionize in water to hydrogen ions and acetate ions, $C_2H_3O_2^-$. If vinegar is mixed with a base such as baking soda, $NaHCO_3$ (sodium bicarbonate), the products are water, CO_2 gas, and a solution of Na^+ and $C_2H_3O_2^-$ ions.

Table 2.3 Common Industrial Acids.

Name	Formula	Comments
Sulfuric	H_2SO_4	Most important industrial chemical
Hydrochloric	HCl	"Concentrated" acid is about 37%
Nitric	HNO_3	Strong oxidizer; may passivate
Phosphoric	H_3PO_4	Used in fertilizer, rust-proofing
Acetic	$HC_2H_3O_2$	Pure acid called "glacial"
Carbonic	H_2CO_3	Solution of CO_2 gas in water

pH

pH is the scale used to measure acidity or basicity of a solution, rather than writing out the hydrogen ion concentration. Mathematically, it is approximately the negative of the logarithm of the hydrogen ion concentration:

$$pH = -\log_{10}[H^+]$$

where $[H^+]$ is the hydrogen ion concentration expressed as moles/litre (the molarity). On this scale a solution is neutral, neither acidic nor basic, at pH 7 at room temperature. Acid solutions have a pH less than seven, from about 0 to 6.9, while basic solutions will have a pH from 7.1 to around 14,

although higher pH's are occasionally found. On this logarithmic scale, a pH of 5 has ten times as much H^+ as a pH of 6. A pH of 4 has ten times the acidity of pH 5, and so on. Likewise, a pH 10 solution is 100X as basic as pH 8, or put another way, a pH 10 solution has only $\frac{1}{100}$th as many hydrogen ions as pH 8.

Pure water at room temperature ionizes slightly to equal amounts of H^+ and OH^- ions, specifically a concentration of $10^{-7}M$ each. The exponent $^{-7}$ means the pH is 7.

Example: Carbonated soft drinks contain flavoring plus CO_2 gas dissolved in water, which makes carbonic acid. The pH is around 3.3, so how acidic is this, compared with a pH 4 solution?

Answer: pH 3.3 means the H^+ concentration is $10^{-3.3}$, or, working that out on a calculator, $5 \times 10^{-4}M$. This then is five times as much H^+ as a $10^{-4}M$ solution of pH 4. (It is also only half as acidic as a pH 3 solution: $5 \times 10^{-4}/10^{-3} = 0.5$.)

Bases

Bases are substances that release hydroxide (OH^-) ions in solution or neutralize acids to form water. Water-soluble bases are sometimes called *alkalies* and, if very strong, they may be termed *caustics*. An example would be a lye, also known as "caustic soda," NaOH. Bases commonly have a "soapy" feel because they react with the oil on your skin to make a soap.

Table 2.4 Common Industrial Bases.

Name	Formula	Comments
sodium hydroxide	NaOH	White pellets, usu. dissolved
potassium hydroxide	KOH	Pellets or flakes, dissolved
calcium hydroxide	$Ca(OH)_2$	"Slaked lime," cheap
aluminum hydroxide	$Al(OH)_3$	Used in water purification
ammonium hydroxide	NH_4OH	NH_3 gas dissolved in water
sodium carbonate	Na_2CO_3	"Soda ash," in water softening

Salts

Salts are not just common table salt, NaCl, but all the compounds that can be produced along with water when an acid and a base react. For example, common salt is produced when hydrochloric acid is neutralized by sodium hydroxide:

$$HCl + NaOH \rightarrow H_2O + NaCl$$
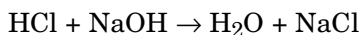
Evaporating the water from the reaction vessel will leave a cake of salt, sodium chloride.

In a chemical formula the valences of the ions must be matched–the negative ion can't have more extra electrons than have been donated by the positive ion:

$$2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$$
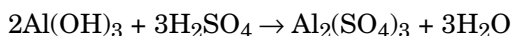
Here, two Al^{3+} ions have combined with three SO_4^{2-} radicals (six electrons exchanged) to make aluminum sulfate.

Solubility

Salts have a solubility limit when dissolved in water. Even sea salt, which certainly has high solubility in water, has a limit. At room temperature you can dissolve up to 35.9 g of pure NaCl (the solute) in 100 g of water (the solvent); add more salt and it will just settle out at the bottom of the container, regardless of how vigorously you stir the mixture. Solubilities of some salts are so low as to be almost unmeasurable–limestone ($CaCO_3$) in water is an obvious example.

Temperature affects solubility. Increasing temperature generally increases the solubility limit of salts but decreases the solubility limit of gases in water. This characteristic can be extremely important for corrosion in water containing dissolved oxygen where the O_2 is a crucial reactant. Corrosion of steel in arctic seawater, consequently, is much greater than in equatorial seawater, in spite of the fact that increasing temperature normally increases chemical reaction rates.

Corrosion products that are insoluble in a corrosive solution may help slow down the corrosion reaction by precipitating out on the metal surface. Even a porous rust reduces corrosion by forcing reactants to diffuse through all the fine, twisted pores in the rust, and diffusion rates are often much slower than chemical reaction rates. Consequently, an old rusted pipe usually corrodes more slowly than a new, clean pipe. "Passivating" metals, such as stainless steels, may form an almost perfect, protective layer of corrosion product on the metal surface. On the other hand, if the corrosion products are soluble in the solution, they offer no resistance to further corrosive attack on the metal.

Electrochemical Cells

Corrosion in water and aqueous solutions is an electrochemical "redox" reaction. If you keep in mind the electrochemical cell and the cell reactions involved, you may be able to stop or slow the corrosion.

Electrical Conduction

Electrical current is commonly carried in two ways: by electron movement and by ion movement. In metallic conductors, some of the metal's valence electrons are free to move between the atoms; these moving charged particles are the electrical current. In solutions, electrically charged ions can move to produce a current. In an electric field (a voltage gradient) the positive ions are attracted to the negative side of the field while negatively charged ions move toward the positive side.

The amount of current carried by a conductor is directly proportional to the voltage gradient but inversely proportional to the resistance of the conductor itself. Ohm's Law states this relationship:

$$I = V/R$$

where I is the current in amperes, V is the voltage gradient (volts), and R is the resistance of the conduction path (ohms).

The current is directly proportional to the corrosion rate. <u>More current = more corrosion</u>.

From Ohm's Law, then, it becomes obvious that to reduce corrosion you could:

- reduce the voltage gradient. For example, do not electrically connect two metals that have very different corrosion potentials (voltages) if they could possibly form an electrochemical cell.

- increase the resistance of the conduction path. A coat of paint on metal increases the electrical resistance of the path between the corrosive environment and the metal, and even though the resistance is not infinite, the paint provides some protection by reducing the current.

The electrical resistance of a conductor depends on the material of the conductor and the conduction path, thus:

$$R = \rho l/A$$

where ρ is the electrical resistivity of the conduction path, l is the path length, and A is its cross-sectional area. The S.I. units of resistivity are ohm·m, since l is in metres, A is in m^2, and R is in ohms. Reference tables often show resistivity in μohm·cm (10^{-8}ohm·m). The resistivities of metals generally lie in the range of 2-70 $\mu\Omega$·cm, or 2-70 x 10^{-8} ohm·m. For corrosive environments, soil may vary from about 2 x 10^{-6} to 2 x 10^{-3} ohm·m while seawater is about 0.2 to 1 ohm·m–many orders of magnitude greater than metals, although they certainly are not electrical insulators, which have resistivities of 10^6 to 10^{16} ohm·m.

Question: How would you expect corrosion to be affected in seawater compared with freshwater, compared with distilled water?
Answer: The conduction path for electrochemical corrosion passes through the water as well as through the metal. Therefore, corrosion is greatest in seawater (resistivity lowest), least in distilled water (highest ρ). More ions in the water mean more current can flow.

Cell Components

Electrochemical cells are responsible for corrosion of metals in aqueous solutions. All cells must have four components to function: an anode, a cathode, an electrolyte in contact with both anode and cathode, and an external (metallic) connection between the electrodes. A schematic illustration shows the components:
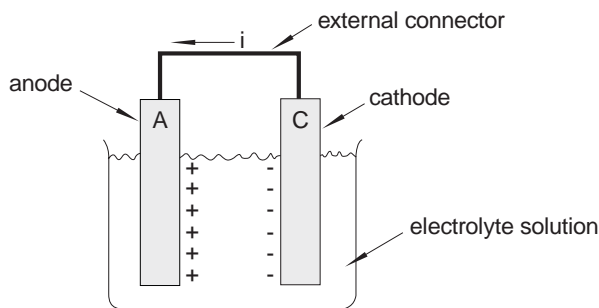
Figure 2.2 Schematic sketch of the components of an electrochemical cell.

The functions that these four components must perform are:
- anode–metal corrodes (reacts)
- cathode–environment reacts on its surface
- electrolyte–current is carried from anode to cathode by movement of ions through the solution: positive ions toward the cathode, negative ions toward the anode.
- external connection–The cell does not function until the electrical circuit is completed. In the external connection, current is carried by movement of electrons from anode to cathode. Since conventional current is considered to be the flow of positive electricity, the positive current is thought of as flowing from cathode to anode.

In actuality, the cell does not have to have a separate anode and cathode. One piece of metal can have both anodic and cathodic areas, as well as serving as the external connector.

Question: In the sketch above of an electrochemical cell, is the circuit of negative charge carriers proceeding in a clockwise or counterclockwise direction? Explain.

Answer: Clockwise. Negative ions move through the electrolyte from cathode toward the anode. At the anode, negatively charged electrons move through the external circuit toward the cathode.

Anode Processes

The anode is the metal that is corroding. This is usually easy to spot when examining a corrosion failure; the damaged region is an anodic area. At the anode, the metal atoms are being oxidized; that is, the atoms are losing their valence electrons and going into solution as ions. The half-cell reaction is:

$$M \rightarrow M^+ + e^-$$

The valence electrons are left behind on the metal. These extra electrons, if left on the anode, would very quickly choke off the oxidation reaction and cause it to reverse. However, in corrosion, the electrons migrate to the cathode where they are used in a reduction reaction.

In the reaction above, M stands for whatever metal is corroding. If it is aluminum, the anode reaction is $Al \rightarrow Al^{3+} + 3e^-$; if iron or steel corrodes, $Fe \rightarrow Fe^{2+} + 2e^-$. The Fe^{2+} compound produced usually oxidizes further to various Fe^{3+} oxide rusts but the damage has been done when Fe^{2+} ions leave the metal. The positive valences produced at an anode are those given in Table 2.1.

Cathode Processes

The reduction reaction at the cathode uses the electrons produced at the anode. The cathode itself does not react; the environment reacts on the cathode surface, picking up electrons and reducing its reactive component. Of course, you will see all sorts of corrosive environments, everything from tomato juice to blood, but the reduction reactions in all these environments are usually one of three common ones, with a fourth category for "everything else":

a. By far the most common cathode half-cell reaction is the one found in nature, in water and soils, where the reactive component is oxygen dissolved in water:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
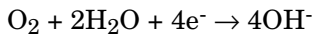
with O_2 being reduced from 0 valence to -2.

b. Acids are also well-known corrosives. In this case, hydrogen ions (+1 valence) are reduced to hydrogen gas (0 valence):

$$2H^+ + 2e^- \rightarrow H_2\uparrow.$$
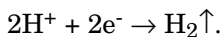
This reaction is unimportant at neutral or basic pH's because so few H^+ ions are available. At pHs above 4 your best bet is O_2 reduction.

c. Occasionally you run across environments that contain both oxygen and hydrogen ions, which are a potent combination able to consume electrons by the reaction:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O.$$
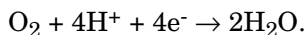
For this reason we usually try to prevent aeration of acids, or we contain so-called oxidizing acids (such as HNO_3 which can decompose, forming O) in metals especially designed for them.

d. In chemical processing, a wide range of reactive oxidizers may be present, available to accept electrons from corroding tanks and piping as well as assisting in the desired processing. A couple of the most common oxidizers are ferric ions which are readily reduced to ferrous ions:

$$Fe^{+3} + e^- \rightarrow Fe^{+2}$$
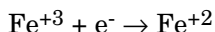
and cupric ions that often are reduced to copper metal: $Cu^{2+} + 2e^- \rightarrow Cu^o\downarrow$.

This copper may plate out on the corroding anode.

Question: If tomato juice corrodes its tin can, what is the most likely cathode reaction?
Answer: If corrosion occurs while the can is vacuum sealed (unlikely), the reduction of H^+ is responsible, since tomato juice is acidic. If corrosion occurs after the can is opened, oxygen from the air has dissolved in the acidic juice so that the cathode reaction is $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$.

Question: Which is the positive electrode–the anode or the cathode?
Answer: That depends on your point of view. If you consider the cell to be a battery, which it is, the source of electrons to the external circuit is the anode terminal, so it should be marked negative. If you are considering the electrochemical process within the cell, the anode is the source of the positive ions and thus is obviously the positive electrode.

Cell Reactions

The overall cell reaction is simply a combination of anode and cathode half-cell reactions. If aluminum is corroding in acid:

$Al \rightarrow Al^{3+} + 3e^-$	anode half-cell reaction
$3(H^+ + e^- \rightarrow \frac{1}{2}H_2\uparrow)$	cathode half-cell reaction
$Al + 3H^+ \rightarrow Al^{3+} + \frac{3}{2}H_2\uparrow$	cell reaction
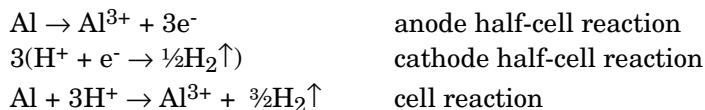
To make a balanced reaction, the number of electrons used in the cathode reaction must equal the number of electrons released by the anode. In the example above, the cathode reaction must be multiplied by 3 to balance.

Exercise: Write balanced cell reactions for the following corrosion situations:
(a) An aluminum canoe corrodes in seawater.
(b) An ancient bronze sword has corroded under blood stains. Bronze is largely copper.
(c) A silver pickle fork has corroded.

Answers:

(a) $4Al \rightarrow 4Al^{3+} + 12\ e^-$

$\underline{3(O_2 + 2H_2O + 4e^- \rightarrow 4OH^-)}$

$4Al + 3O_2 + 6H_2O \rightarrow 4Al^{3+} + 12OH^-$
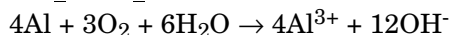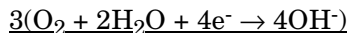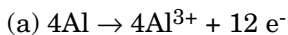
(The salt in seawater improves its ionic conductivity but doesn't take part in the reaction.)

(b) $2Cu + O_2 + 2H_2O \rightarrow 2Cu^{2+} + 4OH^-$
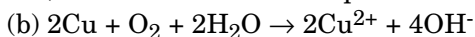
(Blood pH is about 7.4, so H^+ reduction is out.)

(c) $4Ag + O_2 + 4H^+ \rightarrow 4Ag^+ + 2H_2O$
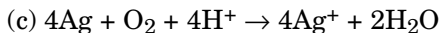
(Silver is too unreactive to corrode in straight H^+ acids, as we will see later, but $O_2 + H^+$ will corrode almost all metals.)

The cell reactions combine the metal ions produced from the anode with the negative ions produced on the cathode surface. The positive ions are attracted to the negatively charged environment around the cathode, and hence are called cations, while the negative ions (anions) head toward the anode. If cations and anions combine to precipitate out as a solid corrosion product, such as rust, they will do so wherever they meet, which may be on the anode, the cathode, both, or somewhere in between. The point is, rust indicates that corrosion has occurred someplace, but not necessarily under the rust. Scrape off the rust and look.

Definition of New Terms

Acid: substance capable of producing hydrogen ions in water.

Alkali: water-soluble base.

a.m.u.: atomic mass unit.

Anode: electrode that oxidizes in an electrochemical cell.

Aqueous corrosion: corrosion in water or in solutions where water is the solvent.

Atom: the smallest particle of an element.

Atomic mass unit (a.m.u.): unit of mass equal to $\frac{1}{12}$ the mass of a C^{12} atom.

Atomic number: the number of protons in the nucleus of an atom.

Avogadro's number: 6.023×10^{23}, the ratio of 1 g/1 a.m.u.; the number of particles in a mole.

Base: substance that will produce hydroxide ions when dissolved in water.

Cathode: electrode on which reduction occurs in an electrochemical cell.

Caustic: extremely strong alkali.

Cell: device producing electricity, containing electrodes and electrolyte.

Compound: different atoms bonded together in definite proportion to form a new substance.

Conductivity: reciprocal of the resistivity of a material. Units: S/m.

Covalent bond: bond formed between two atoms that share a pair of electrons.

Crystal: a three-dimensional array of atoms or ions bonded in a long-range ordered pattern.

Current: the flow of electricity measured in amperes (A).

Dew point: the temperature at which relative humidity reaches 100%.

Electrochemical corrosion: corrosion in which metal is oxidized and some reactant in the environment is reduced.

Electrode: electron conductor in contact with electrolyte in a cell.

Electrolyte: ionic conductor in an electrochemical cell.

Electron: unit particle of electricity, carrying a charge of 1.60×10^{-19}C.

Electron cloud: valence electrons surrounding and bonding metal atoms together.

Electronic conductor: material allowing electron movement through it.

Ion: atom containing more or fewer electrons in its orbitals than it has protons in its nucleus.

Ionic bond: bond formed by the electrostatic attraction between oppositely charged ions.

Ionic conductor: aqueous solution or ionic compound allowing ion movement through it.

Isotope: atom containing more or fewer neutrons in its nucleus than another atom of the same element.

Metallic bond: bond with all valence electrons shared by all the atoms.

Molarity: concentration in moles of solute per litre of solution. Symbol: M.

Mole: Avogadro's number (6.02×10^{23}) of particles, thus giving a mass in grams numerically equal to atomic or molecular weights in a.m.u.

Molecule: atoms bonded together to form the smallest particle of a new substance.

Neutron: basic, uncharged particle in the nuclei of atoms.

Nucleus: the positively charged core of an atom.

Ohm's Law: electrical current is proportional to voltage but inverse to resistance: $I = V/R$.

Organic compound: a covalently bonded compound containing both carbon and hydrogen atoms.

Oxidation: loss of electrons by a substance, thus increasing positive valence. Opposite of reduction.

Passivation: formation of a thin, invisible film of corrosion product on metal surfaces that greatly restricts further corrosion.

pH: scale of acidity or basicity; the negative logarithm of the hydrogen ion concentration.

Proton: basic, positively charged particle in the nucleus of every atom.

Radical: different atoms bonded with excess or deficiency of electrons to form an ion.

Redox reaction: reaction in which one substance gains electrons and is reduced in valence while another substance releases electrons and increases in valence.

Reduction: gain of electrons by a substance, thus reducing its valence.

Resistance: opposition to flow of electric current, measured in ohms (Ω).

Resistivity: electrical resistance of 1 m length and 1 m^2 cross-sectional area of a specific material. Units: $\Omega \cdot m$.

Salt: an inorganic compound composed of cations other than H^+ and anions other than O^{2-} or OH^-.

Solubility limit: maximum amount of solute that can be dissolved in a solvent.

Solute: substance dissolved in a solvent.

Solvent: component of a solution present in the largest amount, or the liquid.

Standard conditions: for gases, measured volumes are commonly recalculated to 1 atm pressure at 273 K.

Valence: the charge, either positive or negative, carried by an ion.

Voltage: electrical potential or potential difference, measured in volts (V).

Questions

1. Classify the following processes as physical or chemical changes.
   a. Copper wire is drawn down to a fine filament.
   b. Steel is melted in a vacuum.
   c. Steel pilings rust in seawater.
   d. Silver tarnishes in air.
   e. Salt dissolves in water.

2. Scandium metal, atomic number 21, atomic weight 45, usual valence +3, has how many electrons? 21, 45, 18, 24, none of these.

3. Mark the most likely chemical formulas for each of the following compounds:
   a. potassium cyanide: KCNS, KCN, K_2CN, PCy, none of these.
   b. sodium sulfite: Na_2SO_4, Na_2S, Na_2SO_3, $Na_2(SO_4)_3$, none of these.
   c. ammonium carbonate: NH_4C, $(NH_4)_2CO_3$, NH_4CO_3, NH_4CO_4, none of these.
   d. cerium sulfate: $Ce(SO_4)_3$, $CeSO_4$, Ce_2SO_4, $Ce_3(SO_4)_2$, none of these.
   e. platinum oxide: PtO, PtO_2, Pt_2O, Pt_2O_3, none of these.

4. Identify the following as atom, simple ion, ionic radical, or compound.
    a. Ni_3C
    b. Nb^{5+}
    c. Li
    d. $CaCl_2$
    e. MoO_4^{2-}

5. What type of bonds would be present in the following materials?
    a. styrofoam: covalent, ionic, metallic.
    b. brass (copper + zinc): covalent, ionic, metallic.
    c. a styptic pencil (aluminum sulfate): covalent, ionic, metallic.
    d. silver tarnish: covalent, ionic, metallic.
    e. wood: covalent, ionic, metallic.

6. Which of the following equations are correct for the corrosion reactions described?
    a. Zinc metal reacts with air to form an oxide.
        $$Zn + \tfrac{1}{2}O_2 \rightarrow ZnO$$
    b. Powdered aluminum reacts with ferric oxide rust (thermite reaction).
        $$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$$
    c. Nickel reacts with an aqueous solution of carbon dioxide.
        $$Ni + H_2CO_3 \rightarrow NiCO_3 + H_2\uparrow$$

7. If a copper heat exchanger tube loses 3 g of metal from corrosion, what mass of CuS corrosion product forms? 3g, 6g, 2.0g, 4.5g, none of these.

8. The equation for corrosion of zinc galvanizing, $2Zn + O_2 + 2H_2O \rightarrow 2Zn(OH)_2\downarrow$ can be broken down to oxidation and reduction parts. Identify each as oxidation or reduction:
    $2Zn \rightarrow 2Zn^{2+} + 4e^-$ oxidation or reduction?
    $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ oxidation or reduction?

9. The concentration of hydrogen ions in your feedwater is $3.7 \times 10^{-8}M$ (moles per litre). What is its pH? 7.4, 3.7, 0.37, 1.00, none of these.

10. If pH 7 is neutral, what is the concentration of OH^- in water? 7, $10^{-7}M$, $^{10}/_7$, 3, none of these.

11. The following reactions are supposed to be neutralizations producing salts. Which are correct?
    a. $Na_2SO_4 + 2HCl \rightarrow H_2SO_4 + 2NaCl$
    b. $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$
    c. $KOH + HCl \rightarrow KCl + H_2O$
    d. $H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + H_2O + CO_2\uparrow$
    e. $Ca(OH)_2 \rightarrow CaO + H_2O$

12. Corrosion tests are sometimes made in 3% NaCl solution to simulate seawater. What is the approximate molarity of this solution? 0.03M, 0.5M, 1.75M, 3M, none of these.

13. If you could double the distance between anode and cathode of a corrosion cell, how will corrosion be affected, assuming the cross-sectional area of the electrolyte is unchanged? Corrosion unchanged, 2X, 3X, 4X, none of these.

14. People are always surprised when they first hear of the "lemon battery." A copper wire and a steel nail stuck into an ordinary lemon create a battery that will light up a flashlight bulb. The lemon contains citric acid which readily corrodes steel but not copper. Which is the positive terminal of this battery? Bulb, copper, lemon, steel, not determinable.

15. Choose the most important anodic and cathodic half-cell reactions for corrosion of a steel automobile muffler from exhaust gases containing H_2O vapor, CO_2, and excess air.

    $2H^+ + 2e^- \rightarrow H_2\uparrow$

    $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

    $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

    $Fe \rightarrow Fe^{2+} + 2e^-$

    $Fe + 2H_2O \rightarrow Fe(OH)_2\downarrow + 2H^+ + 2e^-$
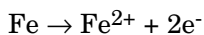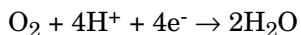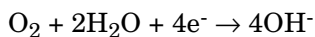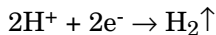
16. Choose the most likely cell reaction for corrosion of steel bridge pilings that form caissons for bridge supports.

    $Fe \rightarrow Fe^{2+} + 2e^-$

    $Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow$

    $Fe + \frac{1}{2}O_2 + H_2O \rightarrow Fe(OH)_2\downarrow$

    $Fe + \frac{1}{2}O_2 + H_2CO_3 \rightarrow Fe(OH)_2\downarrow + CO_2\uparrow$

    $Fe + 2H_2O \rightarrow Fe(OH)_2\downarrow + H_2\uparrow$
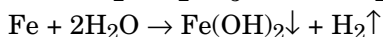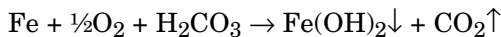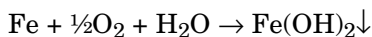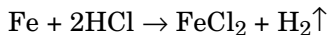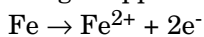
17. If a potential of 1 volt drives an electrical circuit that has a resistance of 500 ohms, what current will flow? 500A, 500VΩ, 2mV/Ω, 2mA, 500 Ω/V.

Chapter

3

BASIC METALLURGY

Different metals corrode differently, of course, but one metal can also corrode at different rates depending on how it has been treated. Was the metal cooled slowly or quickly from the melt? How pure is it, and where are its impurities located? Has it been shaped by working, and at what temperatures? Has it been given a special heat treatment to improve its strength, toughness, or other properties? Has it been welded? These questions must be answered before you have any idea of the metal's corrosion resistance.

The Structure of Metals

The metallic bond, described in Chapter 2, holds metal atoms close to each other by an electron cloud of valence electrons. The electrostatic attraction between the negatively charged electrons and the positive nuclei increases inversely with the square of the distance between them, so that the strongest bond is the shortest bond. Consequently, metal atoms try to fit around each other as tightly as possible.

Metal Crystals

A close packing arrangement of atoms in three dimensions is possible in two different patterns, both found in metals, although why a certain metal prefers one pattern over the other is not completely understood. To complicate the picture further, some metals crystallize in a pattern that is not quite close packed.

The hexagonal close-packed (hcp) crystal structure, shown in Figure 3.1, is favored by a number of high-strength, light-weight metals (see Table 3.1) as well as zinc. Some hcp metals switch to a body-centered cubic (bcc) structure at high temperatures where thermal expansion forces the atoms farther apart.

Face-centered cubic (fcc) crystal structures are preferred by the coinage metals, including aluminum, as well as some others (Table 3.1). This crystal arrangement allows easy, sharply-defined deformation so its advantage in coinage is obvious. The fcc structure is also close packed, although its name doesn't indicate it, and is made up of close-packed planes of atoms just stacked differently than hcp.

Table 3.1 Crystal Structures of Common Metals at 20°C.

FCC	Ag, Al, Au; Co (hcp > 427°C); Cu, Ni; Pb; Pt.
HCP	Be (bcc > 1256°C); Cd; Mg; Ti (bcc > 883°C); Zn; Zr (bcc > 872°C).
BCC	Cr; Fe (fcc 912°-1394°C); Li; Nb; Ta; W.
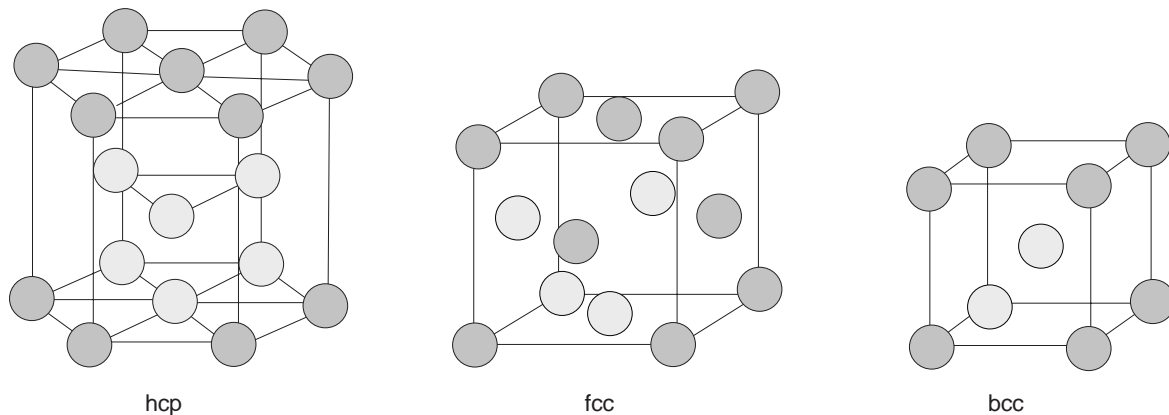
Figure 3.1 Schematic sketches of the three common metal crystal structures, showing atom locations.

Question: A certain homogeneous brass (alloy of Cu and Zn) consists of 75 wt.% Cu, 25 wt.% Zn. What crystal structure does it have and how will the atoms be arranged in the pattern?
Answer: The structure will be fcc because Cu is fcc and is the major component. Zinc atoms will substitute for some copper atoms in the structure–approximately one zinc atom per cube.

Body-centered cubic metals include iron (and steel) at moderate temperatures as well as several less-common metals. Iron, however, changes to the fcc structure when heated to 912°C, then switches back to bcc at 1394°C, and sticks with that structure up to its melting point. The low-temperature bcc structure is commonly called ferrite, the fcc iron structure is austenite, and the high-temperature bcc structure is delta ferrite. Although the bcc crystal pattern is a fairly efficient way to pack atoms tightly together, it is not close packed, as fcc and hcp are.

Figure 3.1 shows the three common metal crystal structures. For clarity, only the atom positions are shown; in reality, the atoms are large enough to touch each other. For example, in bcc structures the center atom touches the eight corner atoms. In fcc the face-centered atoms touch the four nearby corner atoms, and in hcp the center atoms in the top and bottom bases touch the six surrounding atoms in the base.

Question: The crystal pattern for bcc is shown in Figure 3.1. How many atoms are there in each cube? (The crystal is made up of these cubes all packed together so that each corner atom is actually a part of eight cubes.)
Answer: 8 corner atoms ÷ 8 cubes + 1 center atom/cube = 2 atoms/cube.

Crystal Defects

As metals begin to solidify from the melt, nuclei form at various places in the melt and begin to grow into crystals. Within the crystals the repeating pattern of atoms continues almost perfectly in three dimensions, but as two crystals grow up against each other the pattern in one is not aligned with the pattern in another. The result in the solid metal is an agglomeration of crystals, also called "grains," separated by grain boundaries as illustrated in Figure 3.2.

Impurity atoms in the liquid metal will not be exactly the right size for the crystal, may want to bond differently, or for whatever reason may prefer to remain in the liquid, so that many will end up in the last liquid to freeze–the grain boundaries. Consequently, a grain boundary tends to be filled with impurity atoms, and, being a misfit area between tightly-packed crystals, tends to be an easy pathway for atoms to move around.

Question: Which do you think diffuses faster: a vacancy or a substitutional impurity atom? Why?
Answer: Since a substitutional impurity diffuses by simply changing places with a vacancy, you might think that they diffuse at the same rate. However, a vacancy can change places with any of the other atoms on regular crystal sites also, making it much more mobile than an impurity atom.

Interstitial positions and vacancies are not the only paths for atomic diffusion, however. Metals contain dislocations, and small, interstitial atoms especially prefer to run along these dislocation "pipes." Grain boundaries also offer paths for rapid diffusion of all sorts of atoms because of the extra space between atoms and weaker bonding. These short-circuiting paths are only slightly affected by temperature, functioning almost as well at room temperature as at high temperatures.

The fastest diffusion for solids, though, is definitely surface diffusion. Atoms of all sizes are free to move without any squeezing between neighboring atoms. Atom movement over an external surface or internal crack surface is not only rapid, but seems to be almost independent of temperature.

Mechanical Properties

Engineers usually select metal as the material of construction because of its tensile strength and its ductility. Other properties, such as electrical conductivity, may be important, but if a material is not strong enough for the service or cannot be formed into the desired shape it cannot be used. These mechanical properties are usually essential, with corrosion resistance often ranking far down on the list.

Strength

A tensile test commonly measures both strength and ductility. A test sample is gripped in a machine that slowly stretches the material at a constant rate until the sample breaks, while a chart recorder on the machine produces a stress-strain curve showing the entire history of the test. Figure 3.4 is a typical example for a ductile metal.
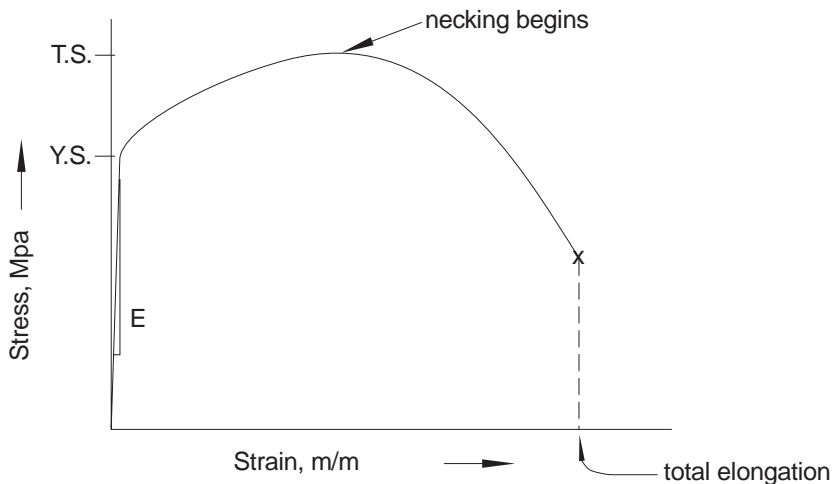
Figure 3.4 Typical tensile test curve for a ductile metal.

Stress is the force exerted on a unit cross-sectional area of the material, with units of MPa or ksi (kilopounds per square inch). Strain is the fractional change in length of the sample, a dimensionless number. In Figure 3.4 strain is shown as m/m but could also have been mm/mm or in./in.

In a tensile test the specimen first stretches elastically, with the stress increasing approximately linearly to produce a small strain. In this region if the force is released, the metal will return to its original length. The slope of this straight-line portion of the graph is the elastic modulus, E, which is a measure of the stiffness of the material.

E = elastic stress/elastic strain.

As stress is increased further, the yield strength (Y.S.) is reached when the metal starts to deform plastically; that is, permanent strain begins. The yield strength must be exceeded to shape the metal by mechanical deformation but usually should not be exceeded in service or you will have a permanently sway-backed bridge, a permanently collapsed spring, or whatever.

Question: For the stress-strain curve shown in Figure 3.4, if the yield strength is 280 MPa at an elastic strain of 0.137%, what is the elastic modulus, E?
Answer: E = elastic stress/elastic strain
E = 280 MPa/0.00137 m/m = 204 Gpa

In permanent deformation the dislocation lines move (called "slip") in response to the applied stress so that only a small increase in stress produces large strains. The sample continues to stretch fairly uniformly until, at the weakest spot in the metal, the dislocations start an avalanche, with moving dislocations dislodging other dislocations that have become temporarily blocked. At this point the sample begins to neck down (see Figure 3.5) so that the load concentrates at this smaller cross-sectional area (higher stress) and the tensile strength has been reached. The tensile strength (T.S. or U.T.S. for ultimate tensile strength) is the maximum stress that the material can handle before it fails.

a.

b.

c.
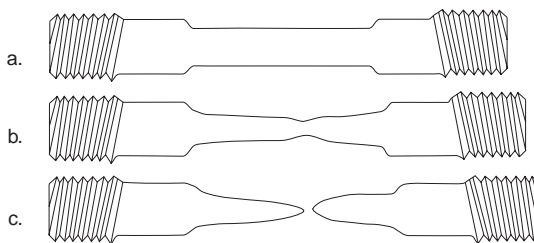
Figure 3.5 Tensile test specimens of a ductile metal:
(a) before loading; (b) necking has occurred; (c) fracture.

Beyond the tensile strength, the stress appears to decrease, but only because the stress is calculated from the original cross-sectional area of the sample. In fact, of course, the cross section at the neck is decreasing so the stress there increases greatly, although the tensile test does not show it. Finally, the sample breaks in the neck and the test ends. Figure 3.5(c) shows a steel tensile specimen that was tested to failure. The ductile metal necked and then fractured.

The description given above applies to a ductile metal; a brittle material behaves differently. Extremely brittle materials fail in the elastic region. Most brittle metals break above the yield strength but before any necking occurs. The fracture stress may be called a tensile strength, but repeated tests tend to show considerable scatter in the values.

The ductility of the test sample can be measured in two ways, although the most common way is simply to use the percent elongation to failure as a measure of ductility. A ductile metal may stretch 25% or more before fracture. In the second method, the diameter of the fractured sample is measured

fatigue. Cyclic stresses, from tension to compression or even from high tension to low tension, cause enough slip to gradually roughen the surface slightly with minute intrusions and extrusions to create a small notch. This first stage may take years to develop. The notch concentrates stress at its tip, the stress causes more slip, and a crack begins to develop and extend by slipping on the various slip planes that intersect the crack tip. As the crack gets longer, the stress at its tip increases so that the crack extends faster, weakening the metal until it finally fails by overload.

A fatigue failure is usually quite distinctive in appearance with a smooth fracture surface showing "beach marks," also called "clamshell marks." These striations form where the crack, temporarily stopped by some obstacle, deviates around it. Figure 3.6 shows a typical fatigue fracture surface. The beach marks often indicate where the crack initiated because they grow in ever-widening arcs as the crack extends. Initiation often occurs at a stress raiser on the metal surface: a sharp notch such as a sharply machined keyway on a shaft, a gouge, a scratch from abrasive wear, or the like.

Figure 3.6 Metal fatigue fracture surface
showing beach marks. (ref. 3).

Rotating shafts may fail by fatigue eventually, especially if they are heavily loaded, as a crankshaft. The torsional stress has a tensile component that opens and extends the crack.

S-N curves show the fatigue resistance of metals. The S stands for the maximum tensile stress in the loading cycle, while the N is the number of loading cycles completed before failure occurs. Figure 3.7 compares S-N curves of a ferrous metal (a normalized steel) with a nonferrous metal, in this case a precipitation hardened aluminum alloy. Two obvious differences appear. First, aluminum alloys tend to be quite susceptible to fatigue, with low stresses able to extend a crack. Secondly, steels appear to have a safe stress level, below which a fatigue crack cannot initiate or grow. This stress, called the endurance limit, appears to be about 320 MPa for the steel in the graph. The aluminum alloy and all other nonferrous metals do not have any endurance limit. For design purposes, engineers specify a fatigue strength, which is the maximum stress which will not cause fatigue failure in a specified number of cycles. The aluminum alloy in Figure 3.7 has a fatigue strength of about 190 MPa for 10^8 cycles.

Question: You need good strength in a joint but a welder suggests silver solder. Will that provide strength?

Answer: Yes, silver "solder" is actually a braze. Silver alloys all melt well above 425°C. Pure silver melts at 962°C (Table 2.1).

Welding causes local melting of the workpieces to achieve the bond between them. A filler metal of similar composition is sometimes used to fill any gap between the pieces. Heat is supplied by combustion of gases, such as with oxyacetylene welding, or by electric arc, electrical resistance, friction, laser, electron beam, or chemical reaction as with thermite welding.

The weld metal that melts and then freezes seldom corrodes preferentially; its composition is often made just slightly more noble than the base metal. Corrosion is very likely, however, in the heat-affected zone (HAZ) just adjacent to the weld. Here the metal has gotten quite hot, although not quite melted, so that cold-worked metal recrystallizes, grain growth occurs in the hottest region, and diffusion takes place throughout the HAZ. Impurities segregate in the grain boundaries and the boundaries are more corrodible than the crystalline grains. The result often is severe corrosion in the HAZ, especially in the fine-grain region at the outer edge of the HAZ, which can be seen clearly in Figure 3.10.
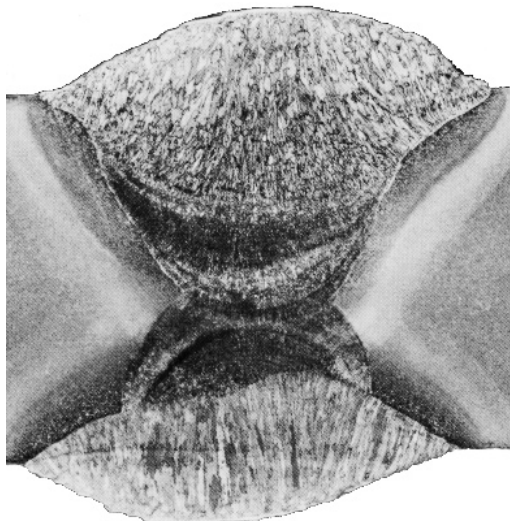
Figure 3.10 Cross section micrograph of an arc butt weld joining steel plates.
(Note heat-affected zone.) Magnification 4X. (ref. 5).

Definition of New Terms

Age: holding an alloy at room temperature for a time sufficient to harden it.

Alloy: metal with two or more component elements.

Anneal: holding material at a temperature high enough to remove internal stresses and/or change microstructure.

Austenite: iron or steel having a face-centered cubic structure.

Bainite: steel microstructure of ferrite with fine dispersion of Fe_3C made by quenching and holding austenite at a temperature slightly above martensite formation.

bcc: body-centered cubic crystal structure.

Beach marks: approximately parallel arcs on a fracture surface indicating steps in fatigue crack growth.

Body-centered cubic: crystal structure, not close-packed, with atoms arranged at the corners of a cube with another atom situated at the center of the cube.

Braze: joining metals below their melting points by another metal melting above 425°C (800°F).

Cementite: iron carbide compound Fe_3C.

Clamshell marks: see Beach marks.

Cleavage: fracture by separating crystal planes, with little or no plastic deformation.

Cold work: permanent deformation of a metal below its recrystallization temperature.

Delta ferrite: body-centered cubic structure of iron near its melting point.

Diffusion: mass transport by atom movement.

Dislocation: flaw in atomic packing extending through a crystal; line defect.

Ductility: ability of a material to be deformed without breaking. Measured in a tensile test as % strain to fracture or as % reduction in area at fracture.

Elastic strain: deformation immediately recovered when stress is removed.

Endurance limit: the maximum tensile stress in cyclic loading that a ferrous metal can withstand indefinitely without fatigue crack initiation.

exp: abbreviation for exponential of e; the inverse of natural logarithm, ln.

Exponential relationship: relationship between two variables a and b by an equation of the form $a = k^b$, where k is a constant.

Face-centered cubic: crystal structure, close-packed, with parallel planes of atoms arranged so that atoms on every third plane lie directly above each other: abcabc...

Fatigue: cracking of a material by cyclic stresses which are at least partly tensile but usually below the yield strength.

Fatigue strength: maximum tensile stress in cyclic loading that a material can withstand for a specified number of cycles without failing by fatigue.

fcc: face-centered cubic crystal structure.

Ferrite: iron having a body-centered cubic structure.

Ferrous metal: one containing more iron than any other metal; iron, steel, stainless steel, cast iron, and the like.

Full anneal: holding metal above its recrystallization temperature to achieve maximum ductility, followed by cooling slowly.

Grain: one of many crystals in polycrystalline materials.

Grain boundary: region of mismatch between adjacent crystals in a polycrystalline material.

Grain diameter: average distance across a grain, passing through its center.

HAZ: heat-affected zone.

hcp: hexagonal close-packed crystal structure.

Heat-affected zone: region of metal next to a weld, not melted but having undergone changes in structure or composition due to weld heat.

Heterogeneous alloy: alloy consisting of two or more phases.

Hexagonal close-packed: crystal structure with densest possible packed planes of atoms arranged so that atoms on alternate layers lie directly above each other: ababab...

Homogeneous alloy: alloy consisting of a single phase.

Hot work: permanent deformation of a metal at or above its recrystallization temperature.

HSLA: high-strength, low-alloy steel.

Interstitials: small atoms located in the spaces between the atoms sitting in regular sites in a crystal pattern.

ksi: thousands of pounds of force exerted on one square inch of material.

Line defect: crystal flaw extending for some distance; dislocation.

Martensite: strongest steel microstructure; body-centered tetragonal crystal structure supersaturated with carbon.

Necking: in a tensile test of a ductile material, intense slip concentrated at one location on the sample.

Questions

1. How many atoms are in each fcc cube in the pattern shown in Figure 3.1? 1, 2, 4, 14, none of these.

2. Nickel silver contains 65% Cu, 25% Zn, 10% Ni but no silver.
   a) What is its crystal structure? bcc, fcc, hcp, none of these.
   b) Which of these elements would fit into this structure substitutionally? Ag, C, Cu, H, Ni.
   c) Which of these elements would fit into this structure interstitially? Ag, C, Cu, H, Ni.

3. Suppose the temperature of a stainless steel is lowered to 0°C. How will diffusion of chromium compare with that at 25°C if the activation energy is 258 kJ/mol? Diffusion will change by a factor of: 1.39×10^4, 1.01, 0.99, 7.2×10^{-5}, none of these.

4. Which will diffuse faster: a substitutional impurity atom or a solvent atom on a regular crystal site? The larger, the smaller, the solvent atom, the substitutional atom, they will diffuse equally.

5. What stress is required to elastically deform a hardened cartridge brass (70 Cu - 30 Zn) by 0.300%? Its elastic modulus is 110 GPa. 37 GPa, 3 GPa, 330 MPa, 37 kPa, none of these.

6. A hardened cartridge brass (see question 5) has a yield strength of 414 MPa (60 ksi) and a 10% elongation to failure. What fraction of the total strain is elastic at failure? 110 GPa/(414 MPa x 10%); 414 MPa/(110 GPa x 10%); (110 GPa - 414 MPa)/10%; (110 GPa + 414 MPa)/10%; none of these.

7. What sort of relationship would you expect between metal hardness and ductility? No relationship, roughly direct, roughly exponential, roughly inverse, none of these.

8. Compared with a steel's fatigue strength, its endurance limit is: often higher, the same, often lower.

9. A 1.1 mm diameter copper wire receives 70% cold work. What is the resulting diameter? 0.92 mm, 0.77 mm, 0.60 mm, 0.33 mm, none of these.

10. Where would zinc atoms in red brass (Zn atoms are larger than Cu) tend to collect around dislocations in the brass? In tensile region, in compression region, avoiding stressed regions.

11. Compare the yield strengths of two recrystallized 65-35 brass parts, one with an average grain diameter of 0.0125 mm and the other 0.0200 mm. The first is: 2.56 times as high, 1.26 times as high, 0.79 times as high, 0.39 times as high, none of these.

12. Comparing bainite with tempered martensite, the bainite structure is: easier to make, stronger, weaker, less likely to have quench cracks, none of these.

13. A gear was tempered too long after precipitation hardening and is now too soft. Is there any way to save it? No; re-solutionize, quench, and temper; re-solutionize and quench; re-temper; none of these.

14. A 50-50 Pb-Sn solder melts over a temperature range of 183°-225°C (361°-437°F). Where will the strength of a soldered joint decrease in this temperature range? 183°C (361°F), around 204°C (399°F), 225°C (437°F).

GENERAL CORROSION

In describing a corrosion problem that has appeared, you will want to report the extent of the damage and also the type of corrosion–whether the metal is uniformly attacked, pitted, cracked, or whatever. Remedies will depend very much on the severity and nature of the corrosion.

Corrosion Classifications

First consider whether the metal is generally corroded over all its exposed surface or whether the attack is localized, with some surface undamaged. Corrosion products may have to be removed before it is evident that the metal underneath is damaged. Particularly in flowing systems, rust or other solid corrosion products may deposit on areas that are unattacked, while corroded areas may be out of sight. Most corrosion, however, is general in nature, with all exposed metal surface corroding.

Example: An engineer was asked to select a better material for a critical stainless steel heat exchanger that had had to be replaced four times. Looking at one of the exchangers on the scrap heap, he saw the tubes were plugged with rust, but under the rust was bright, uncorroded stainless steel. The rust had come from carbon steel equipment upstream. He replaced this steel with a more resistant alloy and the plant operated with scrapped, cleaned heat exchangers for many years.

Types of Corrosion

Corrosion is usually electrochemical, and corrosion in aqueous environments is nearly always electrochemical. Corrosion of metals in most organic liquids cannot be electrochemical, however, because the organic is not an ionic conductor; it is not an electrolyte. In this case the organic molecules exchange electrons directly with metal atoms at the metal surface. The same direct process can occur with metal in some molten salts. Dissolution of a solid metal in a molten metal is another obvious example where the environment is not reduced at a cathode site on the metal surface.

Corrosion in gases is quite complex. A gas molecule may react directly with a metal but if the oxide product builds up on the metal surface, the oxide acts as electronic and ionic conductor, and also as a cathode. All these special corrosion processes will be discussed in later chapters: corrosion in molten salts, molten metals, and gases in Chapter 9, and organic liquids in Chapter 10.

In electrochemical corrosion, if anode sites move around so that the entire surface is fairly evenly removed, the result is uniform attack or general corrosion.

Cathode Processes

The corrosion of a metal surface that is sometimes anode, sometimes cathode, is commonly controlled by the reaction rate of the cathode reaction. Cathode processes are rather involved: the reactant in

the environment (dissolved oxygen, for example) must first diffuse through the solution to the cathode surface, with diffusion rates commonly much slower than reaction rates. Secondly, this reactant must adsorb on the metal, a process involving a slight electron rearrangement for both the metal surface and the adsorbing species, so that the reactant sticks to the surface.

Next comes the reaction itself: transfer of electrons from the metal to the adsorbed species and rearrangement of chemical bonding (for O_2, breaking of the O-O bond and forming O-H bonds with hydrogens of adjacent water molecules). Desorption, the release of adsorbed species (OH⁻ ions for O_2 reduction), may then follow. If H^+ is being reduced, once two H atoms combine, the H_2 molecule can bubble off immediately. The steps in cathode reaction are shown schematically for oxygen reduction in Figure 4.1.
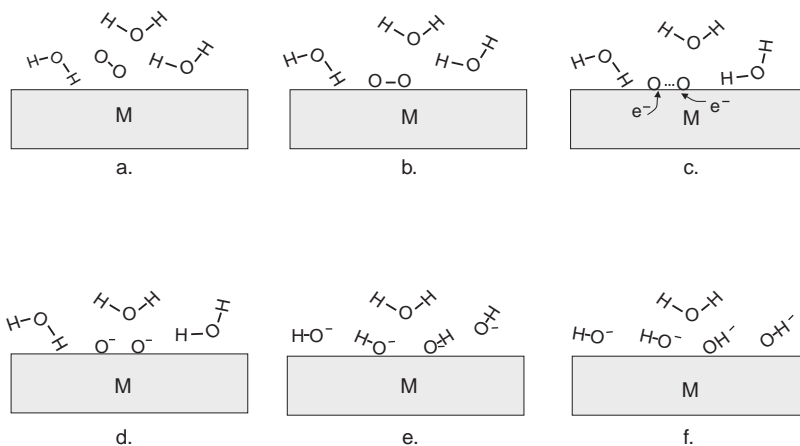
Figure 4.1 Steps involved in oxygen reduction at cathode.
(a) Dissolved oxygen diffuses toward cathode surface.
(b) Oxygen molecule becomes physically attached to cathode surface.
(c) Oxygen-oxygen bond weakens; bonding electrons in metal adjust.
(d) Oxygens receive electrons from metal, thus attracting hydrogens in water.
(e) Hydroxide ions form.
(f) Desorption of hydroxide ions.

Anode Processes

Meanwhile, elsewhere on the surface the anode reaction is occurring: simply the release of metal ions from the metal surface, leaving the valence electrons behind in the metal. As a metal ion leaves the surface it is immediately surrounded by water molecules, the negative (oxygen) ends of the molecules being attracted to the positive metal ion. This is shown schematically in Figure 4.2.

Question: Could diffusion ever become the rate-controlling process for the anode reaction?
Answer: Seldom, but possible. In a restricted environment such as a crevice, a large concentration of metal ions around the anode might inhibit further anode reaction until they can diffuse away; or solvating water molecules may have to diffuse through porous rust to get to the anode.
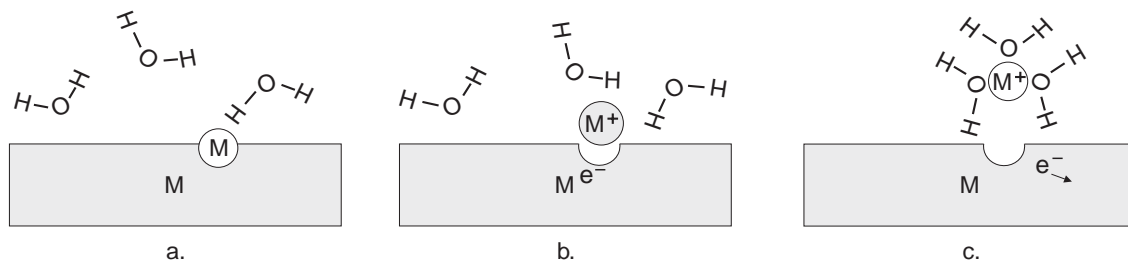
Figure 4.2 Steps in metal corrosion at anode.
(a) Metal surface in electrolyte prior to oxidation.
(b) Metal ion leaves surface; its valence electron(s) stay behind.
(c) Water molecules shield metal ion.

Localized Corrosion

If corrosion products tend to shelter some surface so that water molecules can't reach the surface, the anode reaction is prevented at that site. Then only localized corrosion occurs.

Localized corrosion, whether pitting, crevice corrosion, intergranular corrosion, or some other concentrated attack, quickly becomes a much more serious problem than uniform corrosion. Intensifying attack at one or just a few locations will greatly weaken the metal very quickly. A pinhole in a pipe will not have removed much metal but a flammable liquid spraying out is prelude to disaster.

Localized corrosion is much more difficult to detect than uniform attack. Examining the general condition of the inside of a pipe is awkward; examining every square inch inside for signs of localized attack is impractical in most cases. Often the first indication of trouble immediately becomes a panic situation.

Electrochemical cells that set up so that one place on the metal surface is continually anodic while other places are cathodic becomes the cause of localized attack. These cells can be of two types: (1) the metal differs from one place to another so that some metal is anodic and corrodes while other metal is less corrodible and becomes the cathode, assisting the anode to corrode, or (2) one uniform metal is in contact with two different electrolytes with one more corrodible than the other. The environment differs from place to place on the metal surface.

These two types of localized attack will be discussed separately because the remedies involved in thwarting these two types of cells can be quite different.

Mechanical Action

The worst situation that corrosion personnel must face, however, is the combination of corrosion (usually localized) along with mechanical action. Stresses operating along with corrosion processes may cause sudden failure, even though the stresses may have been below the metal's yield strength and the corrosion may have been minimal. Corrosion fatigue and erosion-corrosion are examples of synergistic action of stresses with corrosion that can bring extremely rapid, unexpected failure.

Question: Is combination with mechanical action, such as corrosion fatigue, caused more by fatigue or by corrosion?
Answer: It may be 90% fatigue, or 50-50, or 90% due to corrosion, but the result is much more rapid failure.

Because the rate usually changes with time, you must specify the duration of any corrosion test. For example "...uniform corrosion of 0.2 mm/y in a two-month test." This same material could very well have a corrosion rate of 0.1 mm/y in a one-year test.

Ways of Combating Corrosion

Basically there are eight ways to deal with corrosion of a metal:

1. Select material that is resistant to the environment.
2. Apply a protective coating to the metal.
3. Change the environmental conditions, such as temperature or velocity.
4. Change the environmental chemistry, its pH, concentration, or aeration.
5. Add an inhibitor to the environment.
6. Apply electrical protection to the metal, either cathodic or anodic protection.
7. Design the equipment with corrosion in mind.
8. Let the metal corrode and repair or replace it when necessary.

People tend to forget the last method but many times it is a viable alternative.

Example: An aircraft company, having ascertained that a certain engine part might fail by corrosive wear after 3000 hours of service, may opt to have the part replaced every 2000 hours.

Which of the eight methods to use in a particular situation depends on (a) the risk to human life if a corrosion failure occurs; (b) potential danger to our environment in the world around us; and, of course (c) the cost of the corrosion control measures, versus costs of downtime, cleanup, and all the rest.

"Cut corrosion protection efforts, and don't be surprised about having to spend ten times the costs to fix corrosion-related problems."–the Heitz report, Germany, 1984.

Definition of New Terms

Adsorption: adhesion to a solid surface by molecules, ions, or atoms.
Anodic protection: corrosion prevention by maintaining corrosion potential of a metal in the passive region.
Atmospheric corrosion: corrosion in the natural, ambient air or weather.
Cathodic protection: corrosion prevention by flow of current from electrolyte onto a metal.
Corrosion fatigue: synergistic combination of metal fatigue with localized corrosion.
Crevice corrosion: severe, localized attack where corrosive environment is stagnant.
Depth of penetration: corrosion rate measure. Units: depth of corrosion/time, such as mm/y.
Desorption: removal of an adsorbed particle; the reverse of adsorption.
Erosion-corrosion: synergistic combination of metal fatigue with localized corrosion.
Inhibitor: chemical added in small amounts to an environment to decrease corrosion.
Intergranular corrosion: localized attack concentrated at metal grain boundaries.
Pitting: intense, localized corrosion of a passivated metal in only one or a few spots.
Rust: solid or semi-solid corrosion product of ferrous metals (irons and steels).
Solvation: attachment of one or more solute molecules to a solvent ion.
Weight loss: corrosion rate measure. Units: mass of metal corroded/surface area·time, such as $g/m^2 \cdot d$.

Questions

1. In comparing uniform corrosion with localized corrosion, which:
    a. is more common?
    b. creates higher stresses?
    c. penetrates more deeply?
    d. is easier to design for?
    e. is the more serious problem?

2. Which is more likely to be rate-controlling (the slow step): the anode or the cathode process?

3. Why would anyone ever select a metal that is known to have a high corrosion rate in the environment it must work in? (Mark all possibly legitimate reasons.)
    a. It is needed only for short-time service.
    b. Replacing it is cheaper than good materials.
    c. Its mechanical properties are superior.
    d. It will be protected, such as with cathodic protection.
    e. Its availability saves time.

4. A copper pipe corrodes at 6 g/m^2·d in a certain environment. What would this rate be if expressed as mm/y? Density of copper = 8.9 g/cm^3.
    0.25 mm/y, 1.0 mm/y, 4.0 mm/y, 5.4 mm/y, none of these.

5. A corrosion rate of 1 mm/y for iron corresponds to what weight loss? Density of iron = 7.86 g/cm^3.
    4.6 x 10^{-2} g/m^2·d; 0.127 g/m^2·d; 1.00 g/m^2·d; 21.5 g/m^2·d; none of these.

6. Stagnant water may use up most of its dissolved oxygen as corrosion proceeds. How would you expect the corrosion rate to change with time? Decrease, increase, indeterminable, remain unchanged.

7. Water containing some copper ions contacts an aluminum gutter so that copper begins plating out. How would corrosion rate change with time?
    a. It decreases because cathode reactant decreases.
    b. It increases because separate copper cathode is created.
    c. It is indeterminate with so little information.
    d. It continues unchanged with time.

8. Which of the curves in Figure 4.4 best illustrate the corrosion of a barbed wire fence? Figure 4.4a, Figure 4.4b, Figure 4.4c, Figure 4.4d.

9. Which of the eight ways of combating corrosion are used to slow corrosion of steel automobile bodies?
    a. (1) Select resistant material;
    b. (2) apply protective coating;
    c. (3) change environmental conditions;
    d. (4) change environmental chemistry;
    e. (5) add inhibitor to environment;
    f. (6) apply electrical protection;
    g. (7) improve design;
    h. (8) let them corrode.

Chapter
5

METAL VS. METAL

Localized corrosion will occur if one metal corrodes while connected to another, less reactive metal that serves as a cathode. An electrochemical cell is set up with only the more reactive metal corroding. The other metal just speeds the corrosion by providing a large cathode surface where the environment can react.

In fact, the cathode need not even be a metal as long as it is an electron conductor. Consequently, graphite connected to almost any metal will cause galvanic, or "bimetallic", corrosion in an ion-conducting solution. Rust and other solid corrosion products are usually semiconductors and therefore can serve as cathodes, helping the attack on any bare metal.

It is not possible to use steel for every purpose. Other metals have better properties for particular service conditions-better electrical conductivity, better wear resistance, or whatever. Consequently, different metals often must be combined to make the best assembly. They can work well together until they contact a corrosive solution.

Galvanic Corrosion

The rate-controlling step in corrosion is usually the process that must take place at the cathode: diffusion of reactant to the cathode surface, adsorption on the metal surface, receiving of electrons from the metal, interaction with other species, and finally desorption or release from the surface.

The interaction and desorption stages may be omitted if the cathode reaction is simply a metal plating on the cathode, such as $Ag^+ + e^- \rightarrow Ag^o\downarrow$, or interaction with the solute may be combined with the electron transfer, as with oxygen reduction: $O_{ads} + H_2O + 2e^- \rightarrow 2\ OH^-$. However, interaction and desorption may be the combining of adjacent adsorbed species, such as $2\ H_{ads} \rightarrow H_2\uparrow$, which is often the slowest stage of the cathode reaction in an acid. Compared with the relatively much simpler anode processes, cathode processes usually dictate the corrosion rate.

A metal corroding by itself must be 50% anode and 50% cathode all the time. If it is to be usable at all, one of the two processes must be reasonably slow. Coupling a corrodible metal (fairly fast anode process) with a different metal that provides a fast cathode process can increase the corrosion rate ten times, or maybe even a hundred times or more. The electrical coupling of two different metals in an electrolyte creates a "galvanic cell."

Example: a tin can is actually a steel can coated with an extremely thin tin layer. Once a can of tomato juice is opened and exposed to the air, $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ becomes the cathode reaction on the tin surface, with the can's cut edges exposing the anodic steel. Soon someone will begin tasting bitter iron ions.

Intergranular Corrosion

Almost all the metals used in industry are polycrystalline, with grain boundaries between the individual crystals (grains). The boundaries tend to collect impurity atoms that don't fit properly within the crystals. Also, since the spacing between atoms is looser than within the regular arrangement of the grains, atoms are freer to move around in the boundaries.

With faster diffusion, atoms have a better chance of congregating and reacting, but the main difficulty in nucleating a reaction product is the high energy of the surfaces being created. In a grain boundary, which is actually the abutment of two surfaces, these surfaces are already present so that precipitates can grow readily.

Sensitization of Stainless Steels

Stainless steels are iron-chromium alloys containing enough chromium (over 10%) to passivate in some environments. Most stainless steels have a low carbon content, but occasionally carbon may accidentally be picked up–a welder may fail to degrease the metal before welding, for example.

The carbon collects at the grain boundaries, so that in the sensitizing temperature range, roughly 500-800°C (900-1500°F), the carbon will react with nearby chromium to precipitate chromium carbide in the boundaries. This depletes the chromium adjacent to the boundaries, creating a microscopic galvanic cell having high-chromium stainless steel grains versus iron alone next to the boundaries. In passivating environments the large cathode/small anode situation eats out the boundary very quickly, allowing individual grains to fall out–sometimes described as "sugaring." An example is shown in Figure 5.4.

Figure 5.4 Intergranular corrosion of a sensitized stainless steel. (ref. 9).

Most stainless steels made today contain less than 0.03% carbon so they should not sensitize unless they have been contaminated with an outside source of carbon. Oxyacetylene welding, for example, must never be used with low-carbon stainless steels because incomplete combustion would charge the metal with carbon.

Question: With a steel containing nonmetallic stringers, which is anode, which cathode?

Answer: Nonmetallic stringers, if electrically conducting, are usually cathodic to steel, i.e., less reactive than metal. If nonconducting, they are inert.

Question: How can stringers "corrode into deep pits" if they are cathodes?

Answer: The metal adjacent to a stringer becomes the anode and corrodes until the stringer falls out.

Figure 5.6 Exfoliation of steel nut on swimming pool fence. (ref. 10).

Stress Cells

Elastically strained metal is anodic to unstrained metal, as the spring in Figure 5.7 evidences, even though the environment is exactly the same at both anodic and cathodic surfaces.

Plastically deformed metal that has been cold worked usually corrodes slightly faster than annealed metal, although the difference is not great. If a piece of metal has some local cold-worked regions, so that anodes are directly adjacent to cathodes, the difference in corrosion rates can be quite obvious. For example, a nail commonly has a cold-worked head and point which can corrode first while its shaft serves as the cathode. A light oiling at the factory usually prevents this problem.

It occasionally happens that cold working actually improves the corrosion resistance of a metal. This happens where impurities that have collected at grain boundaries in the metal become distributed more evenly by heavy cold work. The resulting corrosion is more uniform and less localized.

The most serious problem with cold work, especially light cold work, is that it can create high residual stresses within the metal that can contribute to stress-corrosion cracking (discussed in detail in Chapter 7). Heavy cold working disorders a metal's grain structure badly but *uniformly* throughout.

Do not assume that the temperature of solution is the temperature of the metal surface. In heat transfer situations the surface temperature can be much hotter than the environment in contact with it.

Example: A young engineer, given the task of finding a suitable material for a tar heater, immersed various metals in the hot tar. A stainless steel had essentially no weight loss in the tests but lasted less than 30 hours in service. With heat transfer, the metal was considerably hotter than the tar. As he put it, "I had to go in for a little talk with my boss."

Definition of New Terms

Admiralty brass: alloy of 71 Cu - 28 Zn - 1 Sn.

Area effect: in localized corrosion, the greater the cathode/anode area ratio, the faster the anode corrodes.

Bimetallic corrosion: galvanic corrosion.

Brass: copper alloyed with zinc.

Dealloying: selective corrosion of a reactive component from a solid solution alloy.

Dezincification: selective corrosion of zinc from a brass.

Distance effect: in galvanic corrosion, the further apart the anode and cathode are, the less severe the corrosion, particularly in poorly conducting electrolytes.

End-grain attack: intergranular corrosion on a cut transverse to the direction that a metal has been worked.

Exfoliation: intergranular corrosion along grain boundaries parallel to the metal surface, with corrosion products forcing layers of metal outward.

Fresh water: not saltwater, but not necessarily unpolluted.

Galvanic cell: electrochemical cell in which the anode is a corrodible metal and the cathode is a less-reactive metal or nonmetallic electron conductor.

Galvanic corrosion: accelerated corrosion of a metal connected to a less reactive metal or conducting nonmetal in an electrolyte.

Galvanic series: list of metals and nonmetallic conductors in order of their corrodibility in a specified environment.

Galvanizing: a zinc protective coating, usually on steel.

Graphitic corrosion: corrosion of gray cast iron leaving graphite flakes binding rust which has replaced the iron.

Gray cast iron: Fe-Si-C alloy with a microstructure of numerous graphite flakes in a pearlitic or ferritic matrix.

Oxyacetylene welding: welding with heat generated by combustion of an oxygen-acetylene gas mixture.

Ringworm corrosion: corrosion of the spheroidite microstructure region of a reheated pipe.

Sensitization: making a metal susceptible to intergranular corrosion by holding it in a critical temperature range, as by heat treatment or welding.

Spheroidite: soft steel microstructure of spheroidal globules of iron carbide in a ferrite matrix.

Stress cells: electrochemical corrosion cell in which the electrodes are identical in composition but with the anode more highly stressed.

Stringer: elongated nonmetallic inclusion in a metal, lying parallel to the working direction.

Sugaring: dropping out of individual grains of metal as a result of intergranular corrosion.

Weld decay: intergranular corrosion resulting from sensitization of the heat-affected zone during welding.

Zircaloy™: zirconium alloy with 1.5% Sn plus small, controlled amounts of Fe and Cr.

Questions

1. Where would rust lie in the galvanic series, if it is a semiconductor?
   a. Near graphite.
   b. Near mill scale on steel.
   c. Near mild steels.
   d. Near magnesium.

2. Would a serious galvanic cell be created if passive stainless steel is connected to active stainless steel in an electrolyte?
   a. Yes.
   b. Indeterminable.
   c. No.

3. Is a galvanic cell set up if a brass radiator is soldered with a lead-tin solder?
   a. Yes.
   b. Indeterminable.
   c. No.

4. New pipe, fresh from the mill, is covered with mill scale. Could the pipe be buried, using the mill scale as a protective coating?
   a. Yes, because the mill scale is almost uncorrodible.
   b. Yes, because mill scale will corrode, protecting pipe.
   c. No, because mill scale will break off in some places.
   d. No, because mill scale will detach completely.

5. A housing developer installed bare steel gas lines and copper water lines in the same trenches for a new subdivision, ensuring that the two lines were spaced a few inches apart. Within months, gas was leaking everywhere, Could this have been galvanic corrosion, and if so, how?
   a. Yes, the few inches of soil allowed electron transfer.
   b. Yes, gas and water lines were connected at hot water heaters.
   c. Yes, copper ions plated out on the steel lines.
   d. No, the soil must have been highly corrosive to steel.

6. If the steel gas lines in the preceding question are replaced with factory-applied, epoxy-coated steel, what estimate could you make for their life?
   a. They should last as long as the houses.
   b. No improvement; they will fail within months.
   c. Anode area is reduced. They will fail within weeks.

7. For the corroding gas pipe situation mentioned in Question 5, which would be better: insulating the steel pipe or the copper water line?
   a. Insulate the steel pipe, so it can't lose electrons.
   b. Insulate the copper line, so it can't be a cathode.
   c. Insulate both, to be doubly safe.

8. A nickel alloy reaction vessel is connected to a brass coupling which in turn is fastened to a steel pipe. If seawater flows through the pipe to the reaction vessel, what corrodes?
   a. The nickel alloy vessel corrodes.
   b. The brass coupling corrodes.
   c. The steel pipe corrodes.
   d. The brass and steel both corrode slowly.

ENVIRONMENTAL EFFECTS

An electrochemical corrosion cell can be created with a single, homogeneous piece of metal if it contacts a corrosive solution that differs in concentration at different places on the metal surface. The situation can be sketched as a laboratory cell, shown in Figure 6.1a. The semipermeable membrane shown in the figure is simply a laboratory device to prevent mixing of the two solutions while allowing ionic conductivity. In real situations its equivalent is lack of stirring of the solutions, perhaps with a difference in density that tends to keep the two solutions separated (Figure 6.1b).
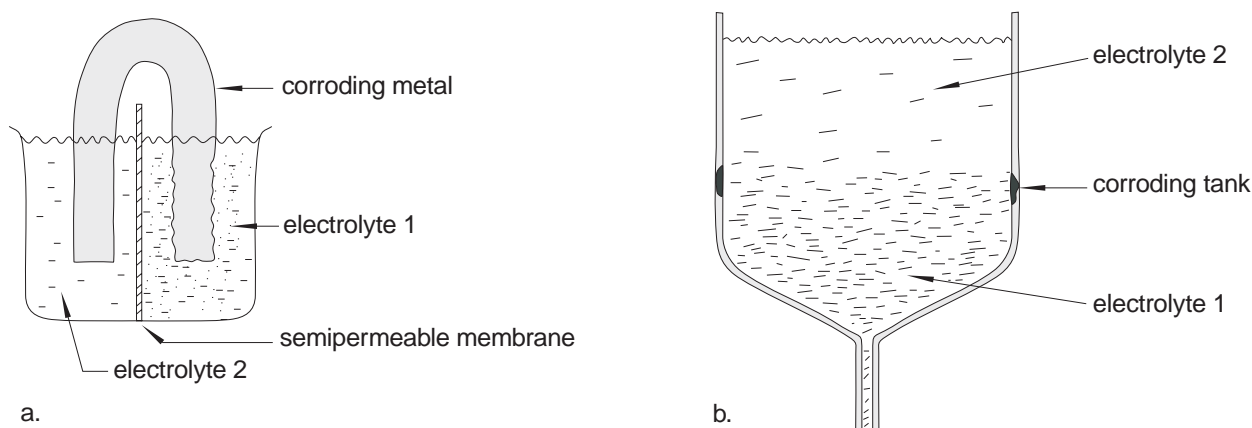
Figure 6.1 Electrochemical corrosion cell consisting of one metal in two connected electrolyte concentrations. (a) laboratory version; (b) more realistic situation.

Concentration Differences

The most common cathode reactions in aerated solutions involve oxygen reduction. A corrosive solution with high oxygen concentration in one region and a lower oxygen concentration elsewhere will set up a localized *oxygen concentration cell* with the cathode being the metal in contact with the high-oxygen solution. The metal corrodes in the low-oxygen region.

A bare pipe buried at about the level of the ground's water table is an example. The upper part of the pipe contacts well-aerated soil while the lower part, in waterlogged soil, corrodes. A film of moisture coats all the soil particles and serves as the electrolyte.

Unmixed salt solutions can show the same effect. A heavy brine in the bottom of a tank has very low solubility for oxygen, but a dilute solution at the top of the tank will dissolve oxygen and become the cathode reactant. The anode will be the metal contacting the dense brine.

On the other hand, unstirred solutions of oxidizing salts ($FeCl_3$, $K_2Cr_2O_7$, and the like) will make a cathode of the metal contacting the stronger oxidizer solution because the cathode reaction will be

reduction of the oxidizer. Similarly with unmixed acids: metal contacting the more concentrated acid will be the cathode.

Question: A pipe carrying plant waste always runs about half full. The pipe is found to be severely thinned inside at the 3 and 9 o'clock positions with very little rusting at top and bottom. Explain.
Answer: Oxygen pickup at the liquid surface has created a cathode region. The pipe wall just below the cathode will be the anode region (the distance effect puts anode very near cathode). This situation is often called "waterline corrosion."

Crevice Corrosion

Over time, crevices develop extremely corrosive conditions where attack is concentrated. Crevices can be created in three different ways:

- *geometric crevices*: metal-to-metal contact where solution can get between the two pieces of metal, such as in threaded connections.

- *metal/absorbent nonmetal*: the absorbent material holds moisture continually against the metal surface. Examples are wood bolted to metal, and sponge rubber gaskets in pipe joints.

- *deposit corrosion*: deposits of sediment, lime, rust, and the like on metal surfaces create a crevice. Deposits that are porous and absorbent often create the worst conditions.

As Figure 6.2 schematically illustrates, with moisture initially in the crevice the corrosion occurs everywhere on the metal surface, in and out of the crevice (Figure 6.2a).

When all oxygen has been used up in the crevice (Figure 6.2b), the production of metal ions can still continue. At this point cathode and anode areas separate: the anode continues inside the crevice, while the cathode reaction occurs on the outer surface where oxygen is plentiful. The situation inside the crevice continues to change, first with precipitation of insoluble corrosion products, such as metal hydroxides, that tend to restrict oxygen diffusion into the crevice even more, and secondly by the migration of Cl^- ions into the crevice, attracted by the large concentration of metal ions there.

Hydrolysis of the metal chloride solution then occurs. By reaction with water,
$MCl + H_2O \rightarrow HCl + MOH \rightarrow H^+ + Cl^- + MOH\downarrow$, the Cl^- is released to form more metal chloride as acidity increases in the crevice. The acid encourages faster anode reaction by cleaning the surface of corrosion products.

Crevice corrosion gradually develops as the oxygen concentration cell becomes established. Chloride ions are not essential to creation of acidity inside the crevice, but because they are so common and diffuse faster than any other anion (except OH^- which eliminates itself by precipitation as an insoluble corrosion product), Cl^- is usually involved. An example of crevice corrosion is shown in Figure 6.3.

Preventing crevice corrosion usually simply involves preventing crevices. Weld two pieces of metal together instead of riveting or bolting, seal crevices with soldering or caulking, use nonabsorbent gaskets, use continual agitation to prevent solids from settling, and frequently clean equipment.
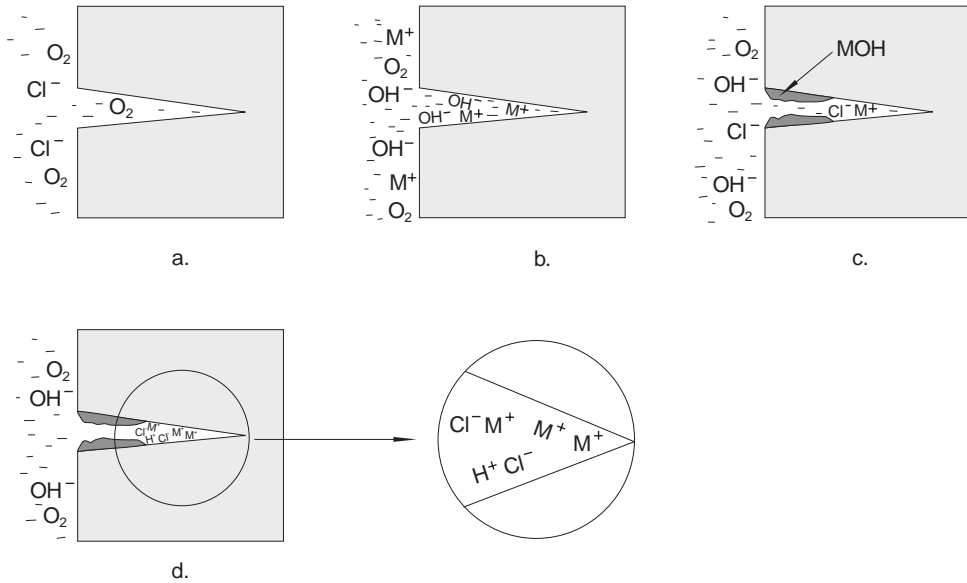
Figure 6.2 Development of crevice corrosion.
(a) Initial situation: oxygen-containing solution inside crevice.
(b) Depletion of oxygen after corrosion begins.
(c) Migration of Cl⁻ into crevice and formation of solid corrosion products.
(d) Hydrolysis of metal chlorides to create acidic conditions in crevice.
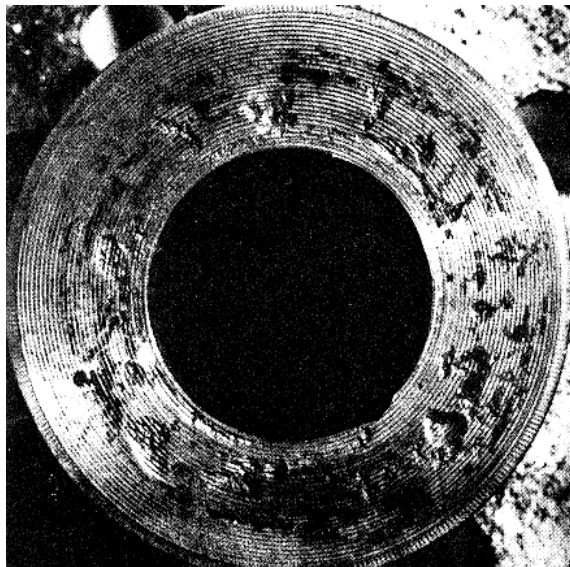
Figure 6.3 Crevice corrosion beneath an absorbent
gasket on stainless steel valve. (ref. 11).

Pitting

Pitting occurs when a protective surface layer is damaged so that the underlying metal is attacked locally. By some definitions a pit must be at least half as deep as it is wide (hemispherical or deeper),

Deposit corrosion: crevice corrosion under sediments, microbial colonies, corrosion products, lime, and other such nonmetallic precipitates and debris.

Dew point corrosion: see Condensate corrosion.

Hydrolysis: reaction of a compound with water where the anion of the compound bonds to the H^+ of the water and the cation bonds to the OH^-.

Microbial corrosion: localized corrosion under deposits of bacterial colonies, algae, or fungi.

Oxidizer: chemical substance which by a reduction reaction facilitates oxidation of another substance.

Oxygen concentration cell: a higher concentration of dissolved oxygen in one region creates a cathode at the metal surface while a lower concentration at another region creates an anode.

Rebar: reinforcing bar, usually steel, embedded in concrete for added resistance to fracture.

Semipermeable membrane: a porous material allowing diffusion of ions through its structure but blocking ionic transport by flow.

Stray current corrosion: corrosion caused by discharge of direct current that was accidentally received by a metal.

Tubercle: knob of rust shielding a colony of iron-oxidizing bacteria.

Questions

1. If a bare, buried pipe had a pit on the outside at the 12 o'clock position, how could that have happened?
    a. A lump of clay touches pipe at 12 o'clock.
    b. The pipe is nearly but not quite full of corrosive solution.
    c. Splashing or condensation left droplets of corrosive solution at 12 o'clock.
    d. A piece of wood or tree root contacts pipe at 12 o'clock.
    e. Soil is more aerated at 12 than at 6 o'clock.

2. Couldn't metal contacting a nonabsorbent nonmetal create a crevice corrosion situation?
    a. It doesn't; however, most nonmetallic materials are absorbent.
    b. Absorbent nonmetallics will hold moisture against the metal longer.
    c. Absorbent nonmetallics will wick away moisture from the metal.
    d. Absorbent nonmetallics release some H^+ into solution.
    e. Absorbent nonmetallics create a tighter crevice.

3. Can hydrogen reduction be the cathode reaction in crevice corrosion?
    a. Yes. H^+ becomes depleted in crevice which then serves as anode.
    b. Yes. H^+ becomes depleted outside crevice, with reduction continuing in crevice.
    c. No. H^+ becomes depleted outside crevice, with reduction continuing in crevice.
    d. No. H^+ diffuses so fast it never is depleted in crevice.

4. Can noble metals pit?
    a. Yes. Passive films could become damaged locally.
    b. Yes. Crevice corrosion could create pits.
    c. Yes. Droplets of condensate could create pits.
    d. No. True pitting requires passive film.
    e. No. Passive films are too tenacious.

STRESS-ASSISTED CORROSION

While general corrosion is the most common corrosion problem, and localized attack causes most of the unexpected, severe corrosion, a combination of localized attack with stress creates the sudden failures that become disasters–the headline makers.

Stress on the metal can be generated by flowing fluids striking the metal surface, by friction, by tensile loading of the metal, such as stretching, bending, or twisting it, or the stress may even be internal, such as that created by heat treatment.

Failures caused by corrosion combined with stress range from severe, extremely corrosive attack over a fairly extensive surface area to a submicroscopic attack at the tip of a crack. The rapidity of failure is due to synergistic and simultaneous action: stress increases the corrosion rate while corrosion increases or concentrates the stress.

Synergism of corrosion and stress is assumed throughout this chapter. A pipe may gradually thin by corrosion until the pressure inside bursts the pipe, but that is merely due to a lack of inspection or monitoring of corrosion, not involving a new corrosion mechanism. With synergistic action between corrosion and stress, the failure comes so suddenly that unique mechanisms of failure are required to explain the causes.

Erosion-Corrosion

A liquid or gas flowing rapidly over a metal surface can erode the metal. When combined with corrosion, the damage can be rapid and severe. The corrosion will tend to protect the metal if solid corrosion products form, but erosion will remove the protective coating to create local anode/cathode areas, as the sketches in Figure 7.1 illustrate.
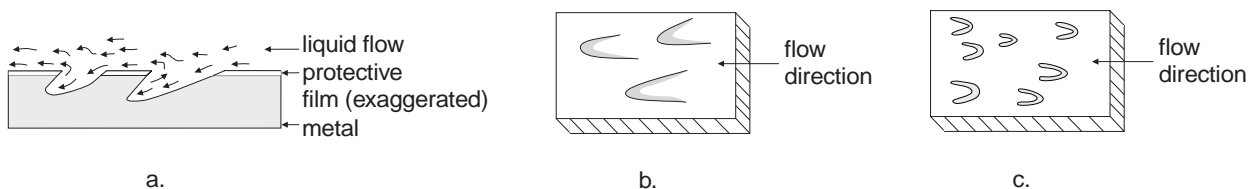
Figure 7.1 Erosion-corrosion,
(a) cross-section illustrating formation of elongated pits;
(b) top view showing comet-shaped pits;
(c) top view showing formation of horseshoe-shaped pits.

Erosion-corrosion begins when fluid velocity exceeds a critical velocity that starts to break down the solid film of corrosion product. The velocity is the relative velocity between metal and fluid, either

Answer: Higher-strength steel will not reduce the corrosion, and so will not be much improvement. A stainless steel replacement reduces corrosion of the elbow but may cause galvanic corrosion of carbon steel pipe. A more gradual curvature of the elbow would reduce impingement and be very effective.

Cavitation

In situations of extreme turbulence, such great pressure differences exist that a liquid may momentarily form a vapor bubble at a low pressure point. In the next moment the bubble implodes, sending out a shock wave of such intensity that it may dent the metal surface. This roughened surface then increases turbulence so that another vapor bubble is likely to form at that spot. Repeated hammering produces a pock-marked patch that rapidly gets rougher and deeper. The fine bubbles become so numerous that water becomes a milky white. Pumps (see Figure 7.5), compressors, and turbine buckets are commonly susceptible.

Figure 7.5 Cavitation of pump impeller in sour crude oil.

Metals that harden readily by cold work resist cavitation, or resilient linings are also effective. Reducing turbulence, flow rate, and vibration are essential.

Question: A small acid pump is giving off popping and cracking sounds. Could this be cavitation?
Answer: Shut it off immediately before it explodes. It is very likely to be cavitation and can be deadly.

Corrosive Wear

Wear by itself can damage metals severely. Combine wear with corrosion and you will see even more serious effects as the wear continually removes protective passive films, allowing corrosion to continue unchecked. Actually, almost all wear is corrosive wear because metals react virtually instantaneously with air when fresh, bare metal is exposed by wear.

Fretting occurs with all tight-fitting parts that are not supposed to slip against each other, but do: shrink-fitted gears on a shaft, bolted or riveted parts that vibrate, or wire rope in vibrating tension. Electrical contacts subjected to vibration may increase their electrical resistance with the oxide formed from fretting.

Fretting corrosion may cut through a protective metal coating to the underlying base metal to cause galvanic corrosion, or it may initiate corrosion fatigue cracks. At the very least it ruins close tolerances.

Lubrication is the most common method of combating corrosive wear. Oils and grease protect the surfaces from corrosion and reduce friction, along with the heat it creates. These lubricants are temporary, however. They become diluted or contaminated, they tend to be forced out of the interface they are supposed to protect, and they may degrade gradually by reaction with the environment. Lubrication must be part of a regularly scheduled maintenance program.

Corrosion Fatigue

Corrosion fatigue combines the standard fatigue mechanism with synergistic corrosion that may initiate cracking as well as speeding crack propagation.

Corrosion fatigue cracks often initiate from pits, stress concentration points on a surface roughened by corrosion, or from fretting corrosion. These cracks propagate much faster than ordinary fatigue cracks and at stresses much below those that cause failure in air. Tough metallurgical microstructures that might halt or slow a fatigue crack are quickly dissolved away in corrosion fatigue.

Cracks are transgranular, usually with no branching. Initiation of many cracks is common, with only one extending any great distance and finally failing. With aluminum alloys, initiation often occurs at sites of intergranular corrosion. Fracture surfaces look much like fatigue failures, with beach marks and corrosion products usually being evident. Figure 7.8 shows initiation and development of corrosion fatigue cracks while Figure 7.9 shows a fracture surface.

Prevention of corrosion fatigue can be achieved by reducing the fatigue or reducing the corrosion. Two common sources of fatiguing stress are vibration and pressure fluctuations due to pumping action. If these can be minimized, it may be possible to avoid corrosion fatigue. Reducing the corrosion by proper material selection, protective coatings, inhibitors, cathodic protection, and the like can greatly prolong service life by preventing rapid initiation of fatigue, but do not prevent eventual failure by fatigue, of course.

Question: A drive shaft has failed after only a year's service. The fracture surface broke like fatigue; it is shiny and clean with telltale beach marks. There is some rust on the outside of the shaft, caused by mist from a nearby leaky pump. Is this straight fatigue or should it be classified in the failure report as corrosion fatigue?
Answer: The presence of a corrosive environment to initiate the crack, plus the short time required for failure, clearly shows corrosion fatigue.

Hydrogen charging can also occur during electroplating of coatings or welding wet steel, which can decompose the water.

Prevention of hydrogen damage is often a matter of proper selection of materials and coatings. High-nickel alloys are much more resistant to hydrogen embrittlement than steels are. If high-strength steels are required, anodic coatings must be avoided. Steels with electroplated coatings should be baked out at around 175°C (350°F) for 3 hours to remove atomic hydrogen. Steels used in H_2S environments must be very ductile, below HRC 22; some oil companies set maximum hardness limits even lower.

Proper design can keep tensile stresses low, or perhaps it may be possible to put the metal in compression and thus eliminate cracking. Cathodic protection can eliminate the corrosion but must be designed very carefully so as not to overprotect. Where possible, anodic protection is safer.
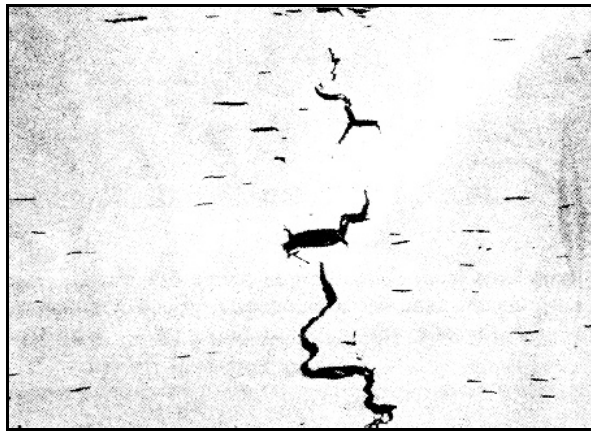
Figure 7.11 Fracture of linepipe steel by hydrogen
stepwise cracking. (ref. 12).

Question: What conditions are required to bring about hydrogen stepwise cracking in a steel?
Answer: A steel with hardness exceeding HRC 22 plus a microstructure containing rolled-in inclusions, atomic hydrogen within the metal, and applied tensile stress. The source of hydrogen is commonly corrosion in a hydrogen sulfide/water solution.

Stress-Corrosion Cracking

A general definition of stress-corrosion cracking (SCC) is the fracture of metal by the simultaneous action of corrosion and sustained tensile stress. This definition excludes failure of metal that first corrodes and then cracks by mechanical overload (not simultaneous), and also excludes corrosion fatigue (stress is not sustained) and probably liquid metal embrittlement (no corrosion), although these other processes are closely related.

Cracking usually occurs with high-strength metals in environments that are not very corrosive, with tensile stresses well below the yield strength. Cracks are fine, usually quite branched, and may be either intergranular or transgranular depending on the metal/environment combination.

Once a crack is initiated it extends very rapidly–a centimetre a day being typical. The branching often observed can be seen in Figure 7.12.

It is quite likely that several of these SCC mechanisms operate simultaneously, with the predominating one being dependent on the particular circumstances.

Protection from stress-corrosion cracking usually involves avoiding metal/environment combinations known to be dangerous. Preventing corrosion with nonmetallic coatings or inhibitors, removal of the damaging species from the environment, lowering temperature, or proper design to keep stresses low have sometimes been successful. Cathodic protection is dangerous for metals that can be embrittled by hydrogen, especially steels, because of the possibility of overprotection causing hydrogen charging.

Question: We have had a metal part break in a slightly corrosive environment. The stress was somewhat fluctuating. Do we call it corrosion fatigue or stress-corrosion cracking?
Answer: If the cracks are intergranular it is SCC. If cracking is transgranular it is usually corrosion fatigue because cracks move so very rapidly with a fatiguing-type stress. If SCC would also give transgranular cracks in this environment, if the crack is branched, and if the fluctuation of stresses is minor, it would be best classified as stress-corrosion cracking.

Definition of New Terms

Abrasive wear: removal of surface metal by grinding action of nonmetallic particles.
Adhesive wear: damage caused by momentary friction welding of two metal surfaces that rub against one another.
Asperities: microscopic and submicroscopic high points on a surface.
Caustic embrittlement: stress-corrosion cracking of carbon steels in alkaline solutions containing OH^- ions.
Cavitation: type of erosion-corrosion involving high turbulence that momentarily vaporizes liquid into minute bubbles.
Corrosive wear: wear greatly increased by synergistic action with corrosion.
Critical velocity: minimum velocity required to cause erosion-corrosion.
Cutting fluid: liquid used as coolant and lubricant in machining operations, often containing corrosion inhibitors.
Erosion: wearing away by fluid flow.
Fretting: damage to heavily loaded metal surfaces caused by very slight lateral movement between them.
Fretting corrosion: fretting in a corrosive environment other than air.
HIC: see Hydrogen-induced cracking.
Hydrogen blister: round bulge on a metal surface caused by accumulation of hydrogen gas in a fissure within the metal.
Hydrogen charging: inducing hydrogen to diffuse into a metal, such as by making it the cathode of an electrochemical cell.
Hydrogen embrittlement: loss of ductility of metal caused by diffusion of atomic hydrogen into the metal.
Hydrogen-induced cracking: embrittlement of metal by internal atomic hydrogen, leading to cracking under low stress.
Hydrogen stress cracking: see Hydrogen-induced cracking.
Impeller: rotor in a pump.
Impingement: striking of fluid against a surface at a sharp angle.
Intergranular cracking: crack following grain boundaries or previous grain boundaries, such as prior austenite boundaries in pearlitic steels.
Laminar flow: smooth, streamline flow of a fluid over a surface.
Liquid-metal embrittlement: rapid cracking of solid metal exposed to certain liquid metals or exposed to solid metals very near their melting point.
LME: see Liquid-metal embrittlement.

SCC: see Stress-corrosion cracking.

Season cracking: stress-corrosion cracking of copper alloys in aqueous ammonia solutions.

Shrink fitting: fastening one metal part over another by heating it to expand it, slipping it on, and allowing it to cool and contract.

Slurry: liquid carrying suspended solid particles.

Sour oil: oil containing dissolved hydrogen sulfide and water, which form acid.

Stepwise cracking: fracture in stairstep path, combining hydrogen blistering with hydrogen embrittlement.

SSC: see Sulfide stress cracking.

Stress-corrosion cracking: fracture of a metal by simultaneous corrosion and sustained tensile stress.

Sulfide stress cracking: hydrogen-induced cracking in solutions containing hydrogen sulfide.

Thermal stress: stress created when materials attempt to expand or contract unevenly due to temperature variations or differing thermal expansions.

Torsional stress: stress developed within a material when it is twisted. Torsion contains a tensile component.

Transgranular cracking: cracks cutting across metal grains along certain crystal planes.

Triaxial stress: stress acting in all three principal directions of space (up-down, left-right, front-back).

Turbulence: flow varying erratically in velocity and direction.

Questions

1. If you know the critical velocity v_c for erosion-corrosion in a straight pipe, can you adjust that for a bend?
    a. Yes. $v'_c = v_c K \tan \theta$ where θ is the bend angle.
    b. Yes. $v'_c = v_c - K \sin \theta$
    c. They are the same. $v'_c = v_c$
    d. No, but v'_c is greater than v_c
    e. No, but v'_c is less than v_c

2. A report on a cavitation problem describes the damage as "a cluster of fine pits." Criticize.
    a. The pits will be widely spaced.
    b. No pits would be observed. The attacked area would be smooth.
    c. Pits formed by true pitting don't cluster together.
    d. Pits would be very coarse.
    e. Confusion between cavitation and pitting could lead to wrong remedy.

3. We plan to put an internal coating in a steel pipe that will carry a water slurry. You would advise:
    a. A hard, strong ceramic coating.
    b. A soft, resilient rubber coating.
    c. A strong, corrosion-resistant metallic coating.
    d. No coating. Any coating would be weaker than the steel pipe.
    e. No coating. Use thick-walled steel pipe.

NATURAL ENVIRONMENTS:
WATER, AIR, AND SOIL

We expect all metals to withstand the normal environments of this earth. Even magnesium, a very reactive metal, holds up well in air and rain. But nature is not always as benign as materials engineers would hope.

Fresh Water

Potable (drinkable) fresh water gets the most precise chemical analyses and controls, but all waters can be quite corrosive under some conditions. The usual cathode reaction is, of course, oxygen reduction.

The dissolved gases O_2 and CO_2 are responsible for much of water's corrosivity, but as corrosion proceeds they become used up, so in closed systems with no contact with air the water becomes less aggressive. Boiler waters and recycled waters in heating and cooling systems usually have the oxygen removed, after it has formed protective films of Fe_3O_4 on steel or Cu_2O on copper. In open systems the O_2 concentration approaches saturation (around 9 ppm at 20°C) at the surface of the water. An example of pitting in stagnant fresh water containing CO_2 is shown in Figure 8.1.
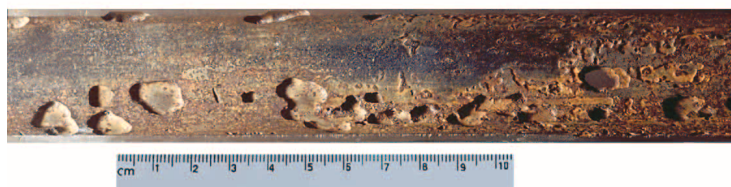
Figure 8.1 Water pipe with flat-bottomed pits,
an indication of CO_2 corrosion.

Dissolved minerals determine the hardness of the water. The major ions in fresh water are the hardness ions, calcium and magnesium, which inhibit corrosion, plus sodium, bicarbonate, sulfate, chloride, and nitrate (see Table 2.2 for formulas of ionic radicals). Ions increase electrical conductivity, hence making corrosion cells more effective, while chloride and nitrate reduce the protectiveness of oxide films. In hard water, bicarbonate will precipitate as calcium and magnesium carbonates, providing a strong, protective layer on the metal surface. Soft waters contain soluble bicarbonate and so are much more corrosive. Water hardness is commonly expressed as ppm $CaCO_3$, with < 50 ppm $CaCO_3$ being very soft and > 350 ppm $CaCO_3$ being very hard. The unit "ppm" stands for parts per million, approximately equal to mg/L, another unit often used to give concentrations of salts in water.

The salts commonly used are NaCl and $CaCl_2$ which increase electrolyte conductivity combined with the chloride damage to protective films on metal. Automobiles splash the slush on each other's painted finish, fender wells, and undercarriage including hot mufflers. Unless promptly washed off, the chloride pits the metal and dooms expensive automobiles to the scrap yard in just a few years. A typical example is shown in Figure 8.3.

Figure 8.3 Automobile corroded by road salt.

Chloride causes paint disbondment and pitting, crevice corrosion, and environmental cracking while also greatly increasing galvanic corrosion and uniform attack. Run-off from the streets also contaminates natural waterways.

Numerous, extensive tests have been made on the use of other salts for deicing or the use of inhibitors with chlorides. They have all reached the same basic conclusions: no other salt is nearly as effective as straight sodium chloride and all others are much more expensive, typically about 20 times as expensive.

A synergism exists between road salts and acid rain or snow. The acid provides the necessary cathode reaction while chloride causes film disruption plus high conductivity. For example, although both Detroit and Montreal use large amounts of road salt, automobile steel corrodes much more in Montreal because of its higher acid deposition.

Reinforcing Steel in Concrete

Reinforced concrete bridges contain steel "rebar" which can corrode dangerously in some conditions. If moisture containing chloride ions penetrates the concrete to the rebar, the steel rusts. The volume of rust created is approximately seven times the volume of steel reacted so that intense pressure builds up to crack the concrete. Cracks allow entry of more water and air so that the rusting continues, often spalling off the concrete (Figure 8.4). Consequently the corrosion damages both the steel and the concrete, and since the steel is required to give the structure tensile strength, a disaster may be in the making.

Chloride is the culprit. Road salt, $CaCl_2$ accelerator sometimes used in cement mixes, sea air, and seawater are possible sources of chloride that damages the strong oxide layer formed by steel in concrete environments. Oxygen from the air is reduced to provide the cathode reaction.

nitrogen oxides in the air that catalyze the reaction of sulfur dioxide to sulfuric acid. Salt deposits on the metal surface also lower the dew point to increase time of wetness.

Atmospheric corrosion is most often combated by protective coatings, either an inert barrier such as paint or a sacrificial type such as a zinc coating on steel. Careful design is also necessary to allow rapid drainage and to avoid crevices.

Example: The Statue of Liberty in New York harbor was repaired in 1986 after an exposure of 100 years. Her 2.5 mm (0.1 in.) copper skin had lost only about 5% of its thickness. The main problem was galvanic corrosion of the iron framework where rust had swelled and pulled rivets through the skin. The iron was replaced by 316L stainless steel which, ten years later, was reported to be holding up well.

Soil Corrosion

Soil is largely made up of insoluble mineral particles that do not directly affect corrosion. The spaces between the particles contain the air and water, dissolved salts, organic matter, and bacteria responsible for corrosion.

Soil is made up of particles of different sizes classified as sand, silt, and clay, from the coarsest to the finest. All the particles have a surface film of moisture, unless arid conditions have completely baked out the soil. Fine clay particles fit tightly against each other, tending to exclude air and oxygen, which would make clay noncorrosive if it were not for anaerobic bacteria and for acidic conditions that often develop in swampy regions. Peats (containing over 50% organic matter), usually found in swamps, decompose organics to produce H_2S and CO_2 gases that dissolve to form acids. Consequently peats and clays are the most corrosive. Light, sandy soils have large pore spaces with plenty of air that allows passivation and uniform corrosion, making them the least corrosive.

Loams, which make up most agricultural land, are mixtures of sand, silt, and clay and thus produce cathodic regions and anodic regions all over the surfaces of buried metals. Oxygen concentration cells, low pH, and bacteria are responsible for much corrosion. The other major factor affecting corrosion is the soil resistivity, which determines the efficiency of electrochemical cells and is quite easy to measure. In general, soils with resistivities below 1,000 μΩ·cm are very corrosive and soils with resistivities over 20,000 μΩ·cm are only slightly corrosive.

Question: Ground rods and steel pilings driven deep into undisturbed soil are often observed to corrode much less than buried pipelines. Why?
Answer: Undisturbed soil tends to be densely packed, often lies below the water table, and contains very little organic matter or oxygen. Water and dissolved salts alone will not corrode metal.

The most serious dangers of soil corrosion are the environmental damage and danger of explosions caused by leaking oil and gas pipelines and leaking storage tanks, both buried and aboveground. These are part of the infrastructure corrosion that, along with bridge corrosion, costs the United States over $250 billion annually.

Example: The clean-up of one leaking gasoline underground storage tank at a service station costs around $100,000, and over a million active tanks are registered with the U.S. Environmental Protection Agency.

The most used method of successfully combating soil corrosion is the use of carbon steel, well coated and cathodically protected, followed by regular monitoring of the metal's condition.

Definition of New Terms

Aerosol: extremely fine liquid droplets floating in a gas.
Catalyst: a substance that speeds chemical reaction without itself being changed.
Deicing salt: salt put on roadways to melt ice and increase traffic safety.
Hardness of water: amount of dissolved minerals that can react to precipitate insoluble products; commonly expressed as ppm $CaCO_3$.
Infrastructure: transportation network (pipelines, railroads, highways, etc.) that ties a nation together.
Loam: soil containing wide variation in size of mineral particles. A typical loam might be 40% sand, 40% silt, and 20% clay.
Peat: soil containing over 50% organic matter.
Potable water: water suitable for humans to drink.
ppm: parts per million (10,000 ppm = 1%), calculated on a weight basis.
Silt: mineral particles in soil, 0.002 to 0.02 mm in average diameter.
$\mu\Omega\cdot$cm: usual soil resistivity unit. 10^8 $\mu\Omega\cdot$cm = 1 ohm$\cdot$metre.

Questions

1. Corrosion rates in water increase approximately linearly with increasing temperature. But reaction rates increase much faster than that: exponentially with temperature. Why does temperature have so little effect in water?
   a. Water molecules are less stable in hot water.
   b. Fewer H^+ ions form in hot water.
   c. Oxygen is less soluble in hot water.
   d. Metal bonding strengthens at higher temperatures.
   e. Diffusion is reduced at higher temperatures.

2. Would a ship traveling at 10 knots have seaweed and barnacles growing on its hull? A knot is a nautical mile (6076 ft.) per hour.
   a. Yes. 10 knots is approximately 5 m/s (16 ft./s).
   b. Yes. Marine growths occur on steel at any velocity.
   c. No. 10 knots is approximately 7.3 m/s (24 ft./s).
   d. No. Marine growth can occur only in stagnant water.
   e. None of the above.

3. Could acid rain create a danger of explosion by generating hydrogen gas from corrosion in a confined space such as a utility manhole?
   a. Yes. Acid + air make an explosive mixture.
   b. Yes. Acid rain will create H_2 gas in corrosion.
   c. No. Acid rain will be neutralized by soil and dirt.
   d. No. H^+ reduction is not a major cathode reaction with acid rain.
   e. None of the above.

4. Automobiles usually corrode from the inside to the outside. Why?
   a. People exhale CO_2 + H_2O which make a corrosive acid.
   b. The cathode reaction works better on the outside.
   c. The inside stays wet longer.
   d. The inside has little or no protective coating.
   e. Bacteria avoid sunlight.

HIGH-TEMPERATURE CORROSION

Corrosion reactions at temperatures well above 100°C (212°F), where water boils, do not have an aqueous environment to act as an electrolyte in an electrochemical cell, although they may still have oxidation and reduction occurring. Anodes are obvious (they're corroding) but the other cell components often become difficult to identify.

Air

Most hot metals in air quickly form a solid oxide coating that greatly slows further oxidation. Obvious exceptions are those oxides that are molten or gaseous, but also unprotective are oxides bonded so strongly that they actually have a smaller volume than the metal volume reacted. The so-called alkali metals, Li, Na, K, Rb, Cs, and the alkaline earth metals, Mg, Ca, Sr, and Ba, all have oxide/metal volume ratios less than one. This ratio of oxide volume/volume of metal reacted is often referred to as the Pilling-Bedworth ratio. Their idea was that when a metal surface reacts with oxygen, the oxide volume must be as large or larger than the metal volume in order to cover the surface completely and protect it from direct reaction with the gas. A complete surface oxide layer would slow further oxidation by requiring solid state diffusion (slow) before reaction.

Question: At high temperatures, copper reacts with air to form the oxide Cu_2O. Would this oxide be protective according to the Pilling-Bedworth criterion? Densities are: Cu = 8.92 g/cm^3, Cu_2O = 6.0 g/cm^3.
Answer: The reaction is $2Cu + \frac{1}{2}O_2 \rightarrow Cu_2O$. That is, two moles of copper will form one mole of oxide. Volume of 1 mole of oxide = (63.55 g/mol Cu x 2 moles + 15.999 g/mol O) ÷ 6.0 g/cm^3 = 23.85 cm^3. Volume of metal reacted = 2 moles of Cu x 63.55 g/mol ÷ 8.92 g/cm^3 = 14.25 cm^3
P-B ratio = 23.85 cm^3 Cu_2O ÷ 14.25 cm^3 Cu = 1.67. Since the Pilling-Bedworth ratio is greater than one, the oxide should be protective.

A further criterion might be added to Pilling and Bedworth's original concept: if the P-B ratio is much greater than two, the oxide *may* become unprotective in time as the oxide thickens, compressive stresses build up within it, and it blisters or cracks.

As solid oxide covers the surface of metal, transport of reactant must occur through the oxide layer so that reaction can continue. Either oxygen must move inward or metal must move outward through the oxide. An oxide with a P-B ratio less than one will be porous or cracked, facilitating the movement of O_2 gas directly to the metal surface. A protective oxide, in contrast, requires solid state diffusion of ions through the oxide layer.

First, oxygen molecules adsorb on the outer surface of the oxide. Next, electrons from the metal's electron cloud leave the metal and migrate quickly through the oxide to the adsorbed oxygen (the

Example: At temperatures above 570°C, iron forms three stable oxides: FeO, Fe_3O_4, and Fe_2O_3. They form in that order on the metal surface, with the Fe_2O_3 on the outside often being incomplete because of its slow growth. This is shown in Figure 9.2.
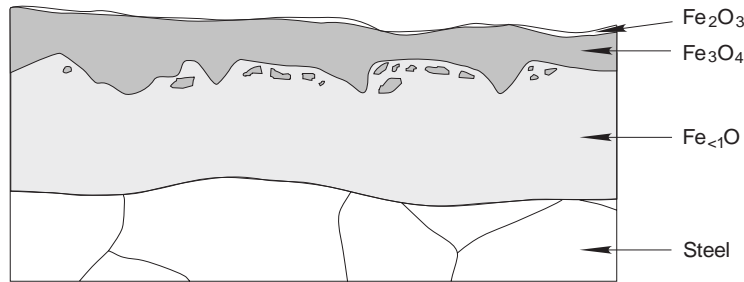
Figure 9.2 Cross-section of oxide scale layers on steel
exposed to air at 1000°C (1832°F).

Oxidation of alloys containing considerable amounts of two reactive metals usually produces two layers of oxide, with the faster-growing oxide forming first. The slower-growing oxide will form on top if metal ions are diffusing outward through the scale, or it will form under the first layer if oxygen ions are diffusing inward.

Combustion Gases

In the combustion of hydrocarbon fuels, metals in equipment such as boilers, internal-combustion turbines, and exhaust piping may suffer serious gas attack, especially above a critical temperature.

In addition to their combustible hydrocarbons, fuels often contain sulfur compounds or inorganic matter that will become ash, either solid or liquid. Coal contains both sulfur and ash. The fuels may be burned either with excess air or with an air deficit. If an excess of air is used, the combustion gases will be O_2, CO_2, and H_2O, along with the unreacted N_2 from the air. With sulfur present in the fuel, SO_2 and SO_3 also form.

If combustion is with an air deficit, the gases will be CO_2, CO, H_2O, H_2, and N_2. Sulfur-containing fuels will also produce SO_2, S_2 vapor, H_2S, and COS oxysulfide.

With fuels that do not contain sulfur or ash, the various combustion gases will oxidize metals much as oxygen or air does:

$$M + H_2O \rightarrow MO + H_2$$
$$M + CO_2 \rightarrow MO + CO$$
$$3M + N_2 \rightarrow M_3N_2, \text{ but } M_3N_2 + \frac{1}{2}O_2 \rightarrow 3\ MO + N_2$$
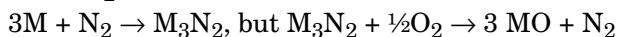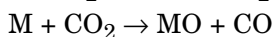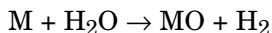
because oxides are more stable than nitrides. (M is just an all-purpose symbol for a metal.) Rates of oxidation in these gases are usually similar, more or less, to reaction with O_2.

Combustion of fuels containing sulfur compounds always produces some SO_2 which will rapidly attack metal to form metal sulfides if the O_2 content of the gas is low. Figure 9.3 diagrams the typical reactions of a metal in a wide range of combustion gas compositions.

Rate constant (k): proportionality constant between amount of reaction and a function of the time.
Scale: thick, visible layer of corrosion product.
Semiconductor: a solid allowing passage of some electric current, intermediate between insulators and electron conductors.

Questions

1. If I calculate the Pilling-Bedworth ratio of beryllium oxide, BeO, as (mol.wt.BeO ÷ density BeO)/(at.wt.Be ÷ density Be), I will have:
    a. the correct ratio.
    b. half the correct ratio.
    c. twice the correct ratio.
    d. the reciprocal of the correct ratio.
    e. none of these.

2. The Pilling-Bedworth ratio of BeO is 1.70. With this ratio, beryllium would be expected to oxidize:
    a. rapidly.
    b. slowly.
    c. slowly at first but perhaps fast after long oxidation.
    d. none of these.

3. If I calculate the Pilling-Bedworth ratio of molybdenum oxide, MoO_3, as (mol.wt.MoO_3 ÷ density MoO_3)/(at.wt.Mo ÷ density Mo) I will have:
    a. the correct ratio.
    b. ⅓ of the correct ratio.
    c. 3 times the correct ratio.
    d. the reciprocal of the correct ratio.
    e. none of these.

4. The Pilling-Bedworth ratio of MoO_3 is 3.27. With this ratio, molybdenum would be expected to oxidize
    a. rapidly.
    b. slowly.
    c. slowly at first but perhaps fast after long oxidation.
    d. none of these.

5. If I calculate the Pilling-Bedworth ratio of yttrium oxide, Y_2O_3, as (mol.wt.Y_2O_3 ÷ density Y_2O_3)/(at.wt.Y ÷ density Y), I will have:
    a. the correct ratio.
    b. ½ the correct ratio.
    c. twice the correct ratio.
    d. 40% of the correct ratio.
    e. none of these.

6. The Pilling-Bedworth ratio of Y_2O_3 is 1.13. With this ratio, yttrium would be expected to oxidize:
    a. linearly.
    b. parabolically.
    c. logarithmically.
    d. at a constant rate.
    e. at a decreasing rate.

Chapter

10

CORROSION IN CHEMICALS

The chemical process industries face some of the nastiest and most varied group of corrosion problems in today's world. Operations that run quite nicely in laboratory glassware often develop new problems when scaled up and put into metal reactors and piping. The most common industrial environments have well-known corrosivities for a wide range of metals, along with precautions and methods of coping with their individual problems. This chapter presents some of this knowledge.

Mineral Acids

Sulfuric Acid

H_2SO_4 is generally acknowledged to be the most important industrial chemical. Often a by-product in scrubbing of flue gases, it is the cheapest and strongest acid, and highly corrosive. Its ancient name was "oil of vitriol," still sometimes used for the industrial grade acid.

For H_2SO_4 concentrations of 70% or higher, carbon steel resists corrosion well and is used for storage and shipment at moderate temperatures. A passive film of $FeSO_4$ forms on steel in the concentrated acid, but once the film is damaged, as with the example in Figure 10.1, attack can be rapid. Steels corrode severely if the concentration drops below 60%.
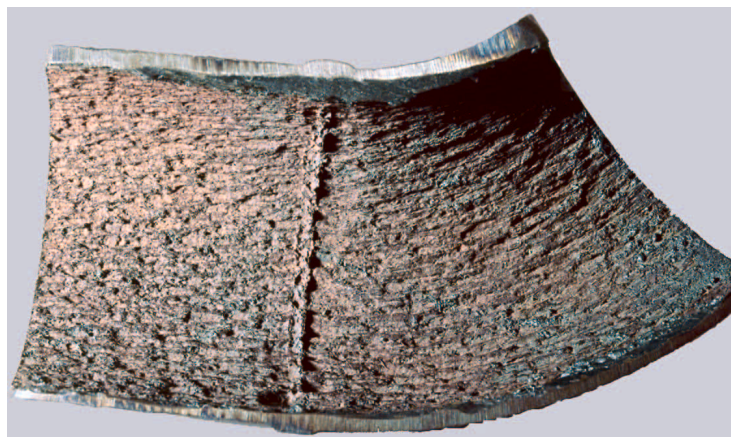
Figure 10.1 Erosion-corrosion at bend of steel pipe in high velocity sulfuric acid.

One precaution must be kept in mind when storing conc. H_2SO_4 in steel: this acid is hygroscopic and will absorb moisture from the air, diluting the acid. In time the acid concentration may drop below 60%, greatly increasing the corrosion rate. Sulfuric acid stored in steel for any great length of time must be prevented from contacting fresh air.

Potassium Hydroxide

KOH or "caustic potash" attacks materials very much like NaOH does, so that materials selection is about the same for both.

Calcium Hydroxide

$Ca(OH)_2$, a lime solution ("slaked lime," "caustic lime"), having only slight solubility in water, is not very corrosive to metals. Steel can contain the solutions.

Ammonium Hydroxide

NH_4OH, a solution of ammonia (NH_3) gas in water up to concentrations of about 30%, creates no great problem for steel if contamination with a little iron doesn't create difficulties. If so, stainless steels can be used. Anhydrous liquid ammonia cracks carbon steel that has not been stress relieved after welding, although as little as 0.2% water in the ammonia will prevent cracking.

Solutions of Dissolved Gases

The gases considered here are CO_2, H_2S, and Cl_2. Dry CO_2 is not corrosive. Hydrogen sulfide gas is noncorrosive at moderate temperature, but at high temperatures it is notorious for corroding expensive nickel alloys. Dry chlorine can be stored in steel at room temperature but with increasing temperature it becomes increasingly corrosive. All gases that dissolve in water decrease in solubility as temperature increases.

Carbon Dioxide

CO_2 dissolved in water makes carbonic acid, H_2CO_3, a weak acid with a pH no lower than 3.5. Hydrogen evolution can occur at pH as high as 5, but with oxygen present a synergistic effect changes the cathode half-cell reaction to a very aggressive oxygen reduction: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ that corrodes steel and copper alloys severely. Corrosion of steel is about the same as for a strong acid of the same concentration. All the stainless steels resist solutions of CO_2, with or without O_2, and thus are the practical choice for most service conditions.

Example: Carbonated water in a soft-drink machine flowed through stainless steel tubing while the syrup flowed through copper tubing. Partial plugging of the outlet nozzle by congealed syrup forced some carbonated water (containing dissolved O_2) back up into the copper line, corroding it through.

Question: Would the corrosion have occurred if dissolved O_2 had not been present?
Answer: Since copper is more noble than hydrogen in the galvanic series, no cathode reaction would be available, and therefore no corrosion would occur.

Hydrogen Sulfide

H_2S can be dissolved in water to about 0.4 wt.% at room temperature, making a weak acid, hydrosulfuric acid (H_2S). It is only mildly corrosive to steel as long as the protective iron sulfide film remains, but sulfide stress cracking is a serious danger to carbon steels and stainless steels.

Oxidizing acid: acid in which the negative radical can decompose, reducing the valence of some atoms. Example: HNO_3 can react so that N receives electrons, reducing its valence.

Scrubbing: removing impurities such as SO_2 from gases.

Slaked lime: lime (CaO) dissolved in water to make calcium hydroxide ($Ca(OH)_2$).

Superferritic stainless: Fe-Cr-Mo stainless steels with bcc crystal structures and with corrosion resistance rivaling the fcc stainless steels.

Vitriol: see Oil of vitriol.

18-8 stainless: austenitic stainless steels with a nominal composition of Fe-18%Cr-8%Ni.

Questions

1. We need a cheap way to neutralize alkaline wastewater before disposing of it. You suggest:
   a. sulfuric acid; it's cheap and strong.
   b. limestone; only water is cheaper.
   c. sodium hydroxide; much stronger than limestone.
   d. acetic acid; this vinegar acid won't damage the environment.
   e. Don't bother neutralizing; alkaline solutions don't create environmental problems.

2. We want to start a new industrial process using hot, concentrated muriatic acid (impure HCl) at high pressure. The question is, what materials should be used for the equipment. You suggest:
   a. carbon steel: easily fabricated and inexpensive.
   b. austenitic stainless steel: designed for corrosion resistance.
   c. glass-lined steel: the lab process worked OK in glass.
   d. rubber-lined steel: hard rubber resists many strong chemicals.
   e. none of the above.

3. We want to start a new industrial process using concentrated caustic potash at high pressure. You suggest:
   a. carbon steel: easily fabricated and inexpensive.
   b. austenitic stainless steel: designed for corrosion resistance.
   c. superferritic stainless steel: resists cracking.
   d. graphite: extremely corrosion resistant.
   e. none of the above.

4. Concentrated ammonium hydroxide is about to be shipped in a steel tank truck. You are asked to okay this:
   a. No problem.
   b. Steel is satisfactory if high purity alkali is not required.
   c. Add water to avoid cracking the carbon steel.
   d. Use stainless steel tanker to avoid contamination.
   e. Use glass-lined tanker to avoid highway catastrophe.

5. Propane gas is burned with an excess of air and the exhaust gases are passed through water. This hot water can then be carried in pipes made of:
   a. steel.
   b. austenitic stainless steel.
   c. ferritic stainless steel.
   d. copper.
   e. brass.

TESTING AND MONITORING

Very likely situations will arise where you will want to try out new materials in a corrosive environment or test materials being received to make sure they meet requirements. Or you may need to find out how changing conditions will affect the equipment ("We can raise our operating temperature a few degrees. Right?") or simply how long equipment will survive before the inevitable disasters strike. This chapter describes the test methods commonly used to answer these questions.

Plant and Field Tests

These tests use the real environment with all its unpredictable fluctuations as the corrosion medium. The advantage, of course, is that no environmental variable that could affect results will be overlooked. The disadvantage is that the exact test conditions can never be precisely repeated; comparison with previous or future studies will always contain some uncertainty.

Actual Service Tests

Using a new piece of equipment in real service is by far the most convincing test of all. If it works well, your problem is solved. If not, try something else. This approach, for someone trying out $250,000 pumps, is time-consuming, expensive, and maybe even dangerous. However, if you want to find the best type of nail to use with pressure-treated wood containing a new preservative, you might build a picket fence using every type and brand of nail on the market. Examination after a few years of service in real weather will show which is superior.

Example: A steel company developed a new coated steel for automobile mufflers. Every employee driving a certain model of car was offered a free muffler, to be exchanged after one year for a conventional type. In this way the company compared their steel with the competition's, under a wide variety of driving conditions.

Service tests provide the definite, unquestionable answer that everyone wants. Their success must be weighed against the time involved, the cost, and possible dangers.

Coupon Tests

Tests of small, identical samples ("coupons") can be made in plant process streams or in outdoor exposure to the weather, ocean, or the like. This allows testing of large numbers of samples (for example, several different metals with various heat treatments, surface finishes, or coatings, with and without crevices, welded or not, etc.).

A wide variety of racks and frames are used to hold the coupons so they do not contact each other or any electron-conducting material, in order to prevent galvanic corrosion. The racks must also be

arranged so that corrosion products from one specimen do not settle on another. Figure 11.1 shows a typical corrosion test spool used for plant or field tests.

Figure 11.1 Corrosion test spool. (ref. 15).

It sometimes happens that inserting coupons, examining them, and removing them would be too disruptive to the industrial process involved. In this case side streams may be built into the equipment so that the coupons are tested in the real environment but not in the actual operation.

For outdoor exposure, racks are often set up so that coupons are at a slight angle from horizontal to allow drainage of water, with a known orientation with respect to sunlight, prevailing winds, distance from the seacoast, or any other important variable. Testing times are typically several years. An example of such test facilities is shown in Figure 11.2.

Figure 11.2 INCO test racks at Kuré Beach, NC. (ref. 16).

Figure 11.5 Typical U-bend test specimen with cracking showing danger of SCC.
Carbon steel sample partly immersed in hot caustic solution was expected to crack
readily and did, so that behavior of other metals could be compared.

Heat transfer conditions, where the metal surface is considerably hotter than the solution contacting it, often give much higher corrosion rates than would be found by simply immersing metal in the solution. Simulation of heat transfer can be achieved by electrical resistance heating of wires, fastening a coupon to an electric soldering iron, or a more elaborate heating arrangement.

Accelerated Tests

Speeding up tests to get quick answers is the most despised approach in corrosion testing. It never gets corrosion rates right, even if samples with known rates are included. It often doesn't even rank different materials in the right order. But nevertheless it is often necessary. How else can a choice be made for canister metal to contain radioactive waste with a half-life of several hundred years? How else can a material be chosen to replace failed equipment when downtime is costing $1,000 an hour?

Example: "Here's what we're going to do, and I know your corrosion testing would take too long, but we won't have any trouble, will we?" This chemical company was going to lower pH from 7 to 2 to triple output. A quick electrochemical test showed that their new plant would last one week.

Accelerating lab tests by increasing corrosive conditions is unreliable. Raising the temperature, adjusting concentrations and pH, or increasing aeration are all tried, usually with only limited success. A salt-spray test, for example, combines much salt, much water, and much aeration to give rapid corrosion, but it doesn't correlate well with most real service except offshore oil rigs, where the corrosion acceleration is only about a factor of three.

instruments are equipped with a computer that integrates the output to show corrosion in real time. ER probes work best at constant temperature because electrical resistance of metals changes with temperature. If temperatures fluctuate, a probe with an internal resistance wire must be used, with corrosion rate calculated from the difference in resistance between the internal wire and the exposed wire loop.
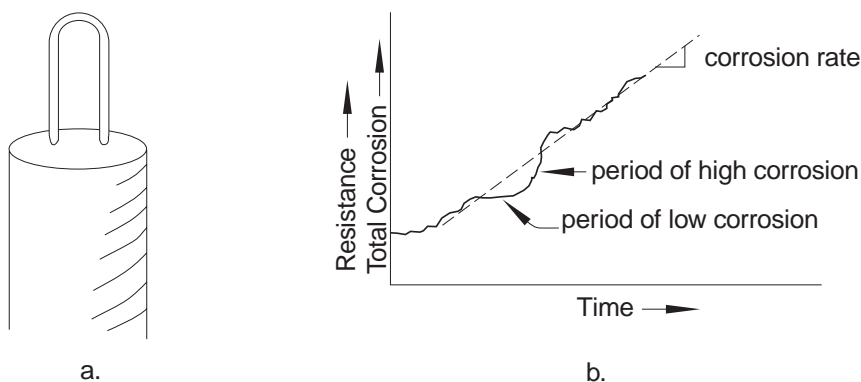
Figure 11.8 (a) Sketch of electrical resistance probe. (b) Graph of output of probe.

Linear Polarization Resistance Probes

LPR probes, the second-most common type, consist of two identical prongs of metal as electrodes (a third electrode is sometimes added for extremely low corrosion rates). A small potential difference (5 or 10 mV) is impressed on the electrodes, as might be found between adjacent anode and cathode sites on a metal surface. The current flow between the electrodes is proportional to the corrosion rate at that moment. Consequently, LPR probes show any high corrosion excursions, making them excellent for troubleshooting.

Sketches of the various electrode arrangements of the probes and a graph of the sort of precise data obtainable are shown in Figure 11.9. This type of probe can only be used in an electrolyte.
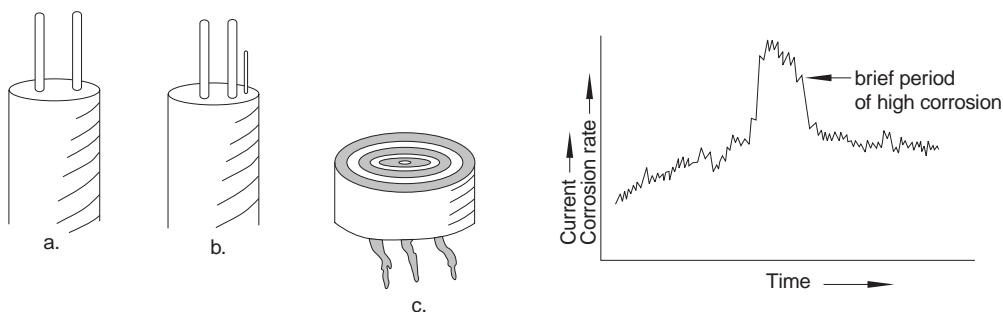
Figure 11.9 Linear polarization resistance probes.(a) two-electrode type;
(b) three-electrode type; (c) flush-mounted type; and (d) graph of output of LPR probe.

Hydrogen Probes

Devices to detect hydrogen in solution or within steel are particularly important where a danger of sulfide stress cracking or other SCC hydrogen cracking exists. The original hydrogen detector consisted simply of a hollow tube with a steel plug at one end and a pressure gauge at the other. A pressure buildup indicated hydrogen.

Linear polarization resistance probe: device measuring instantaneous corrosion rate by imposition of a small potential difference between two electrodes.

LPR probe: see Linear polarization resistance probe.

Patch probe: hydrogen detector consisting of an electrochemical cell fastened to the outside of a vessel. Current through the cell measures hydrogen in the metal. See Barnacle probe

Polarization: change in potential of a metal, caused by the flow of current.

Potentiostat: electronic device allowing the potential of an electrode to be held constant at any set value.

Rest potential: natural potential developed by a metal in solution, with no applied current. See Corrosion potential.

Service test: test of material by using it in equipment in real service conditions.

SSRT: Slow Strain Rate Test for stress-corrosion cracking. Also called CERT test.

Waterline attack: corrosion at or near the liquid/vapor interface where oxygen content of the liquid is at a maximum.

Questions

1. In the 1920's the National Bureau of Standards buried short lengths of many different types of pipe in various kinds of soils all over North America. These tests would be classified as:
   a. field tests.
   b. service tests.
   c. coupon tests.
   d. pilot plant tests.
   e. lab tests.

2. Highway departments sometimes test paints by painting many stripes across a highway. These tests are:
   a. true service tests.
   b. accelerated service tests.
   c. accelerated wear tests.
   d. weathering tests.
   e. field tests.

3. Our outdoor structure will consist of painted carbon steel sheet fastened with galvanized steel bolts. The most information would be gained by making a test of the painted steel and galvanized steel:
   a. separately in lab tests.
   b. fastened together in lab tests.
   c. separately in field tests.
   d. fastened together in field tests.
   e. fastened together in accelerated weathering tests.

4. Rectangular flat metal test coupons in one lab were identified by simply nipping off one corner. The identification method:
   a. prevents calculation of corrosion rate because surface area is reduced.
   b. is limited because only four different types can be identified.
   c. permits up to 12 types to be identified if more than one corner is also cut.
   d. is likely to introduce SCC.
   e. is ambiguous.

Chapter

12

INSPECTION AND FAILURE ANALYSIS

Since corrosion is inevitable, the question to be answered by inspection is "When?" When must equipment be repaired or replaced, or how must conditions be altered to safeguard the metals' life? With failure analysis, the principal question is "Why?" Too many reports concentrate on "how," but the cause of the corrosion and ways of preventing a repeat performance are much more important.

Example: In one famous study of a chemical plant explosion, the investigators built a five story test facility to duplicate plant service, showing exactly how a pipe ruptured. The combination of corrosion, high temperature, and stress could then be avoided in redesigning the facility, although perhaps that combination should be avoided anyway.

Inspection

Visual Inspection

Visual examination will spot more problems and potential problems than any other method. During shutdowns, a thorough inspection of all metal gives a good idea of expected life of the equipment as well as revealing locations needing immediate repair. Corrosion products may have to be scraped off to examine the condition of the metal surface. A strong light and a low-power (5X - 20X) magnifying lens help.

During plant operation, the continual, routine inspections should concentrate on possible cracking in high stress areas, "minor" leaks, hot spots, coating failures, and unusual noises.

Complete inspection reports for each piece of equipment *must* be made and kept on file. Failure to keep thorough records is one of the most costly mistakes a corrosion engineer can make.

Corrosion Monitoring

Crucial equipment often needs continual corrosion measurement for which electronic probes (described in the previous chapter) serve ideally. Probes may be installed permanently in trouble-prone locations with readings taken from them periodically or, more commonly now, the probe outputs go continually to recorders in a central control station. In remote locations a computer may store probe output data to radio it to a central location upon command.

Some operations still prefer insertion of weight-loss coupons into plant streams, with periodic removal for examination and weighing, and replacement with new coupons. Electrical resistance probes generally agree better with weight-loss coupons than linear polarization resistance probes do, but keep in mind that no indirect monitoring method always reveals the complete truth about equipment corrosion.

metal if it is free of defects but redistribute around defects, with some lines leaking out into the surrounding medium. The eddy current technique is similar, detecting defects by the perturbations of eddy currents produced within the magnetized steel.

Radiography is widely used for flaw detection, especially at welds. Photographic film covering one surface of the metal is exposed by a radioactive source on the opposite surface. Flaws and thinned metal show up as dark regions on the film negative.

Pipelines have been cleaned for many years by "pigs" that fit snugly inside the pipe and are pulled or pushed through it. Containing revolving scrapers and brushes, they removed wax, rust, and deposits. In time, feeler gauges were added to measure variations in wall thickness. Now, "smart pigs" carry ultrasonic equipment or magnetic field sensors or other sophisticated measuring devices to map the condition of the entire pipeline.

Failure Analysis

"We never makes the same mistake twice," Albert the Alligator confidently assumed, in the old comic strip "Pogo." But like Albert, we are very likely to repeat our mistakes unless we learn from them.

Sampling

The first major problem to be solved in failure analysis is finding the failed metal. Typically, repairs are made as quickly as possible, and the scrap metal has no value. "Oh, it's probably around here somewhere" is the general attitude of the production personnel. The investigator must get to the failure site immediately or insist that the failed parts be brought in from the field with no delay. After the failure, weathering and mechanical damage can confuse or at least obscure the diagnosis.

If on site, first photograph everything, preferably in color. Photograph the failure from every angle, photograph the adjacent metal, nearby equipment, pipes, whatever. Never again will this opportunity be available. Photographs are absolutely essential where litigation may be involved.

Large sections of failed metal are often removed with a cutting torch. Avoid sampling near these heat-affected regions with their altered microstructures and perhaps also altered chemistry. Even saw cuts can overheat the metal unless done very slowly and carefully.

Small samples can be cut from larger pieces for chemical analysis, metallographic examination, and testing. Each sample must be carefully labeled and the exact location it was taken from recorded. It often helps to mark the metal showing where cuts will be made, with each sample identified, photograph it, and then cut it.

Chemical Analysis

To make sure that the metal is the one it was supposed to be, it's a good idea to start the investigation by taking samples of the environment and the metal for chemical analyses. While minor deviation from alloy specifications is unlikely to be significant, all too often failure has been due to a mix-up of materials. Wet chemistry, spectrographic analysis, and the myriad of modern analytical techniques are all capable of identifying the alloy.

Note: Metals that served satisfactorily in the past sometimes corrode excessively now. Modern metallurgical technology makes them purer and controls their compositions at the low end of the specs so that their corrosion resistance may be inferior in some environments.

Examination of Failure

After visual examination, look at the failure with a binocular microscope at magnifications up to 50X. The excellent depth of field reveals much more than any photograph can. For high magnification, the scanning electron microscope also provides excellent depth perception. The metal microstructure–grain size and shape, distribution of precipitates and inclusions, and the like–will be observable with a metallograph at magnifications of 100X to 600X.

Magnetic particle inspection can often trace cracks to determine origin, path (intergranular or transgranular), and branching. Ferromagnetic materials, such as carbon steels, ferritic and martensitic stainless steels, and many nickel alloys, can be magnetized and coated with a slurry containing ferromagnetic powder that collects at even the finest cracks to reveal them. For nonmagnetic metals, dye penetrants seep into cracks to delineate them.

Mechanical Testing

Failures involving mechanical action as well as corrosion require an investigation of the metal's strength and ductility. The hardness test is the simplest to make and reveals the strength of the metal quite well. Hardness tests can even be made with portable testers on equipment in service.

To establish that the metal was mechanically suitable for the service conditions it was subjected to, tensile tests, fatigue tests, or impact tests may be required. Small samples will have to be cut from the failed metal, with specimen orientation matching the stress situation in the failed part. For example, if a pipe has ruptured circumferentially, test specimens should be cut in the longitudinal direction. In many cases the specimens will have to be very small, so multiple tests can be performed giving more meaningful results.

If testing shows that the metal is mechanically satisfactory, laboratory corrosion tests combined with stress may be necessary to simulate service conditions. Tests will include other alloys also to provide data for any recommended replacement materials.

Information Searches

"There is nothing new under the sun," the Bible says, and certainly corrosion began causing metals to fail almost as soon as humans began using metals. Consequently, it is not only likely that a particular problem has appeared before, but it is also possible that a solution to the problem has been published. Information already available can greatly speed an investigation.

The first and most difficult part of a literature search is to compile a list of key terms to search. These terms define the problem, including the cause of failure, the corrosive environment, the equipment, and the metal. It might be something like:

Corrosion fatigue	Archimedes' screw
Seaweed	Auger
Seawater	Stainless steel
Bromide	Austenitic stainless steel
Chloride	Stainless steel, austenitic

During the search it will quickly become obvious that some terms can be eliminated. "Stainless steel" will give hundreds of references, so it is too broad to be of any help. "Auger" may not show up at all.

Questions

1. A record should be made on each piece of equipment when it is:
   a. replaced.
   b. repaired.
   c. inspected.
   d. cleaned.
   e. taken out of service.
   f. returned to service.

2. The corrosion monitoring method proven most reliable in virtually all cases is:
   a. LP probe.
   b. LPR probe.
   c. weight-loss coupons.
   d. potentiostatic corrosion rate measurement.
   e. none of the above.

3. Measurement of a corroding metal's potential can show:
   a. corrosion rate.
   b. immunity.
   c. severe corrosion.
   d. regions receiving or discharging stray currents.e. none of the above.

4. Nondestructive test methods such as acoustic emission, ultrasonic tests, magnetic flux leakage, and radiography are used to show:
   a. the presence of corrosion.
   b. the instantaneous corrosion rate.
   c. the extent of corrosion.
   d. how corrosion rate is changing with time.
   e. location of defects within the metal.

5. A "smart pig" is used to:
   a. find truffles.
   b. locate corroded regions inside pipelines.
   c. locate corroded regions on pipeline exteriors.
   d. locate welding defects on pipelines.
   e. find corrosion rates of pipelines.

6. Ideally, the sequence of actions that might be taken in a corrosion investigation should be:
   a. Cut out samples of metal for chemical analysis.
   b. Photograph failure and surroundings.
   c. Conduct literature survey.
   d. Go personally to the failure site.
   e. Talk with equipment operators.
   f. Take samples of the environment.

Chapter
13

MATERIALS SELECTION

Proper materials selection prevents corrosion before it ever starts. But materials selection is not simply choosing a corrosion-resistant material. The material must possess other properties, too–strength, ductility, thermal conductivity, a specified thermal expansion, weldability, electrical conductivity, or whatever. In addition to all these properties, the cost must be acceptable.

Metals

Steels and Cast Irons

Carbon steels are the most common materials of construction, not because of their corrosion resistance, which is usually fair to poor in most environments, but because of their excellent mechanical properties and their cost. When used in corrosive environments, steels usually require auxiliary protection, such as protective coatings or cathodic protection. The carbon content, which is so important for mechanical properties, usually has very little effect on corrosion resistance.

Thick sections of steel are used in aqueous solutions where considerable corrosion can be tolerated and where some iron in the solution creates no serious problem. Steel forms a thin, protective rust scale in alkaline solutions, so it is often used to store and ship caustic solutions. Caustic embrittlement may occur in hot solutions, particularly if the caustic can concentrate in crevices or hot spots.

Weathering steels, developed to have approximately four times the atmospheric corrosion resistance of ordinary carbon steels, are low-alloy steels (less than about 2% total alloy content), low in carbon, and contain around 0.4% Cu, Ni, Si, and Cr. During the first year or two of exposure, weathering steels rust much like any other steel but gradually develop a very protective, dark brown scale. While primarily used for bridges and highway guardrails, they are sometimes used for building facades because of their unusual architectural appearance. They corrode excessively if they stay wet for long periods of time or if their surfaces collect large amounts of industrial particulates. Although more expensive than plain-carbon steels, these low-alloy steels are also considerably stronger so they are quite economically competitive. A cross-section of the scale layers formed is shown in Figure 13.1.

High-strength alloy steels, with over 2% alloy content, provide strength but must be protected from corrosion. Furthermore, they are quite susceptible to stress-corrosion cracking in numerous environments.

Cast irons have the advantage of low cost and thick sections that withstand a lot of corrosion despite their fairly high corrosion rates in many environments. Gray cast iron contains graphite flakes that serve as cathodes in the gradual process of graphitic corrosion in stagnant conditions, particularly in soils. High-silicon cast iron (14.5% Si) can withstand brines and sulfuric acid at concentrations up to 100% and temperatures up to boiling. It is often used for impressed-current anodes in cathodic

protection where it forms an extremely resistant silica layer. High-silicon cast iron, while strong and hard, is nearly as brittle as glass and is shaped by casting, not by sawing or welding.
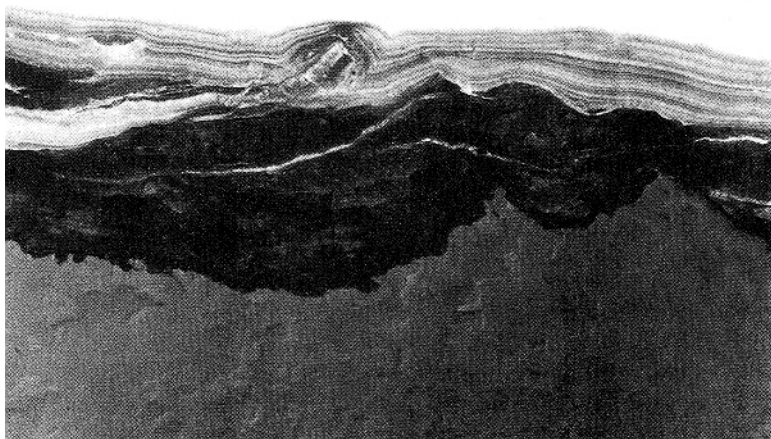
Figure 13.1 Protective scale that has formed on weathering steel. (ref. 19).

Stainless Steels

Stainless steels are iron-chromium alloys containing more than 10% Cr plus other alloying elements sufficient to allow passivation in some environments. The thin, invisible, passive film consists primarily of Cr_2O_3 strengthened by solid solution of iron and the other elements. In many cases it is not more than ten atoms thick and usually under 50 atoms, but it is extremely strong and tough once it forms over the entire metal surface. While stainless steels passivate on exposure to air, a passivation wash with warm, dilute nitric acid or other oxidizing solution (see ASTM A380) produces a stronger, thicker film.

Stainless steels are usually divided into five types according to their structures: martensitic, ferritic, austenitic, duplex, and precipitation-hardenable. Table 13.1 lists some of the most common grades along with an indication of their resistance to uniform attack, pitting, and SCC.

Martensitic stainless steels contain enough carbon to harden by a quench and temper. Chosen where high strength is essential and corrosion resistance is secondary, they are often used for machine parts and cutlery.

Ferritic stainless steels cannot be strengthened by heat treatment and only moderately by cold work. Being virtually immune to stress-corrosion cracking, they are often used for storage tanks. The new "superferritic" alloys are made with extra-low carbon and nitrogen, along with 1.5-2% Mo to give them excellent pitting and crevice corrosion resistance.

The austenitic stainless steels contain nickel (and sometimes Mn) to keep them fcc at all temperatures, also making them non-ferromagnetic. The old 18-8 workhorse contains 18% Cr and 8% Ni, although now more commonly made as 18-10, termed 304L, with the L designating low carbon (< 0.03%) to avoid sensitization. This is the most widely used, and consequently one of the least expensive, stainless steels available today. Chemical processing and food handling equipment are major applications. Superaustenitics include the SMO ("six-moly") alloys with around 6% Mo and

austenite grains. The duplex alloys, especially the high-Cr alloys, have strengths well above the common austenitic stainless steels.

Precipitation-hardenable stainless steels are strengthened by a heat treatment that produces a finely divided precipitate distributed evenly throughout the grains. Strengths achieved in this way compare with those of martensitic stainless alloys, but the corrosion resistance is usually not much better. Uses include aircraft parts as well as valves and pressure vessels.

Nickel Alloys

Where stainless steels don't hold up well, engineers commonly turn next to the high nickel austenitic alloys. Most of these alloys are formulated to resist certain specific corrosives rather than a wide range of corrosive conditions. In general, the nickel alloys resist stress-corrosion cracking much better than iron-based stainless steels. A list of major alloying elements and their effects on corrosion (Table 13.2) describes the alloying principles.

Table 13.2 Major Effects of Alloying Elements in Austenitic Alloys.

Cr	resists oxidizing environments and pitting.
Cu	resists HF; cheaper than Ni.
Fe	resists oxidizing environments; much cheaper than Ni.
Mo	resists reducing environments, pitting, and SCC.
N	reduces pitting; economical substitute for some Ni.
Ti, Nb, Ta	improved corrosion resistance of weld HAZ.
W	resists reducing environments, pitting, and SCC.

The Monels™ (Alloy 400 and its variations), based on 70Ni-30Cu, resist brines, sulfuric acid, and hydrofluoric acid exceptionally well, while very few materials can withstand HF at all.
Nickel-molybdenum alloys (B-2 and other B alloys), based on 70Ni-30Mo, resist hydrochloric acid–virtually the only metals that do. They do not resist oxidizing solutions, not even aerated HCl.

Nickel-chromium-iron alloys (such as 600, 800, and 20) are similar to stainless steels but contain much higher Ni (35 to77%) to make them more resistant to reducing conditions as well as oxidizing conditions, even at high temperatures.

The nickel-chromium-molybdenum alloys (such as 625, C-22, and C-276) can withstand mixed environments, oxidizing and reducing, organics, high temperatures, and SCC conditions that would crack the best austenitic stainless steels. They are often the only choice in environments as varied as waste incinerator gases.

Aluminum Alloys

The standard designations developed by the Aluminum Association (AA) consist of four numbers where the first indicates the major alloying element:

1XXX = no alloy	4XXX = Si	7XXX = Zn
2XXX = Cu	5XXX = Mg	8XXX = Miscellaneous
3XXX = Mn	6XXX = Mg + Si	

The next number indicates any control over impurities, and the last two numbers indicate the specific commercial alloy. The UNS system merely precedes these four numbers by A9. For example,

Miscellaneous Metals

Magnesium and its alloys, with their extremely high strength-to-weight ratios, find service principally in atmospheric environments where a passive oxide protects the surface. In aqueous environments they tend to pit or corrode severely, particularly if connected to another metal. Remarkably, magnesium shows virtually no corrosion in anhydrous hydrofluoric acid (HF) or dry chlorine gas.

Tantalum, usually considered the most resistant of all metals in corrosive chemicals and suitable even at high temperatures, finds little use except as thin linings because of its cost. At temperatures above 300°C (570°F) oxygen or hydrogen embrittle the metal. Like glass, tantalum cannot resist hydrochloric acid or strong alkali solutions.

The precious metals, silver, gold, and platinum, like tantalum, offer corrosion resistance in specific environments where less expensive metals cannot. They can handle anhydrous hydrogen bromide (HBr) at high temperatures, for example, and are the only metals that can do so. Hydrogen iodide solutions attack stainless steels and even silicon iron, but platinum can withstand them. Gold-platinum alloys resist sulfuric acid at all concentrations up to the boiling point. Silver finds extensive use in the pharmaceutical industry because of its excellent resistance to organic compounds. Gold, being quite soft, frequently serves as gasket or O-ring metal. For high-temperature corrosive service, platinum, with a melting point of 1772°C (3222°F), often becomes a practical choice.

Plastics

Plastics generally withstand aqueous solutions far better than metals. In atmospheric exposure, ultraviolet light tends to degrade plastics, and they are limited to moderate temperatures. Most are hydrocarbons, although silicones (silicon-oxygen polymers) are becoming increasingly important.

Plastics can be divided into three groups with different structures and different properties: the flexible thermoplastics, rubbers with their unique elastic properties, and the hard, strong thermosets.

Thermoplastics consist of high molecular weight (typically 20,000 or more) molecules, usually in a noncrystalline, tangled mass although some of the simpler molecules can be partially crystallized. Different formulations produce different molecular weights, different degrees of crystallinity, or different amounts of cross-linking between molecules to give mechanical properties varying all the way from very soft to quite rigid. They soften upon heating, hence the name thermoplastics.

Rubbers have coiled molecules that can be stretched to several hundred percent elastic deformation. They can be vulcanized, which is a cross-linking by sulfur between molecules to prevent excessive softening upon heating, and can even be vulcanized so extensively that they become hard, rigid thermosets.

Thermosets consist of a noncrystalline network of carbon and hydrogen atoms so completely covalently bonded that each plastic part is actually only one giant molecule. They usually form into a hard, rigid mass when reactants are heated, giving them the name thermosets. Reheating never softens them; exposed to high temperatures they gradually char.

Concrete

Concrete consists of an inert aggregate, usually sand and gravel, bonded together by cement. Portland cement is a mixture of finely divided calcium aluminate, calcium silicates, and other minerals that undergoes a hydration reaction when mixed with water, producing a solid gel and binding the aggregate. While the concrete sets in a few hours, it normally take several weeks of curing to reach full strength.

Concrete usually resists the natural environments of air, water, and soil quite well, but being alkaline it is attacked by acids. Even carbonic acid in acidic waters will leach out lime from the cement. Magnesium ions in an aggressive environment may exchange with calcium ions in the cement to destroy the bonding. Sulfates react with the calcium aluminate to form high-volume salts within the concrete, causing it to spall and fracture. Some organic solvents that react with calcium ions can also attack concrete. The most serious damage occurs with corrosion of rebar in reinforced concrete, discussed in the Specific Corrosion Problems of Chapter 8.

Surface treatments of concrete can make it more resistant. Fluoride washes remove any surface ions that could be readily attacked. Sodium silicate, called "water glass," can be painted on the concrete surface to reduce porosity.

Polymer concretes, using binders such as polyesters and epoxies, have approximately 13 times the permeability resistance of portland cement concretes and have comparable strength. Although expensive, they are finding use for bridge overlays, geothermal piping, and acid-resistant sewer piping.

Other Materials

Carbon and Graphite

Carbon and graphite, although extremely fragile, withstand temperatures that would destroy all materials except ceramics and withstand environments that destroy even ceramics.

Carbon, as distinguished from graphite, is an amorphous (noncrystalline) solid that is weak at room temperature but increases greatly in strength with increasing temperature. It can be used up to vaporization temperatures, about 3600°C (6500°F) in non-oxidizing atmospheres, and resists thermal shock very well. Carbon can withstand concentrated sulfuric acid, hydrofluoric acid, and strong alkalies. It is a thermal insulator, with porosity as high as 30%.

Graphite is a crystalline form of carbon, also usable up to about 3600°C. It has the advantage of being self-lubricating and has excellent thermal conductivity (about ten times that of some stainless steels). However, it is not strong and has high porosity.

"Impervious graphite" has been developed to improve graphite's strength. Graphite pores are impregnated with thermosetting resin, such as epoxy or phenolic, and then sealed by polymerizing the resin with heat to produce graphite containing about 10% thermoset. Impervious graphite keeps graphite's high thermal conductivity but cannot be used above the service temperature of the polymer, approximately 180°C (350°F), and is still fairly fragile. It is used for high-purity hydrochloric acid manufacture, can handle HF concentrations up to 60% and sulfuric acids at concentrations up to the very most oxidizing.

Feldspar: natural minerals of aluminum silicates containing Na, K, Ca, or Ba.

Fiberglass: glass fibers.

Filler: substance mixed with plastics and cements to improve certain properties, and in some cases to lower cost.

Fireclay: clay particularly resistant to high temperatures.

FRP: fiber-reinforced plastic.

Glass: noncrystalline ceramic material.

Graphite: the stable crystalline form of carbon.

Hardwood: wood from deciduous trees.

HDPE: high-density polyethylene.

Heartwood: the dense center part of a tree.

Lignin: material cementing the cell walls of wood.

Lime: strong caustic, principally calcium oxide, CaO.

Matrix: continuous phase in an alloy with two or more phases.

Monel: trademark for nickel alloys containing approximately 30% copper.

Neoprene: synthetic rubber particularly resistant to petroleum products.

Nylon: any of several synthetic polyamide polymers.

PE: polyethylene thermoplastic, $(CH_2CH_2)n$.

Porcelain: nonporous ceramic consisting of crystalline mineral particles in a glassy matrix.

Portland cement: mixture of finely divided calcium aluminate, calcium silicates, and other minerals that will set to a strong, rigid solid when hydrated.

PP: polypropylene thermoplastic, $(CH_2CH_2CH_2)_n$.

PTFE: polytetrafluoroethylene thermoplastic, $(CF_2CF_2)_n$.

PVC: polyvinyl chloride thermoplastic, $(CH_2CHCl)_n$.

Pyrex: trademark for a borosilicate glass.

Resin: polymer base; also natural secretion in wood.

Sapwood: the outer growth of a tree.

Silica: SiO_2, crystalline or glassy.

Silicone: thermoplastic containing principally silicon and oxygen.

Silicon iron: corrosion-resistant cast iron containing approximately 14.5% Si.

Softwood: wood from coniferous trees.

Stoneware: low-porosity ceramic consisting of crystalline particles with a glassy binder.

Superaustenitic: austenitic stainless steels containing molybdenum additions and very low interstitials.

Superferritic: ferritic stainless steels containing molybdenum additions and very low interstitials.

Teflon: trademark for a group of thermoplastics containing carbon and fluorine.

Thermoplastic: synthetic, chain-type polymer that softens when heated.

Thermoset: synthetic, network-type polymer that does not soften when heated.

Vulcanization: cross-linking rubber with sulfur to improve properties.

Water glass: Na_2SiO_3 dissolved in water to make a viscous syrup.

Weathering steel: low-alloy steel containing Cu, Ni, Si, and Cr, having high resistance to atmospheric exposure.

Wood flour: finely divided wood particles, much finer than sawdust.

Questions

1. Carbon steel is the material most used in corrosive environments because:
    a.   it is cheaper than most materials.
    b.   it is stronger than most materials.
    c.   it is more corrosion resistant than most materials.
    d.   it can be formed and welded readily.
    e.   it is readily available in every form.

2. Stainless steels are renowned for their resistance to:
    a. chloride-containing solutions.
    b. oxidizing environments.
    c. reducing environments.
    d. stress-corrosion cracking.
    e. caustic solutions.

3. Nickel alloys are often the materials of choice where:
    a. cost is important.
    b. the environment is caustic.
    c. stainless steels might suffer SCC.
    d. fluorides are present.
    e. either oxidizing or reducing conditions may exist.

4. Aluminum and its alloys are often selected where:
    a. solutions are high in chlorides.
    b. solutions are caustic.
    c. dilute nitric acid is present.
    d. high strength-to-weight ratio is required.
    e. the environment is the atmosphere.

5. Copper and its alloys are often selected for environments of:
    a. fresh water.
    b. seawater.
    c. dilute nitric acid.
    d. ammonia solutions.
    e. sewage.

6. Thermoplastics generally are:
    a. organic compounds.
    b. increased in tensile strength with increasing temperature.
    c. recyclable.
    d. network polymers.
    e. more resistant to aqueous solutions than most metals.

7. Thermosets generally are:
    a. organic compounds.
    b. recyclable.
    c. network polymers.
    d. suitable for higher temperatures than thermoplastics.
    e. good in alkaline aqueous solutions.

8. Most glass used in corrosive conditions is good in environments involving:
    a. thermal shock.
    b. mechanical shock.
    c. fluoride.
    d. alkalies.
    e. high heat transfer.

PROTECTIVE COATINGS

Steel is the metal most commonly coated to improve its corrosion resistance. Other materials as well as steel are coated for high-temperature resistance, wear resistance, or for appearance.

Before coatings are applied, the base metal surface must be thoroughly cleaned. For mill-applied coatings, the metal is commonly pickled in an acid bath to remove any oxidation and surface contamination and then rinsed thoroughly. In the field, the base metal is usually cleaned mechanically by wire brushing or grit blasting.

Metallic Coatings

Heavy linings and overlays of corrosion-resistant metals, whether applied by welding metal sheets on the steel, weld overlay, explosive bonding, or rolling will basically perform as the surface metal does.

Cladding by roll-bonding a thin sheet of high-purity aluminum onto a strong but corrodible aluminum alloy is called Alcladding. The pure aluminum becomes quite corrosion resistant because it forms a strong passive film.

Thin metal coatings are much more widely used than cladding. Thin layers are applied by techniques such as hot dipping, electroplating, and thermal spraying.

Metal coatings can be either cathodic or anodic to the base metal. If the coating is cathodic it must be perfect. Any minute flaw that allows corrosive solution to penetrate to the base metal sets up a galvanic cell with a high cathode/anode area ratio.

If a coating is anodic to a steel base, the coating is sacrificial, protecting the steel. But, the coating usually must corrode more slowly than steel would if it were uncoated. Otherwise, it would be cheaper just to use thicker steel and let it corrode.

Hot Dip Coatings

Galvanizing consists of immersing steel articles in a bath of molten zinc. When removed, excess zinc runs off to leave a complete zinc layer that is bonded metallurgically to the steel. The zinc must be a minimum of 0.1 mm (4 mils) thick (ASTM A 123), with thicker coatings giving proportionally longer service lives.

The very ductile zinc deforms readily if the steel must be bent after being coated. Zinc also acts as a lubricant, allowing bolts to be torqued more tightly than would be possible with the friction of steel against steel. Hot-dip galvanizing is shown in Figure 14.1.

Chemical Conversion

Chromate and dichromate coatings have been widely used on aluminum and magnesium and on electroplated zinc and cadmium to provide excellent corrosion resistance. Steel sheet may be chromated to provide protection and to provide a base for polymer lacquer in "tin-free" cans. A problem with chromate coatings is the disposal of effluent with its risks of environmental pollution.

Phosphate conversion coatings, produced by spray or dipping with phosphoric acid or metal phosphate solutions, provide an excellent base for paints and offer some protection, although a following chromate treatment greatly improves corrosion resistance. These coatings have been widely used in the automotive industry in places on car and truck bodies where minor corrosion may occur. Thick manganese phosphate coatings are porous, not very protective, but can absorb inhibited oils so they are commonly used for steel bolts, nuts, and screws.

Bluing of steel produces a beautiful finish on firearms but offers little corrosion protection. The porous Fe_3O_4 layer absorbs oils and waxes that can provide the actual protection. Traditional bluing involved heating the steel to around 300°C (575°F) until high-temperature oxidation produced the oxide. Chemical bluing occurs when the steel is immersed in a hot alkali bath. Bluing has largely been superseded by phosphate conversion coatings, particularly for military weapons.

Rust converters are widely sold with the claim that the solutions will transform the rust on steel to an adherent, protective layer. The formulations contain tannic and phosphoric acids plus surfactants and corrosion inhibitors. They do convert the various rust compounds to the more stable and better adhering magnetite (Fe_3O_4) form, if the rust is no more than 2.5 µm (0.1 mil) thick. They do not remove moisture and salts that may have been trapped in the rust, so they are satisfactory for mild service conditions or for temporary protection only.

Nonmetallic Coatings, Linings, and Tapes

Coatings can protect metals in several ways, the most important being:

1. a barrier layer, preventing the environment from contacting the metal;
2. an electrically resistive layer, imposing such a high resistance between anodes and cathodes that corrosion current is effectively stifled;
3. an inhibitor layer, containing chemicals that restrict anode and/or cathode reactions;
4. a cathodically protective layer, containing metal powder that corrodes preferentially to preserve the substrate metal.

Linings and tapes are thick enough to serve as barrier layers, needing no other mechanism to stop corrosion, whereas paint films are too thin and porous to be effective barriers. Paints, which are applied as liquids that solidify on the metal surface, use one or more of the other mechanisms to protect the metal. Paints all serve as electrically resistive layers; in fact, the electrical resistivity of the paint film is used as a measure of its protective qualities.

With today's concerns about environmental pollution and health dangers, coatings may also have requirements other than protecting the metal. Among them are:

*   antifouling characteristics to discourage growth of barnacles, mussels, sea grass, and the like. Since toxic coatings are now prevented by law, silicone-based, slippery coatings are being used.

*   coatings that can seal old lead-based paint coats, to avoid their difficult and very costly removal.

Table 14.1 Comparison of Paint Systems.

Coating	Preparation[1]	DFT[2]	Cost[3]	Years[4]	Solvents[5]
Alkyd primer/topcoat	3	4	0.14	4	1
Coal tar epoxy	3	16	0.31	10	8
Epoxy 100% solids	Brush	6	0.21	6	N
Epoxy, water-based	3	6	0.39	10	5
Epoxy/acrylic urethane[6]	2	3	0.31	10	4
Zinc-rich, inorganic	3	3	0.19	16	19
Zinc-rich, organic	3	3	0.21	7	16

Notes:

1. Preparation = NACE surface preparation number. Brush = wire brushing, hand or power.
2. DFT = minimum dry film thickness in mils. To get μm, multiply by 25.
3. Cost (approximate) for paint per square foot in 1996 US$ for spraying. To get $/m^2, multiply by 10.8.
4. Years service expected in moderate industrial atmosphere before maintenance repainting is required.
5. Solvents = years of resistance to splashes and spills of hydrocarbon solvents and gasoline. N = not recommended.
6. Epoxy primer/acrylic urethane topcoat.

Source: primarily G.H. Brevoort, M.F. MeLampy, and K.R. Shields, MP 36, no. 2, p. 39 (1997).

Zinc-Rich Paints

As Table 14.1 shows, zinc-rich paints provide superb corrosion protection. They contain 90-95% zinc powder held together by a binder that can be an inorganic silicate or an organic such as epoxy. The organic zinc can be topcoated for additional protection but the inorganic zincs perform best when left exposed to the environment, as long as the pH remains near neutral (pH 5 to 10).

With inorganic zinc coatings, the binder forms zinc silicates where it contacts the zinc powder particles. Air and moisture from the environment penetrate coating pores to form insoluble zinc hydroxides and carbonates which plug pores and flaws. The zinc silicates are believed to form chemical bonds with the metal surface, preventing undercutting of the coating at flaws–the cause of most coating failures. An example of undercutting followed by paint blistering is shown in Figure 14.3.

Figure 14.3 Pipe coating undercut by corrosion at small surface abrasions. (ref. 27).

and flushed. High-density polyethylene linings are squeezed down so that they can be pulled through the pipes for up to about 800 m (about half a mile). The linings are then allowed to expand to the pipe wall by running hot water through them so that they return to their original shape. Nylon liners, instead of HDPE, have been used where higher melting point, additional strength, and better resistance to organics are required.

In cities, lining buried water pipes, gas lines, and such, without having to dig up all the streets, has been the only practical way to provide these municipal services.

To protect the outside of pipes, as well as bridge and jetty piles, from soil and water, heavy shrink-fit plastic wrap with an inner coating of a sealant such as coal-tar epoxy provides the barrier to seal out the corrosive environment. An alternative is the spiral wrapping of heavy polyethylene tape, also with a sealant, often with up to 50% overlap to give essentially a double tape thickness. These wraps are commonly applied at the pipe mill where good surface preparation is easiest. Ends of the pipe sections are left uncoated for welding in the field, followed by shrink-fit polyethylene sleeves or tape over the welds.

Inspection and Maintenance

For paint coatings, a touch-up is usually required at failed and damaged areas about one-fourth of the way through a coating's life and a maintenance repaint coat about halfway through. Paints fail by undercutting at scratches in the coating and at sharp edges and corners of metal because the paint is thinnest there. Figure 14.5 shows a rather typical test panel with failure beginning at the edges.

Figure 14.5 Edge corrosion on a painted
test coupon in marine atmosphere. (ref. 29).

While coating failures occasionally occur because the wrong coating was specified for the service conditions actually encountered, most early failures can be blamed on either poor surface preparation or improper application. Comparison with small standard samples makes inspection of surface preparation relatively easy; either the surface meets the specs or it must be recleaned.

Definition of New Terms

Alclad: aluminum alloy bonded to corrosion-resistant, pure aluminum cladding.

Anodizing: protective oxidation of a metal surface by making it the anode in an electrochemical cell.

Antifouling coating: coating formulated to prevent attachment and growth of marine organisms such as seaweed and barnacles.

Coating: protective solid film on metal, less than 0.5 mm (20 mils) thick, when differentiated from linings.

Conversion coating: coating formed on metal by reacting its surface to leave an adherent metal compound for protection.

DFT: abbreviation for dry film thickness of paint after it solidifies on a surface.

Galvalume: alloy of 55Al-43.4Zn-1.6Si, more resistant than zinc to atmospheric corrosion.

Grit blasting: cleaning of metal surface by spraying it with sand or other hard grit at high velocity.

Hot dipping: applying a coating to metal by dipping it in a molten bath of a more corrosion-resistant metal.

Inorganic zinc paint: paint with silicate binder and zinc powder pigment.

Lining: protective coating greater than 0.5 mm (20 mils) thickness.

Organic zinc paint: paint with an organic polymer binder and zinc powder pigment.

Primer: in painting, the first coat, chosen to bond well with the substrate.

Roll bonding: fastening sheets of two different metals by rolling them together under high pressure.

Rust converter: coating designed to react with surface rust in forming a more protective layer.

Sherardizing: coating of metal parts by tumbling them with heated zinc dust.

Slip: slurry of ceramic and glassy powders in water.

Slushing compound: inhibited oil, wax, or grease in which metal parts are dipped for temporary corrosion protection.

Spangle: shiny crystal on metal surface, such as on hot-dipped galvanized steel.

SSPC: abbreviation for Steel Structures Painting Council.

Tenting: tendency of plastic tapes to stretch straight over a rough surface instead of following surface contours.

VOC: abbreviation for volatile organic compounds.

Zinc-rich paint: paint containing pigment of zinc metal powder.

Questions

1. Galvanizing applies a coating of these metals:
   a. aluminum.
   b. lead.
   c. tin.
   d. zinc.
   e. none of the above.

2. Uneven plating in an electroplating bath would likely be related to:
   a. cathode/anode area ratio.
   b. distance effect.
   c. electronic conductance.
   d. ionic conductance.
   e. potential difference between electrodes.

Chapter

15

INHIBITORS AND CHEMICAL TREATMENT

Corrosion inhibitors are chemicals usually added in small amounts to the environment, but are sometimes included in protective coatings or alloyed in the metal to be protected. Their purpose is to interfere with corrosion reactions–the anode reaction, the cathode reaction, or both. The inhibitors may react with the metal surface as passivators and inorganic precipitation inhibitors do, or they may merely adsorb on the metal surface, as the organic filming inhibitors and cathodic poisons do. Inhibitors prevent general corrosive attack; most are not effective in preventing localized attack such as pitting or in stopping cracking.

A different approach to corrosion control is chemical treatment to modify the environment, making it less corrosive by removing much of the cathode reactant. If the dissolved oxygen or hydrogen ions are tied up, they will be unavailable to receive electrons from the metal cathodes, and corrosion practically ceases.

Inhibitors

Inhibitors reduce corrosion by altering the metal surface, either covering the surface completely so that the environment cannot contact the metal, or affecting specific surface sites. These sites may be cathode sites where reactants would try to adsorb or anode sites where water molecules would try to attach to dissolving metal ions.

Passivators

Passivators react with the metal surface to form a complete, but thin, layer of reaction product, a passive film of hydrated oxide.

Direct passivators are strong oxidizers that react with the metal surface to form a complete passive layer on the surface. They are anodic inhibitors: that is, the anodes react rapidly until they are all covered with the passive film. That also means that the inhibitor must be maintained at the proper concentration and continually circulated to ensure that all anodes remain passivated. Insufficient passivator could let the corrosion potential drop to the active peak and greatly *increase* corrosion!

This is illustrated in the sketch of the polarization curve shown in Figure 15.1. Also note on this curve that anodic inhibitors such as passivators raise the corrosion potential of the metal considerably–the obvious indication that it is an anodic inhibitor. Cathodic inhibitors would lower the corrosion potential, while inhibitors that affect both anode and cathode sites would have little effect on potential.

The critical concentrations of passivators such as chromates (CrO_4^{2-}), nitrites (NO_2^-), molybdates (Mo_4^{2-}), and tungstates (WO_4^{2-}) are fairly low, in the range of 0.1%, but passivators do get used up in

The organic inhibitors consist mostly of straight hydrocarbon chains, typically about 18 carbons long, with a polar end that will attach to the metal surface, something like the sketch in Figure 15.3a.
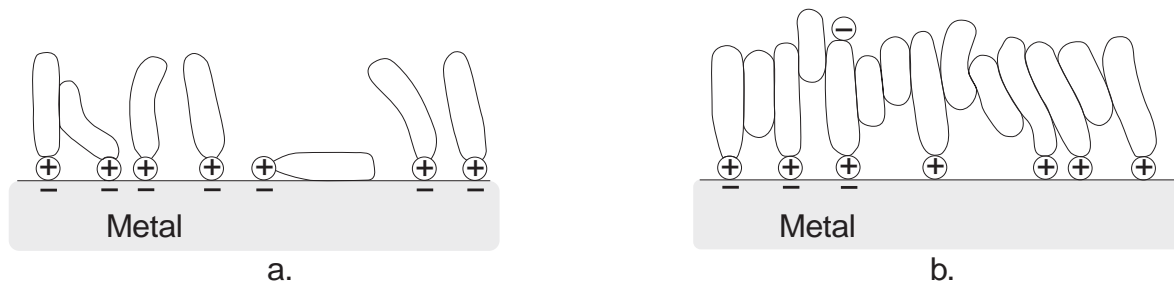
Figure 15.3 Schematic showing arrangement of organic adsorption inhibitor molecules on metal surface, for (a) a single type of polar organic compound; (b) a mixture of organic molecules.

The polar end may be either positive or negative. Amines, with their slightly positive nitrogen, are favorites. Molecules with negative polar ends include thio compounds —S^-), aldehydes (—O^-), and alcohols (—OH^-). Adsorption usually covers the entire metal surface although a few inhibitors adsorb mainly at anode or at cathode sites on the metal.

Addition of other organics to the blend may include molecules that are not polar but cling particularly well to polar molecules (sketched in Figure 15.3b), thus building up a much more complete barrier layer. Also, an organic inhibitor must be dispersed in an aqueous solution as an emulsion of extremely small micelles. Additives will be needed to aid in forming these micelles and keeping them dispersed. Surfactants improve wettability and adherence to the metal surface.

Adsorption inhibitors find their major use in protecting metals from strong acids, although some inhibitors are designed for neutral environments. One essential qualification must be made: the system must be clean–no dirt, no deposits, no corrosion products. These adsorption inhibitors adsorb on any surface (and porous rust has a tremendous surface area). A dirty system can soak up thousands of dollars of inhibitor with no effect on the corrosion whatever.

Example: A Prudhoe Bay, Alaska pipeline lost 70% of its inhibitor within 24 ft. of the injection point due to adsorption on production sand entrained in the crude oil.

In spite of cost, inhibitors can be quite practical. In one test on four oil wells, addition of an inhibitor at a cost of $5,000 reduced corrosion and increased production to give combined savings and earnings of $420,000.

Vapor-Phase Inhibitors

Vapor-phase inhibitors, most of which are the organic adsorption type, protect metal surfaces from atmospheric corrosion during storage and shipment. Extremely small amounts can evaporate to fill an entire warehouse and prevent rusting of the steel stored inside. Or machined parts may be shipped in plastic bags which have been impregnated with a vapor-phase inhibitor.

A few vapor-phase inhibitors protect by reacting rather than by adsorbing. Some organic nitrites react with moisture on the metal surface to passivate, or a vapor-phase inhibitor may be injected into sour gas pipelines to react with the hydrogen sulfide in the gas to form protective sulfide on the inside of the pipe.

Cathodic Poisons

As was mentioned in the discussion of hydrogen embrittlement caused by the sulfide ion (Chapter 7), S^{2-} adsorbed on cathode sites will prevent removal of adsorbed H atoms as H_2 gas molecules. Cathodes become clogged with sulfide and unpaired H atoms, essentially shutting down corrosion. Elements other than sulfur can adsorb at cathodes: phosphorus (P), arsenic (As), and antimony (Sb) being the most important.

Example: Sulfuric acid can be inhibited by addition of a small amount of arsenic trioxide. Reaction at cathode sites of a steel surface would be:

$$As_2O_3 + 6H_{ads} \rightarrow 2As_{ads} + 3H_2O.$$
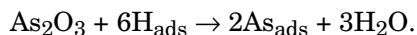
Cathodes now have arsenic plated on them, protecting the steel from corrosion.

Cathode poisons would not be used to protect metals where danger of hydrogen embrittlement exists, as with high-strength steel.

The cathodic reduction of dissolved oxygen can also be poisoned. To improve the corrosion resistance of brass in seawater, addition of 0.1% As, Sb, or P was made to Admiralty brass. When inhibited Admiralty brass corrodes, O_2 at cathode sites produces OH^- ions which react with dissolved As to adsorb $As(OH)_4^-$ on cathodes, preventing further O_2 adsorption. Table 15.1 shows the variety of inhibitors that can be used to protect steel in various environments.

Table 15.1 Typical Inhibitors for Steel in Industrial Applications.

Environment	Inhibitor	Inhibitor Type
Potable water	Polyphosphates	Indirect passivator, conversion layer former
Cooling water	Calcium bicarbonate	Inorganic precipitation
Engine coolant	Borax	Indirect passivator
Brine	Quaternary amines	Adsorption
Pickling acid	Thiourea	Adsorption
Nitric acid	Dichromate	Direct passivator
Cement	Calcium nitrite	Direct passivator

Chemical Treatment

Chemicals added to solutions in order to reduce their corrosiveness include oxygen scavengers and neutralizers that remove the cathode reactants, as well as biocides that reduce the threat of localized attack caused by algae and bacteria.

Oxygen Scavengers

Oxygen scavengers eliminate the cathode reactant, dissolved oxygen, from neutral and basic solutions by tying the oxygen up in innocuous compounds. Common scavengers include sulfites which react with the oxygen to make the more stable sulfates: $SO_3^{2-} + O_{2(soln)} \rightarrow SO_4^{2-}$. Sulfites are often added to water floods in secondary recovery for crude oil production. Corrosive brines in the rock formation will then have no effect on the steel piping.

Proprietary compounds containing hydrazine (N_2H_4) are commonly added to high-temperature boiler waters:

$$N_2H_4 + O_{2(soln)} \rightarrow N_2\uparrow + 2H_2O$$
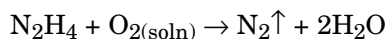
eliminating enough oxygen so that porous, unprotective ferric oxide (Fe_2O_3) scales will not form, but leaving enough oxygen so that the protective magnetite (Fe_3O_4) scale does form.

Adsorption inhibitors are often used along with scavengers but passivating inhibitors are not, since dissolved oxygen would aid passivation.

Neutralizers

Neutralizing acids by removal of hydrogen ions obviously eliminates the cathode reactant to form a noncorrosive solution. Strong bases such as sodium hydroxide (NaOH) can neutralize acids quickly and inexpensively.

Acidic vapors such as hydrogen chloride are often neutralized with ammonia (NH_3) gas where precipitation of solid crystals of the product, NH_4Cl, will not cause crevice corrosion.

More difficult problems, and very common ones, occur in gas streams containing water vapor plus carbon dioxide, or in vapors of organic acids. These often condense at inaccessible locations in the equipment and the neutralizer must condense along with them. Amines (organic nitrogen compounds) that will condense at the same temperature as the acid are often selected as neutralizers because amines are mild bases.

For boilers, the steam usually contains some CO_2 formed by decomposition of carbonates in the water. To neutralize carbonic acid (H_2CO_3) in the condensate, a short chain amine that is water soluble (not a filming inhibitor), such as morpholine, is commonly added to the boiler feed water.

Biocides

Biocides prevent fouling by algae, fungi, and bacteria that could initiate localized corrosion by the various mechanisms discussed in the section on bacterial corrosion in Chapter 6. A good example of the problem to be faced is the fouled heat exchanger shown in Figure 15.4. Ordinary organic adsorption inhibitors cannot be used to control microbially-induced corrosion (MIC). Bacteria need organic matter in their metabolic processes and greedily consume most organic inhibitors.
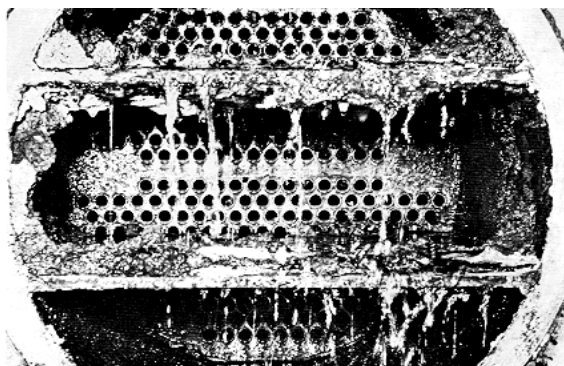
Figure 15.4 Biological growths in a heat exchanger. (ref. 31).

Questions

1. A scavenging inhibitor used in an oxidizing acid such as nitric acid would:
    a. be suitable for an acid-resistant metal such as copper.
    b. be suitable for protection of steel.
    c. be unsuitable.
    d. require frequent replenishment.
    e. slow corrosion but not stop it.

2. A passivating inhibitor could protect a steel tank containing:
    a. brine.
    b. deaerated water.
    c. hydrochloric acid.
    d. a permanganate oxidizing solution.
    e. a thiosulfate reducing solution.

3. A system to be protected with an adsorption inhibitor should be cleaned first because:
    a. circulation of inhibitor is improved by laminar flow.
    b. inhibitor may protect dirt.
    c. rust will react with the inhibitor.
    d. rust would adsorb inhibitor.
    e. stockholders want to see profits.

4. Compared with one-component inhibitors, proprietary adsorption inhibitor formulations:
    a. are easier to select by inexperienced personnel.
    b. are less expensive.
    c. disperse more uniformly in solution.
    d. form a more complete surface film.
    e. need to be added only once.

5. Poison inhibitors may block:
    a. adsorption of dissolved oxygen.
    b. adsorption of hydrogen ions.
    c. anode reaction.
    d. cathode reaction.
    e. both anodes and cathodes.

6. Neutralizers may:
    a. convert metal surface to a protective compound.
    b. form a barrier between metal and solution.
    c. increase pH of condensate.
    d. increase pH of solution.
    e. remove acidic components from gases.

7. Scavengers may change solution composition by removing:
    a. acid.
    b. hydrogen ions.
    c. inhibitors.
    d. metal ions.
    e. oxygen.

CATHODIC AND ANODIC PROTECTION

Electrical protection can slow corrosion or even stop it completely. Protection can be retrofitted with the metal already in service, and is usually far less expensive than other methods. Protection can be achieved in any electrolyte, but not in vapor, organic liquids, or any environment that cannot carry electrical current.

Cathodic protection reverses the current of electrochemical cells so that anodic areas on the metal are no longer able to release metal ions. The metal to be protected, usually steel, becomes entirely a cathode, and thus doesn't corrode. The environments for cathodic protection are soil, water, or dilute solutions.

Anodic protection is almost the opposite; a passivating metal is made the anode in an electrochemical cell, passivating the metal to reduce corrosion to an extremely small rate. Although not used nearly as much as cathodic protection, anodic protection can be employed in very corrosive environments that become impractical for cathodic protection.

Cathodic Protection

In an electrochemical corrosion cell, positive currents (metal ions) flow from anode sites into the electrolyte. Cathodic protection reverses this flow, forcing current onto anodes to buck out any current that tries to escape from the metal. In theory, cathodic protection only needs to prevent any current flow; in practice, the current flowing onto the metal exceeds the current flowing off, so that the metal surface becomes a cathode everywhere.

Cathodic protection protects from both uniform corrosion and localized attack, whether from galvanic or environmental composition cells. It prevents the corrosion component of stress-corrosion failures, but not the mechanical component. So, while corrosion fatigue is stopped, the metal can still fail eventually from fatigue.

Two types of cathodic protection are available: sacrificial (also called galvanic) cathodic protection and impressed-current cathodic protection. Each has its advantages and limitations, and on some complicated structures such as offshore oil platforms, both systems may be used.

In general, however, sacrificial cathodic protection is more likely to be used on small structures, for short-term protection, or where electrical power is not available. Impressed current is more often used for extensive systems and systems where corrosion conditions must be known at all times.

Sacrificial Cathodic Protection

Steel is protected if a metal more corrodible than steel is fastened to it in the corrosive environment. The metals commonly used as galvanic anodes are magnesium and some of its alloys or high-purity
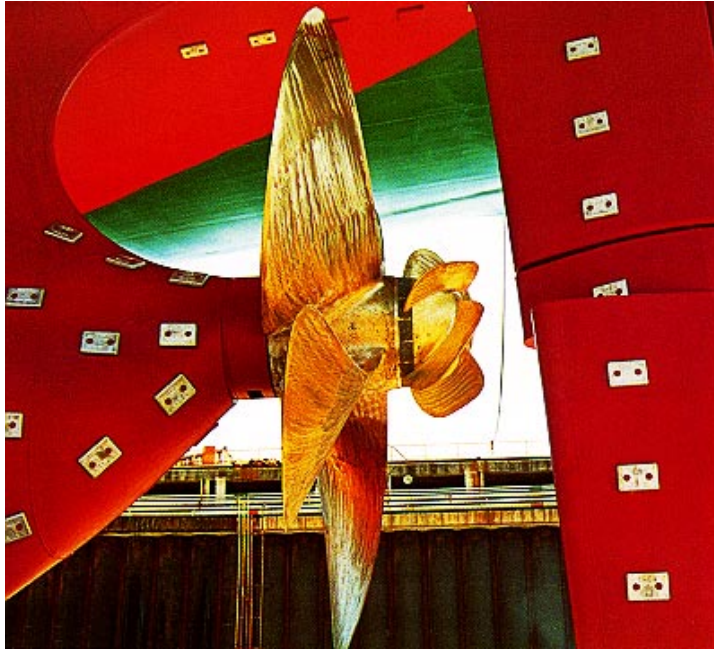
Figure 16.2 Zinc anodes on merchant ship to protect propeller and rudder. (ref. 32).

Impressed-Current Cathodic Protection

To overcome the voltage limitation of sacrificial cathodic protection, the electrochemical cell set up between the protected steel cathode and the anode can have a DC power source added to the external circuit. In this way, any desired amount of current can be forced onto the steel to protect it. To avoid rapid anode consumption, noncorroding anodes are used, rather than sacrificial anodes.

The anode reaction of the cell is no longer the dissolution of the anode but now becomes oxidation of some species in the electrolyte. For most solutions this will be the formation of oxygen gas from the water:

$$2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^-$$
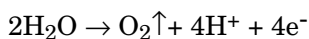
as the anode half-cell reaction. At the protected metal cathode the corrosion reaction should just be reversed:

$$M^+ + e^- \rightarrow M\downarrow$$
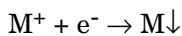
while any excess protective current generates hydrogen:

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$$
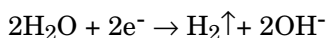
with alkaline conditions developing around the cathode. Calcium ions and other cations also move to the cathode so that a cathodically protected structure gradually develops a calcareous crust on it which contributes some additional protection as a coating.

The electrical arrangement for impressed-current cathodic protection is shown schematically in Figure 16.3. Where a power line is available, the direct current power source is a rectifier that

converts AC to DC In remote areas, the power is usually taken from batteries that are kept charged by a motor generator, windmill, solar cells, or the like. For protection of natural gas pipelines, thermoelectric generators sometimes provide the power.
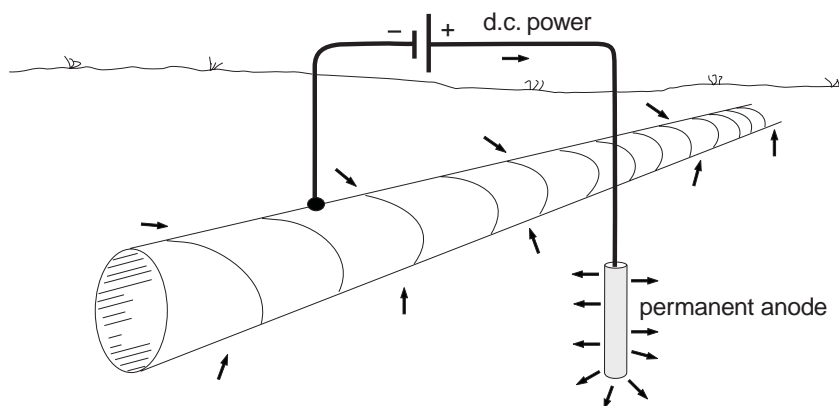
Figure 16.3 Schematic diagram of impressed-current cathodic protection of a buried pipeline. Arrows show direction of positive current flow. Current flows to any flaws in the pipe coating.

Permanent anodes have most commonly been graphite or high-silicon cast iron, although in recent years magnetite (Fe_3O_4) and sintered metal oxides on platinum, the so-called ceramic anodes, have become important. These semiconducting oxides can sustain extremely high voltages without decomposition. Conductive polymeric cable, the impressed current analog of ribbon anodes, can be run parallel to buried pipelines. The cable looks like ordinary insulated copper cable but the polymer coating has graphite filler to make it electrically conducting.

Impressed-current anodes are buried in soils with a backfill of coke breeze, a finely divided carbon that helps produce a very even current distribution over the length of the anodes. Deep-bed anodes are often used in oil fields, with anodes packed into holes at depths typically of 30-90 m (100-300 ft.) to distribute more current in high conductivity strata where corrosion of oil well casings is greatest.

On large systems, anodes are connected together in groups of 10 or 20 in anode beds located near the rectifier. On long-distance pipelines the anode beds are located several miles from the pipeline and up to 50 miles apart. Power can be increased or decreased on the various sections of the line as conditions change—rain will increase soil conductivity, requiring less voltage to drive the protection current. Current requirements decrease with time as the structure becomes well polarized and calcareous deposits build up.

Locating the anode beds is the most difficult part of designing an impressed-current cathodic protection system for a pipeline. The sites must have good soil conductivity, should be near electrical power, and the anodes must be arranged to provide uniform protection to the entire line. Selection of anode sites, anode arrays, and sizing of rectifiers requires considerable experience, although computer programs are helpful. Installation must be followed by corrections to the system for several months after installation.

Although bare steel can be completely cathodically protected, the metal usually is coated to reduce power requirements, typically to 10% or less, compared with bare steel. Complete protection is determined by the resulting potential of the structures: for coated steel in soil the standard criterion is a potential of -850 mV versus a $Cu/CuSO_4$ reference electrode; in seawater, -800 mV versus the Ag/AgCl half-cell is sufficient. Other criteria are used when special circumstances require them.

large amounts of hydrogen, some of which may diffuse into the steel and embrittle it. Overprotection can also disbond coatings, as Figure 16.4 shows.

Excessive protective current may also escape from a poorly designed system and flow to nearby structures, causing interference (stray current) corrosion. When an impressed-current cathodic protection system is to be started up, all nearby owners of buried metal should be notified with the suggestion that corrosion conditions be monitored. Corrective action can then be taken before any great amount of damage is done.
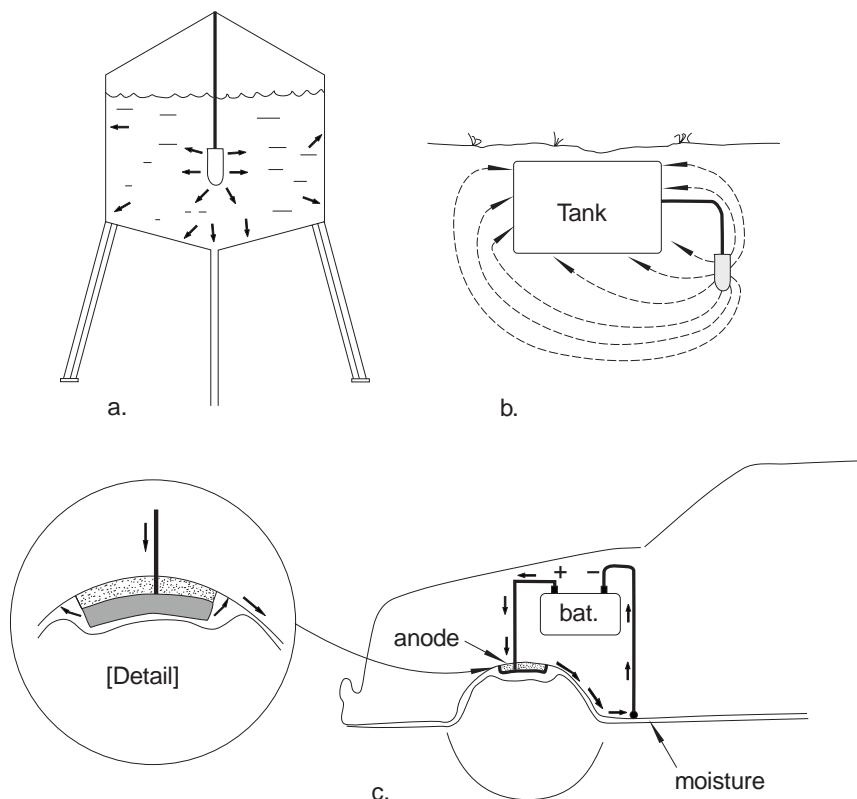
Figure 16.5 Examples of shielding that prevent complete cathodic protection.
 (a) Mg anode in municipal water tower fails to protect inside the pipe.
 (b) Shallowly buried tank has its top shielded by the soil surface.
 (c) Automobile "cathodic protection" (sic) device fails to flow current
   through a thin film of moisture.

The worst mistake that can be made in cathodic protection is a failure to keep complete and up-to-date records, maps, and status of the system.

Cathodic protection is not used in extremely corrosive environments, for instance hot, concentrated acid. While cathodic protection could theoretically stop corrosion even here, it is impractical. Sacrificial anodes would dissolve immediately and have to be replaced every few minutes. Impressed-current cathodic protection would incur tremendous power costs. This is a situation where anodic protection can be used.

2. The following metals would be suitable for sacrificial anodes:
    a. aluminum.
    b. bronze.
    c. high-silicon cast iron.
    d. manganese.
    e. zinc.

3. In impressed-current cathodic protection, the half-cell reactions at the electrodes can be:
    a. anode: decomposition of water.
    b. anode: oxidation of metal.
    c. anode: reduction of metal.
    d. cathode: decomposition of water.
    e. cathode: oxidation of metal.

4. For complete cathodic protection, the protected structure should have:
    a. current flowing off its entire surface that is contacting electrolyte.
    b. current flowing onto its entire surface that is contacting electrolyte.
    c. no current flowing to or from its surface.
    d. a sufficiently positive potential compared with a reference electrode.
    e. a sufficiently negative potential compared with a reference electrode.

5. Cathodic protection will not drive current:
    a. along a film of moisture on metal.
    b. down a long pipe.
    c. through alcohol.
    d. through a vapor.
    e. through whiskey.

6. Anodic protection can:
    a. be applied to any metal.
    b. be combined with cathodic protection for complete protection.
    c. be used in extremely corrosive environments.
    d. passivate metal.
    e. stop all corrosion.

7. For an anodically protected metal:
    a. current flows off its entire submerged surface.
    b. current flows onto its entire submerged surface.
    c. its half-cell reaction is the generation of hydrogen.
    d. its half-cell reaction is the generation of oxygen.
    e. its half-cell reaction is $M \rightarrow M^+ + e^-$.

Chapter

17

DESIGNING TO CONTROL CORROSION

Careful design of equipment can do more to prevent corrosion problems than any other aspect of engineering. Analysis of industrial corrosion failures shows that 58% of them were due, at least in part, to poor design–even more common than incorrect choice of materials or incorrect application of protective treatment (poor paint jobs and the like). Proper design can eliminate or minimize most corrosion problems.

Because corrosion is the reaction between a metal and its environment, both must be controlled. And since corrosion failures are greatly worsened by mechanical stresses, stresses also must be controlled by design.

Environmental Design

Corrosion is not instantaneous, so the design should minimize the attack time that the environment contacts the metal. Variations in solution concentrations, velocities, and temperatures also contribute to corrosion, but careful design can minimize these variations.

Minimize Attack Time

If solutions don't have to contact metal continuously, see that they don't. Provide complete drainage to tanks, as illustrated in Figure 17.1. Stagnant liquids trapped in dead space, such as for the tank in Figure 17.1a, may pit if they are at all aggressive or will certainly continue general corrosion if they are not. Pipes should not be horizontal but should slope slightly so that they drain completely. Even equipment designed to be full of liquid continuously during operation must be able to be drained completely during shutdowns.
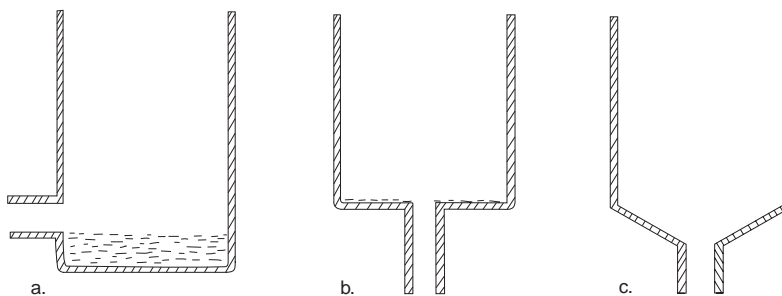
Figure 17.1 Location of tank drain.
(a) Poor design, leaving liquid never able to drain.
(b) Film of moisture on tank bottom does not drain.
(c) Tank can drain completely.

Figure 17.8 Drip skirt on tank bottom.

Maintain Reasonable Velocities

A passivated vessel containing a corrosive solution, especially one with chloride or acid which tend to attack passive films, is very likely to pit if the solution sits stagnant. Careful design of stirring or flow components will keep solution velocity above the minimum at which pitting can initiate. Intermittent flow should be avoided also because settling of dispersed solid particles is likely to result in crevice corrosion.

Maintain Uniform Temperature

Hot spots in boiler tubes become anodes that not only corrode very rapidly but may allow momentary evaporation of liquid, concentration of corrosive chemicals, and possible stress-corrosion cracking. While frequent cleaning may solve the problem once it appears, proper design could have spread the flame or hot exhaust gases more evenly over the tubes.

Cold spots cause almost as much trouble as hot spots. Vapors may condense and create pits under droplets of the condensate. The pits will grow rapidly as more vapor condenses in them. In Figure 17.9a, the cold, uninsulated legs of a tank act as cooling fins that cause cold spots inside the tank. While tank metal may withstand the vapors, it is likely to corrode in the condensate. To prevent the cold spots, the designer should specify that the legs are also to be insulated.

In Figure 17.9b, an insulated pipe has a break in the outer plastic wrap, allowing moisture to penetrate the insulation and produce a cold spot. The vapor in the pipe condenses at this cold spot. The plant should be designed so that moisture won't drip on insulated pipes, the plastic wrap should be stronger, and perhaps protected by a metal jacket. A slight increase in vapor temperature might have prevented condensation even with the faulty insulation.
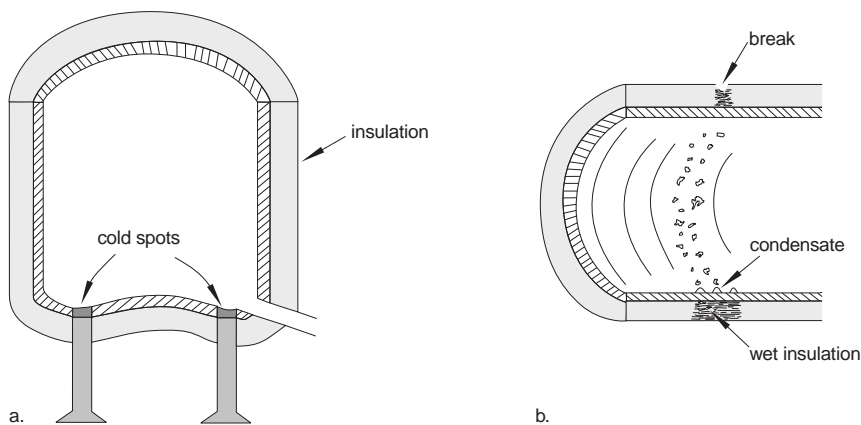
Figure 17.9 Examples of cold spots in chemical processing equipment containing hot vapors.
    (a) Insulated tank with condensation at leg locations.
    (b) Insulated pipe carrying vapor. Plastic wrap around insulation has a break
        that allows moisture to penetrate. Condensate forms at cold spot.

Large diesel engines, such as those on trains and ships, have often suffered severe corrosion of their exhaust mufflers from the acids in condensed exhaust gases, even though the mufflers are made of stainless steel. Improved design added an outer stainless steel jacket with thermal insulation between the muffler and the jacket, keeping the gases hot enough to allow them to escape from the muffler before the steam condensed.

The Metal

Allowing for uniform corrosion is always part of a design engineer's plan, and most people working around corrosion are aware that putting two different metals together can be dangerous, but few go beyond that. Realistic designs cannot be monolithic; they consist of different parts connected together. And somehow corrosion must be controlled.

Make Allowances for Corrosion

After proper materials selection, the chosen metal will have a suitably low corrosion rate in its environment. Enough metal must be left when the metal part nears the end of its expected service life that the part still functions properly. It must still be strong enough, stiff enough, have enough conductance, or whatever, that it does not fail to perform its job. The design engineer plans from the known corrosion rate of the metal.

Example: Having decided on the dimensions needed to give a part the necessary strength for the service and adding on a safety factor, a corrosion allowance is also added. If the corrosion rate in the expected environment as listed in the handbooks is 0.1 mm/y (4 mpy) and the part must have a service life of ten years, then multiplying the annual rate by ten years gives an additional 1 mm (40 mils) that must be added to each surface of the part as a corrosion allowance. Note that while it is true that a metal that corrodes at a certain rate in one year will probably corrode less in subsequent years, if we have no data we can't count on that.

Ensure Galvanic Compatibility

When different metals are used in an electrolyte, galvanic corrosion can still be reduced by careful design. If the metals can be electrically insulated from one another, no galvanic corrosion will occur, but that is often difficult to achieve. Keep in mind that metal A must not only be insulated from metal B but also from metal C if C touches B, even if C is not even in the electrolyte.

If the cathodic metal surface can be made very small in comparison with the anode surface area, any galvanic effects are minimized. Figure 17.10 illustrates a galvanic corrosion cell between steel and copper. A small anode (Figure17.10a) corrodes severely, whereas a small cathode (Figure 17.10b) does little damage to a large anode. In Figure 17.10c, a metal of intermediate corrodibility is placed between a very cathodic metal and an anodic metal. The result is that the intermediate metal corrodes slightly but does almost no damage to the most anodic metal.
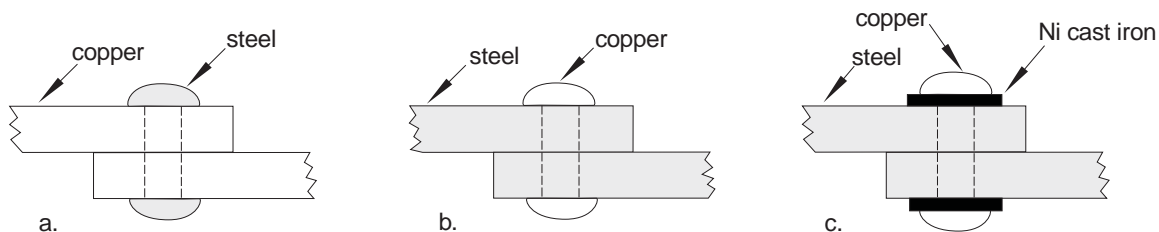
Figure 17.10 Effect of cathode/anode area ratio in galvanic corrosion.
(a) Copper plates riveted with anodic steel rivets will cause severe corrosion of rivet heads and premature failure.
(b)   Steel plates riveted with cathodic copper rivets will cause minor corrosion of the plates around the rivet.
(c)   Nickel cast iron washers, intermediate in corrodibility between steel and copper, reduce galvanic corrosion of steel.
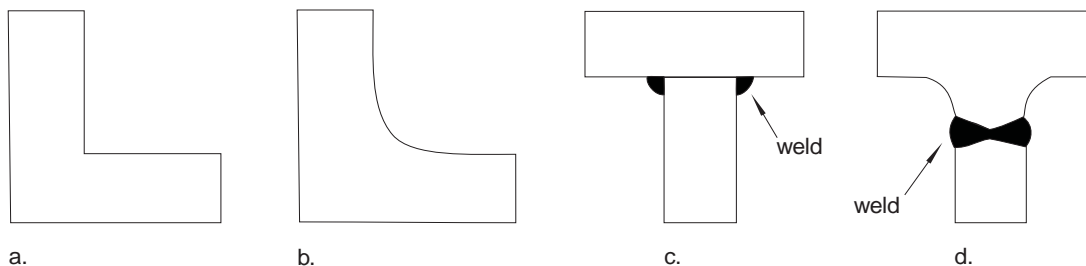
Figure 17.17 Designs that concentrate stress or disperse stress.
(a)   Stress concentrates at sharp notch.
(b)   Fillet spreads out stress.
(c)   Stress concentrates at welds where intergranular corrosion is likely.
(d)   Weld is removed to low stress area.

Figure 17.18 Cut threads (a) concentrate stress in the sharp grooves.
Rolled threads (b) spread out stresses more evenly.

Components put into compression cannot crack. Designing compressive stresses into critical parts, even if tensile stresses overwhelm the compression, reduces the possibility of crack initiation. Shot peening of axles, for example, is used to prevent corrosion fatigue as well as fatigue. Other methods, such as inhibitors or coatings, can reduce corrosion enough to keep the compressive surface layer from corroding away.

Inspection and Maintenance

A corollary of Murphy's Law states that when a failure occurs, it will occur in the least accessible location. This is not just a pessimistic attitude–it is completely logical: that least accessible location is the place that nobody keeps an eye on or repairs before complete failure occurs.

Monitoring

After a careful materials selection and a good design, a component is put into operation in a corrosive solution. No one can assume that the handbook corrosion rates, measured under controlled conditions, are completely correct, and no one should assume that localized attack couldn't possibly be happening here. The corrosion at critical locations and at inaccessible locations should be monitored.

The equipment design should include ports for insertion of coupons or, more commonly now, electronic probes whose outputs are fed to a central console. In this way the corrosion situation throughout the system can be followed continuously during regular operation, the occasional upheavals, shutdown, and start-up.

The designer must always keep the possibility of human error in mind. Multitudes of corrosion disasters have occurred when people turned the wrong valve "because it was there." Many plants are designed for versatility, but as all mechanics know, a multipurpose tool isn't really good for much of anything. And in equipment design, each component should be allowed only one way–the proper way–of functioning. As computer control becomes widespread, this task becomes easier, but human beings still program computers.

Definition of New Terms

Corrosion allowance: oversizing to allow for metal lost to corrosion.
Drip skirt: extension below the bottom of a tank to carry off external spills.
Ferrule: a thin sleeve inserted in the end of a tube.
Filler metal: metal added during welding to fill the joint between metal workpieces.
Fillet: concave connection between two metal plates or sheets.
Gasket corrosion: crevice corrosion under a porous or loose fitting gasket.
Inlet tube corrosion: erosion-corrosion from turbulence at the inlet end of heat exchanger or boiler tubing.
Jumper wire: a short wire providing electrical continuity between two metals.
Laminar flow: streamlined flow without turbulence.
Lap joint: connection between two sheets or plates that overlap.
Murphy's Law: "Anything that can go wrong, will go wrong."
Skip weld: weld extending for short lengths with unwelded spaces in between.
Tube sheet: heavy plate through which heat exchanger tubes pass.

Questions

1. Corrosion attack time is often reduced by:
    a. adding drip skirts to tanks.
    b. sloping horizontal sections.
    c. eliminating crevices.
    d. frequent cleaning of equipment.
    e. providing rapid evaporation.

2. Adding concentrated corrosive solution to the center of a tank will:
    a. cause splashing on tank walls.
    b. eliminate the need for a drip skirt.
    c. reduce corrosion attack.
    d. reduce crevice corrosion.
    e. speed mixing.

3. Splashing liquid on a hot metal surface:
    a. can be prevented by a drip skirt.
    b. concentrates the corrosive liquid.
    c. evaporates the liquid.
    d. strengthens the metal.
    e. tempers the metal.

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Chapter
18

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ECONOMIC CALCULATIONS IN CORROSION

Do we use stainless steel or try to get by with carbon steel at one-fifth the price? Do we use bargain paint or go for the expensive stuff that lasts longer? Do we cathodically protect? If so, how? And when? Where human safety is involved or where the environment could be seriously damaged, the decisions are obvious. But in other cases the choices simply come down to which will save the most money *in the long run*.

Time is an important factor. For one thing, decisions put off for a year or two can be made with a clearer picture of the future, but more important, a dollar spent a year from now costs less than a dollar spent today.

The Time Value of Money

The investment of $100 in a bank paying 5% interest will bring in $105 a year from now. Or, as the economists say, the "present worth" of that future $105 is $100.

In mathematical terms, the present worth, P, is related to the future worth, F, by the equation

$$F = P(1+i)^n$$

where i is the annual interest rate expressed as a decimal, and n is the number of years. Substituting in numbers:

$$F = \$100(1+0.05)^1 = \$105$$

That is to say, the future worth of $100 is $105 next year. This is the time value of money.

Daily or continuously compounded interest rate calculations might seem to be more accurate than using an annual interest rate, but corrosion estimates are unlikely to be so precise as to warrant the extra math.

Should $10,000 be spent now to improve our plant design and reduce cost of maintenance by $1500 per year? The life of the project is ten years and the interest rate is projected to be 7%. A simple approach would be to say that the $10,000 cost now is much less than the $15,000 to be spent over ten years. But is it? The cost of $10,000 now can't be compared with $15,000 ten years from now. The costs of the two proposals must be compared at the same time.

The two plans could be compared at the end of ten years. The future worth of $10,000 could be compared with the future worth of all the annual $1500 costs. Table 18.1 shows this.

Table 18.1 Comparison of large initial cost with smaller annual costs.

Years Elapsed	Plan A (improved design)		Plan B (annual maintenance)	
	Cash outlay	Interest	Cash outlay	Interest
0	$10,000	0	0	0
1	---	$700.00	$1500	0
2	---	749.00	1500	$105.00
3	---	801.43	1500	217.35
4	---	857.53	1500	337.56
5	---	917.56	1500	466.19
6	---	981.79	1500	603.83
7	---	1050.51	1500	751.09
8	---	1124.05	1500	908.67
9	---	1202.73	1500	1077.28
10	---	1286.92	1500	1257.69
Totals	10,000 + 9,671.52 = **$19,671.52**		15,000 + 5724.67 = **$20,724.67**	

The improved design does turn out to be less expensive than continual maintenance, but only marginally so. Taxation differences between capital expenditures and maintenance costs may tip the scales in favor of maintenance.

Economic Analysis Methods

Present Worth

The present worth method is the easiest and the one most used in engineering economic calculations. It is sometimes termed the "discounted cash flow method."

Example: $88.65 invested today at 5% interest will allow four annual payments of $25. Here's how:
  1st year: $88.65 (1.05) - $25 = $68.08 remaining.
  2nd year: $68.08 (1.05) - $25 = $46.48 remaining.
  3rd year: $46.48 (1.05) - $25 = $23.80 remaining.
  4th year: $23.80 (1.05) - $25 =   0   remaining.
  So $83.65 invested at 5% is "equivalent to" four annual payments of $25.

The equation relating an equivalent annual cost, A, to the present worth is:

$$P = A\left[\frac{(1+i)^n - 1}{i(1+i)^n}\right]$$

This is where that $88.65 in the example above came from. The A in the equation was the $25 annual cost.

For the comparison in the previous section of the $10,000 design cost vs. maintenance costs, instead of calculating the future worth of both alternatives, the present worth of the maintenance program could be calculated. With the equation above, and using $1500 for the annual cost, A, the present

Double-declining balance depreciation: constant percentage depreciation using a percentage that is twice that of straight line depreciation.

F: symbol for future worth.

Future worth: value of today's sum of money at some time in the future, including interest.

P: symbol for present worth.

Present worth: today's value of some future sum of money that would have included accumulated interest.

Straight line depreciation: depreciation of an asset by the same amount each year.

Sum-of-digits depreciation: a depreciation accounting method that depreciates very rapidly at first and much less toward the end.

Write-off: a book value of zero after an investment is fully depreciated.

Questions

1. The present worth of a $5 expenditure to be made 5 years from now, with an annual interest rate of 5% is:
   a. $3.92
   b. $4.17
   c. $4.45
   d. $5.55
   e. $6.38

2. Future worth is the value of an investment:
   a. after it has accumulated interest.
   b. after it has been depreciated.
   c. in equipment when it is scrapped.
   d. made today, calculated as if it appreciated in value.
   e. to be made in the future, expressed in today's dollars.

3. The symbol A in economic calculations refers to:
   a. actual principal invested in an enterprise.
   b. annual expense.
   c. annual interest rate.
   d. sum of money paid out at regular periods.
   e. future value of an investment made today.

4. If present worth is $100, interest rate is 7%, the value of F for one year is:
   a. 0
   b. $7
   c. $93
   d. $100
   e. $107

5. When interest rates are high:
   a. continual maintenance is attractive.
   b. continual maintenance is unattractive.
   c. large capital investments are attractive.
   d. large capital investments are unattractive.
   e. the cheapest way to go is attractive.

Appendix

A

UNITS OF MEASUREMENT WITH CONVERSIONS

(SI units follow ASTM E380, Standard for Metric Practice)

The International System (SI) of Units

Table A.1 SI Base Units.

Quantity	Name	Symbol
Length	metre	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Amount of substance	mole	mol

Table A.2 Derived SI Units with Special Names.

Quantity	Unit	Symbol	Formula
Celsius temperature	-	°C	K-273.15
force	newton	N	$kg \cdot m/s^2$
pressure, stress	pascal	Pa	N/m^2
energy, work	joule	J	$N \cdot m$
power	watt	W	J/s
quantity of electricity, electric charge	coulomb	C	$A \cdot s$
electric potential, potential difference, electromotive force	volt	V	W/A
electrical resistance	ohm	Ω	V/A
electrical conductance	siemens	S	A/V

Table A.3 SI Multiple and Submultiple prefixes.

Symbol	Prefix	Factor
G	giga	10^9
M	mega	10^6
k	kilo	10^3
m	milli	10^{-3}
μ	micro	10^{-6}
n	nano	10^{-9}

Table A.4 Conversions.

To convert from:	Multiply by:	To find:
Length		
mil	2.540×10^{-2}	mm
in.	25.4	mm
ft	0.3048	m
Area		
in.^{2}	6.452×10^{-4}	m^2
ft^2	9.290×10^{-2}	m^2
Volume		
in.^{3}	1.639×10^{-5}	m^3
ft^3	2.832×10^{-2}	m^3
gal. (U.S. liquid)	3.785×10^{-3}	m^3
Mass		
lb	0.4536	kg
oz	2.835×10^{-2}	kg
Density		
lb/in.^{3}	2.768×10^{4}	kg/m^3
lb/ft^3	16.02	kg/m^3
Temperature		
ºF	ºC = (ºF - 32)1.8	ºC
ºC	K = ºC + 273.15	K
Pressure		
atm.	101.3	kPa
mm Hg	0.1333	kPa
psi	6.894	kPa
torr	0.1333	kPa
Energy		
Btu	1055	Joule (J)
cal.	4.190	J
ft-lbf	1.356	J
Current Density		
A/ft^2	10.76	A/m^2
A/in.^{2}	1550	A/m^2
Corrosion Rate		
mpy	0.0254	mm/y
ipy	25.40	mm/y
mdd	0.1000	g/m^2·d

APPROXIMATE EQUIVALENT HARDNESS NUMBERS AND TENSILE STRENGTHS FOR STEELS

HV	HRC	HRB	HB	T.S.(ksi)	T.S.(MPa)
680	59.2	-	(638)	355	2450
670	58.8	-	(630)	348	2400
660	58.3	-	620	342	2360
650	57.8	-	611	336	2320
640	57.3	-	601	328	2270
630	56.8	-	591	323	2230
620	56.3	-	582	317	2190
610	55.7	-	573	310	2140
600	55.2	-	564	303	2090
590	54.7	-	554	298	2050
580	54.1	-	545	293	2020
570	53.6	-	535	288	1990
560	53.0	-	525	283	1950
550	52.3	-	517	276	1900
540	51.7	-	507	270	1860
530	51.1	-	497	265	1830
520	50.5	-	488	260	1790
510	49.8	-	479	254	1750
500	49.1	-	471	247	1700
490	48.4	-	460	241	1660
480	47.7	-	452	235	1620
470	46.9	-	442	228	1580
460	46.1	-	433	223	1540
450	45.3	-	425	217	1500
440	44.5	-	415	212	1460
430	43.6	-	405	205	1410
420	42.7	-	397	199	1370
410	41.8	-	388	193	1330
400	40.8	-	379	187	1290
390	39.8	-	369	181	1250
380	38.8	(110.0)	360	175	1210
370	37.7	-	350	170	1170
360	36.6	(109.0)	341	164	1130
350	35.5	-	331	159	1100

HV	HRC	HRB	HB	T.S.(ksi)	T.S.(MPa)
340	34.4	(108.0)	322	155	1070
330	33.3	-	313	150	1030
320	32.2	(107.0)	303	146	1010
310	31.0	-	294	142	980
300	29.8	(105.5)	284	138	950
290	28.5	(104.5)	275	133	920
280	27.1	(103.5)	265	129	890
270	25.6	(102.0)	256	124	860
260	24.0	(101.0)	247	120	830
250	22.2	99.5	238	115	790
240	20.3	98.1	228	111	760
230	(18.0)	96.7	219	106	730
220	(15.7)	95.0	209	101	700
210	(13.4)	93.4	200	97	670
200	(11.0)	91.5	190	92	640
190	(8.5)	89.5	181	88	610
180	(6.0)	87.1	171	84	580
170	(3.0)	84.5	162	79	550
160	-	81.7	152	75	520
150	-	78.7	143	71	490
140	-	75.0	133	66	460
130	-	71.2	124	62	430
120	-	66.7	114	57	390

Hardness values in parentheses are beyond standard range.

HV = Hardness Vickers.

HRC = Rockwell C Hardness (150 kg load, diamond indenter).

HRB = Rockwell B Hardness (100 kg load, 1/16 in. ball).

HB = Hardness Brinell (3000 kg load, 10-mm ball, WC ball above 470 HB).

T.S. = Tensile Strength.

Sources: Metals Handbook, 8th ed., American Society for Metals. vol. 11, p. 425 (1976), and other
          sources.

ANSWERS TO QUESTIONS

Chapter 1

1.a. No. A piddling amount not worth troubling over.
  b. No. This would just be a minor problem.
  c. Correct, plus at least another $1000 for the indirect costs.
  d. No. This would be as much as the average family's income.
  e. No. Corrosion is a serious problem but not "the ultimate catastrophe" as Zorba the Greek defined marriage.

2.a. Right. We should save more than ¼ of the direct costs.
  b. No. Materials are not free and none are totally uncorrodible.
  c. No. Corrosion will occur as long as we use metals, so equipment must be over-designed, and some downtime is required for replacement.
  d. No. We do not live in the best of all possible worlds.
  e. Of course. Improvement is possible.

3.a. No. Haven't you seen the piles of steel in scrap yards?
  b. No. Corrosion is much more serious than this.
  c. No. You're underestimating the magnitude of this natural disaster.
  d. No, but you're close.
  e. Yes. Fortunately most steel production comes from scrap.

4.a. Certainly. This is a serious problem confronting all cities.
  b. Of course. Gasoline does not taste good.
  c. Yes. Example: those hundreds of casualties in Mexico.
  d. No. Gasoline always contains some entrained water that will separate and corrode.
  e. No. We can and sometimes do prevent corrosion.

5.a. No, most workers in corrosion have other backgrounds.
  b. No. Only two or three colleges in the world offer such a degree.
  c. No. All the metallurgical engineers in the world could not supply the demand for knowledgeable corrosion personnel.
  d. Yes. Experience is still the best teacher.
  e. No. Industry is not grinding to a halt.

6.a. No, although occasionally you'll run across people with this attitude.
  b. Yes, indeed. If you try to make yourself and your memory indispensable, you'll be stuck in the same job forever.
  c. This is the "Damn the torpedoes. Full speed ahead." approach.
  d. No. Dream on.
  e. No. Steel is cheap, and our industries could not survive without it.

7.a,c,d. No. Consider the effect that the plated copper will have.

b. Yes, the copper cathode will increase aluminum's corrosion.

8.a. Yes. First, corrosion products on the zinc coating slow the corrosion. When the zinc is all corroded, rust will still slow the corrosion somewhat.

b. No, the zinc coating doesn't truly passivate although it does form protective corrosion products.

c. No, corrosion products on the zinc coating or rust on the steel have an effect.

d. No, solid corrosion products form on the metal.

9.(1) No, steel is quite corrodible.

(2) Of course. An unpainted automobile would quickly rust, and who would buy it?

(3) No, the rain, snow, mud, and slush haven't changed much in the last hundred years.

(4) Not to any extent, although efforts are underway to use less salt on icy highways.

(5) No, inhibitors are simply too expensive.

(6) No, this does not work. Figure 16.5c shows such an attempt.

(7) Yes. Shielding from splashing in fender wells, elimination of crevices and water traps, and many other design improvements have greatly extended automobile life.

(8) Definitely not. Safety must not be compromised.

10.(1) No, steel is normally used for pipelines.

(2) Yes. All major pipelines today are coated.

(3) No, the principal corrosive is the soil, left unchanged.

(4) No, the principal corrosive is the soil, left unchanged.

(5) Not usually, although sometimes inhibitors are added to very corrosive gases.

(6) Yes, cathodic protection is used on all large gas pipelines to protect them from corrosion by the soil.

(7) Not primarily, although the design must allow immediate response to leaks or rupture.

(8) Definitely not. Safety must not be compromised.

Chapter 5

1.a. No, rust is fairly uncorrodible but Fe^{2+} ions in it can be oxidized further to Fe^{3+}.

b. Yes. Mill scale and rust both contain both Fe^{2+} and Fe^{3+} ions.

c. No, rust contains Fe^{2+} and Fe^{3+} ions that have already been oxidized.

d. No. Magnesium is very reactive while rust has already reacted.

2.a. Correct. Active and passive stainless steels are quite far apart in the galvanic series.

b,c. No. Compare the positions of active and passive stainless steels in the galvanic series.

3.a,b. No. Compare the positions of the two alloys in the galvanic series.

c. Correct. The two alloys are bracketed together in the galvanic series.

4.a. Wrong. This idea was tried on large pipeline. Result: disaster.

b. Wrong. The mill scale is cathodic to (less corrodible than) the steel pipe.

c. Right. This sets up anode and cathode regions on the pipe.

d. Wrong. Although the scale is brittle it is metallurgically bonded to the steel. That is, it has reacted with, and grown right on, the steel.

5.a. No. Soil is not an electron conductor at moderate voltages.

b. Correct. The long electron path didn't matter because metals are such good electron conductors.

c. No. Copper is the cathode and doesn't corrode.

d. Incorrect. The soil was corrosive but galvanic corrosion occurred.

INDEX

(**Bold numbers** refer to pictures; *italic numbers* refer to tables and definitions.)

USING ACROBAT® READER WITH SEARCH

Navigating

Tool Bar Icons
Paging Through a Document
   Go to the Next Page
   Return to the Previous Page
   Move One Screenful at a Time
Browsing with Thumbnails
   Jump to a Page Using its Thumbnail
Browsing with Bookmarks
   Jump to a Topic by its Bookmark
Following Links
Retracing Your Steps
   Retrace Your Viewing Path
Magnifying the Page View
   Increase Magnification
   Decrease Magnification
Working with Large Pages (Hand Tool)
Choosing a Page Layout for Scrolling Ease

Main Menu   Next Page

Searching

Navigating

Tool Bar Icons

Select a tool by clicking the icon.

Click the **Page Only** icon to close the overview area of the window.

Click the **Bookmarks and Page** icon to open the overview area and display bookmarks created for the document. Click a bookmark's name to go to the location marked by that bookmark.

Click the **Thumbnails and Page** icon to open the overview area and display thumbnail images of each document page. Click a thumbnail to go to the page marked by that thumbnail.

Use the **Hand** tool to move a document page on-screen when it does not fit within the window. Drag the hand tool in the direction you want to move the page.

Tool Bar Icons (Continued)

Use the **Zoom** tools to magnify and reduce the page display by a factor of 2.

This function is not available with this CD-ROM.

The **Browse** icons (arrows) with the vertical line, advances the document to the first or last page of a document, whereas the browse icons without vertical lines move the document forward or back one page at a time.

Use the **Go Back** and **Go Forward** icons to retrace your steps in a document, moving to each view in the order visited. Go Back also returns you to the original document after you click a link to another document.

Click the **Actual Size** icon to display the page at 100 percent.

Tool Bar Icons (Continued)

🔲 Click the **Fit Page** icon to scale the page to fit within the window.

🔲 Click the **Fit Width** icon to scale the page width to fill the width of the window.

🔍 The **Find** tool searches for part of a word, a complete word, or multiple words in a document.

🔍 The **Search** tool searches indexed PDF documents for single words, phrases, parts of words, or combinations of words.

📇 The **Search/Results** tool displays the results of your cross document search.

Paging Through a Document

Acrobat Reader provides a number of ways to page through a document.

Go to the Next Page

Choose one of the following:
- Click the **Next Page** button ▶ in the tool bar.
- Press the **Right Arrow** or **Down Arrow**.
- Choose *View, Next Page.*

Return to the Previous Page

Choose one of the following:
- Click the **Previous Page** button ◀ in the tool bar.
- Press the **Left Arrow** or **Up Arrow**.
- Choose *View, Previous Page.*

Move One Screenful at a Time

- Press the **PageDown** key, **Enter**, or **Return** to move forward.
- Press the **PageUp** key, **Shift+ Enter**, or **Shift+ Return** to go back. Use the horizontal scroll bar in the status bar to scroll the page right or left.

Browsing with Thumbnails

A thumbnail is a miniature view of each document page which you can display in the overview area. You can use a thumbnail to jump quickly to a page and to adjust the view of the current page.

Jump to a Page Using its Thumbnail

Click the **Thumbnails and Page** button ▦ or choose *View, Thumbnails and Page* to display thumbnail images. Click a thumbnail to move to the page it represents. The point you click determines the center of the page display.

Browsing with Bookmarks

Bookmarks can mark parts of a document for quick access.

Jump to a Topic by its Bookmark

1. Click the **Bookmarks and Page** button 📑 or choose *View*, *Bookmarks and Page* to display bookmarks in the overview area. If a triangle appears to the left of the bookmark, click the triangle to show or hide subordinate bookmarks.
2. To go to the destination specified by a bookmark, click the bookmark text or double-click the page icon to the left of the bookmark name. A bookmark can also change the page view, play a movie, reset a form, or perform other actions.

Following Links

Links can connect parts of a document, jump to other PDF documents, open another application file, play a movie or sound, enter an article, hide or show an annotation, import form data, and reset or submit a form.

1. Move the pointer over a linked area. The pointer changes to a pointing finger when positioned over a link.
2. Click to follow the link. Clicking a link can also change the page view, play a movie, reset a form, or perform other actions.

Retracing Your Steps

The **Go Back** button traces your viewing path through a document or series of documents. You can go back up to 64 views. **Go Back** will reopen closed documents if necessary.

Retrace Your Viewing Path

- Click the **Go Back** button ◀◀ or choose *View*, *Go Back* to return to the previous page, document, or magnification level.
- Click the **Go Forward** button ▶▶ or choose *View*, *Go Forward* to reverse direction and return, one view at a time, to the view where you first used *Go Back*.

Magnifying the Page View

You can use the **Zoom** tool, the **Magnification Box** in the status bar, or the **Actual Size**, **Fit Page**, and **Fit Width** tool bar buttons to change the screen magnification. The maximum magnification level is 800%. The minimum magnification level is 12%. If you zoom in on a large document, use the hand tool to move the page around on-screen or in a thumbnail . Acrobat Reader also offers magnification level choices that are not related to a specific percentage, but to the look of the page on-screen:

- **Fit Page** ▣ scales the page to fit within the main window.
- **Fit Width** ▣ scales the page to fit the width of the main window.
- **Fit Visible** fills the window with the page's imaged area only (text and graphics).

Magnifying the Page View (Continued)

When you select any of the **Fit** options, the magnification level resulting from the selection is displayed in the status bar.

The Fit options, **Fit Page**, **Fit Width**, and **Fit Visible,** are in a *sticky state*, which means they don't change as you page through a document unless you change the zoom level.

Increase Magnification

Choose one of the following:
- Select the **Zoom** tool 🔍 and click on the document page to double the current magnification.
- Select the **Zoom** tool 🔍 and drag to draw a rectangle, called a marquee , around the area you want to magnify.
- Click the **magnification box** in the status bar, and choose a magnification level. If you choose **Zoom To**, type in the magnification level and click *OK*.

Decrease Magnification

Choose one of the following:
- Select the **Zoom** tool 🔍 while holding down Ctrl (Windows and UNIX) or Option (Macintosh), and click at the center of the area you want to reduce.
- Select the **Zoom** tool 🔍 while holding down Ctrl (Windows and UNIX) or Option (Macintosh), and drag to draw a rectangle, called a marquee , around the area you want to reduce.
- Click the **Magnification Box** in the status bar, and choose a magnification level. If you choose **Zoom To**, type in the magnification level and click *OK*.

Working with Large Page Sizes

If you need to magnify a page to a size larger than the Reader window, you can use the **Hand** tool to move the page around so that you can view all the areas on it. Moving a page around with the **Hand** tool is like moving a piece of paper around on a desk with your hand.

Choosing a Page Layout for Scrolling Ease

Acrobat Reader has three page layout options: Single Page, Continuous, and Continuous-Facing Pages. Continuous and Continuous-Facing Pages facilitate page scrolling so that you can see the bottom of one page and the top of another.

- **Single Page layout** displays one page in the document window at a time.
- **Continuous layout** arranges the pages in a continuous vertical column.
- **Continuous-Facing Pages layout** arranges the pages to appear side by side. This configuration accommodates two-page spread display and multiple-page viewing in the viewer window. If the total page count of a document is greater than two pages, the first page is displayed on the right to ensure proper display of two-page spreads. To see two-page spreads most efficiently in this page layout, choose *View*, *Fit Width*.

Choosing a Page Layout for Scrolling Ease (Continued)

Choose one of the following:
- Click the **Page Size Box** in the status bar, and choose one of the page layouts from the menu.
- Choose *Single Page*, *Continuous*, or *Continuous-Facing Pages* from the *View* menu.

Search

Use the Search command to perform full-text searches of indexed PDF document collections.

The Search command has powerful tools for limiting and expanding the definition of the term you are searching for.

A full-text index is a searchable database of all text in a document or collection of documents. Searches of full-text indexes are very quick.

The Find command works with a single document and reads every word on every page, and is slower than the Search command.

Searching

Perform a Full-Text Search

1. From the Main Menu click on Search, or at any time from the menu bar you may choose *Tools*, *Search*, *Query* or click the *Search Query* button 🔍 on the tool bar to open the Search window. Type the text you want to find in the *Find Results Containing Text* box, and click *Search*. The text can be a single word, a number, a term, or a phrase. When you click *Search*, the Search window is hidden, however, the search results can be seen by clicking on the 📄 icon located on the tool bar. The Search Results window displays the number of hits for the search.

2. Use the *Search Next* button 📄 and *Search Previous* button 📄 to go to other matches in the document. Alternatively, redefine the query by typing new text or by using other techniques to expand the search to more documents or to limit the search to fewer hits. If you want to do this without having to redisplay the Search windows, change the default preference that hides it "on view."

Defining Search Queries

You can search for a word, a number, a term, or a phrase made up of several terms. You can also use the other techniques listed below to define a search query.

Searching for a Term or Phrase

To find matches for a single term, type the term in the text box labeled *Find Results Containing Text* and click *Search*. The term can be a word, a word with wild-card characters, or any combination of letters, numbers, and symbols.

- If the phrase includes the word *and*, *or*, or *not* used in its ordinary sense (not as a Boolean operator), put the phrase in quotes. The search phrase "*rock or mineral*" finds all occurrences of the phrase *rock or mineral*, not all occurrences of *rock* and all occurrences of *mineral* as it would without the quotes.

- If the phrase includes punctuation (other than the apostrophe) or special characters such as @ and *, they are ignored. For example, either of the terms *up-todate*, *up to date* finds all occurrences of both *up-to-date* and *up to date*.

Expanding a Search

If a search returns too few hits or no hits at all, make sure you are searching the appropriate key words. Also, make sure that settings left over from a previous search aren't limiting the current one.

Using Search Options

Query Techniques

- The **Word Stemming** option finds words that share a stem with a search word.
- The **Sounds Like** option finds different spellings of proper names.
- The **Thesaurus** option finds words that have meanings similar to the meaning of a search word.
- **Match Case** finds text only when it has the same capitalization as the text you type.
- **Proximity** limits AND searches so that words must be within three pages of each other.
- **Boolean OR, AND, NOT** operators between key words can narrow or expand searches.
- Using **Operator Names** and **Symbols** Literally
- **Wild-card** characters, such as * or ?, in the search text increase the number of matches for the text.

The options in the Search window expand or limit the results of searches with single terms and phrases and with Boolean expressions. All options are initially disabled in the window by default.

```
Options
☒ Word Stemming    ☐ Thesaurus   ☐ Match Case
☐ Sounds Like                    ☐ Proximity
```

The **Word Stemming**, **Thesaurus**, and **Sounds Like** options expand searches. (Before you perform a search with one of these options, you can see the effects of using it with the **Word Assistant**.)

The **Match Case** and **Proximity** options limit searches.

Main Menu   Using Acrobat Reader   Next Page

Word Stemming Option

The **Word Stemming** option expands the search by finding words that share a word stem with the search word you type.

Example: with Word Stemming selected, searching for *engineering* finds *engineer* and *engineers* as well as *engineering*.

Before searching with the **Word Stemming** option, consider using the **Word Assistant** to see whether the option would find too many irrelevant words to be practical. The Word Stemming option:

- Applies to single words, not phrases.
- Does not apply to words that contain wild-card characters.
- Finds words that end in **ing**, **ed**, **s**, **ion**, and so on (but not **er**).
- Cannot be used with the **Match Case** option.

Sounds Like Option

The **Sounds Like** option expands the search for a proper name by finding words that begin with the same letter as a search word and that share some phonetic feature with it.

Example: with Sounds Like selected, searching for *color* also finds *colour* and *colore*.

Searching for *color* with the **Sounds Like** option also finds *clear* and *chaleur*. Before searching with the option, try using the **Word Assistant** to see whether the option will find relevant words.

The Sounds Like option:
- Applies to single words, not phrases.
- Does not apply to words that contain wild-card characters.
- Cannot be used with the **Match Case** option.

Thesaurus Option

The **Thesaurus** option expands the search by finding words with meanings similar to the meaning of the search word.

Example: with **Thesaurus** selected, searching for *begin* finds *start.*

Searching for *begin* with the **Thesaurus** option also finds *attack* and *produce.* Before searching with the option, try using the **Word Assistant** to see whether the option will find relevant words.

The Thesaurus option:
- Applies to single words, not phrases.
- Does not apply to words that contain wild-card characters.
- Cannot be used with the **Match Case** option.
- Finds only the similar words that appear in the documents you are searching, not all the similar words you might find in a complete Thesaurus.

Match Case Option

The **Match Case** option limits the results of the search by finding only those documents that contain words with the same capitalization as the search word or phrase you type.

Example: with Match Case selected, searching for *Metal* finds all occurrences of *Metal*, but not occurrences of **m**etal.

You can use the **Match Case** option with a Boolean expression or with terms that use wild-card characters. Characters matched by wild-card characters can be either uppercase or lowercase. You cannot use the **Match Case** option with the **Word Stemming**, **Thesaurus**, or **Sounds Like** option.

Proximity Option

The **Proximity** option limits the results of simple AND searches to one pair of matches closest together. The two matches must be within three pages or fewer of each other. The option is useful for locating a search that concentrates on some topic of interest.

Example: searching for information about *arc welding* with *arc* AND *welding* would be less likely to locate information about *mig welding* or *circle arcs* if the **Proximity** option was used.

Proximity will not work with complex AND searches, for example, *welding* AND (*arc* OR *mig*).

Searching with Boolean AND

Use AND to find two or more search terms.

Example: *installation* AND *instructions* finds only those hits that contain both *installation* and *instructions*.

You can also use the ampersand (&) to specify an AND search.

Example: *installation* & *instructions*.

Choosing the **Proximity** option changes the way AND searches work. Without the **Proximity** option, items in an AND search can be anywhere in a document.
With the **Proximity** option, items in an AND search must be within three pages of each other to be found.

Searching with Boolean OR

Use OR to find hits containing any of two or more search terms.

Example: *metal* OR *alloy* finds all hits that contain either or both *metal* and *alloy*.

You can also use a comma (,) or a vertical bar (|) to separate items in an OR search.

Example: *metal*, *alloy* and *metal* | *alloy*.

Combining Boolean Operators

Be careful when combining operators to build Boolean expressions because it is easy to build an expression that does not mean what you think it means.

When you combine AND and OR in the same expression, AND is evaluated before OR.

Example: *alloy* OR *metallurgy* AND *stainless* finds all documents that contain *alloy* or that contain both *metallurgy* and *stainless*.

You can use parentheses to change the default order of evaluation for Boolean operators.
Example: (*alloy* OR *metallurgy*) AND *stainless* finds all documents that contain either *alloy* and *stainless* or that contain *metallurgy* and *stainless*. Parentheses can be nested, i.e., parentheses can be placed within parentheses.

Using Operator Names and Symbols Literally

When you use a literal phrase that contains an operator name, a symbol for an operator name (such as & for AND), or parentheses, the phrase must be enclosed in quotation marks.

Example: *"salt and rock"* finds all hits that contain the phrase *salt and rock*, not all hits that contain either the word *salt* or the word *rock*. The phrase *salt & rock* also needs quotes to be interpreted literally.

Searching with Wild-Card Characters

You can use **wild-card** characters to find words that contain a word fragment or all the terms that match a character pattern:

- * asterisk, matches zero, one, or more characters
- ? question mark, matches any one character

You can use wild-card characters in a term that is part of a Boolean expression. You cannot use wild cards to represent separator characters such as the hyphen (-) and the slash (/).

Examples:
geo* matches geodesic, Geoffrey, and geothermal
*tic matches austenitic and ferritic
?ight matches light and might but not bright
S3???? matches all six-digit alphanumerical sets with the S3 prefix, e.g., S30403, S30400
pr?m* matches prime, primary, and primed

Limiting a Search

If a search returns too many hits or provides too many matches in individual searches, try any of these query techniques:

- A **Boolean AND operator** between two words returns only hits containing both words.
- The **Proximity** option limits AND searches so that words must be close to each other – within three pages or fewer.
- The **Match Case** option finds text only when it has the same capitalization as the text you type.

Word Assistant

Use the **Word Assistant** to build a list of terms that will appear when the search of a document uses the **Sounds Like**, **Word Stemming**, or **Thesaurus** option. The list will show you whether the option you are using is likely to be helpful in the search. If the list is too long or full of irrelevant words, you can quickly construct a list of words to find with the option turned off by copying words from the **Word Assistant** dialog box and pasting them into the Search window.

Look up the effects of a search option on a search word:
1. Choose *Tools*, *Search*, *Word Assistant*.
2. Enter the search word in the **Word text** box.
3. Select the **Search** option from the **Assist** menu.
4. Click on **Look Up**. All the words that will be found in a search for this word with this option are listed.

Word Assistant (Continued)

Search with words copied from the Word
Assistant dialog box:
1. If the **Search** window is closed, click the
   Search Query button 🔍 on the tool bar
   to open it.
2. Use the **Word Assistant** to look up the
   effects of a search option on a search word
   and to display a list of related words.
3. Double-click a word in the list that you
   want to use in a search. The word
   appears in the **Word** text box.
4. Double-click the word to select it, and
   copy it to the clipboard (Ctrl + C).
5. In the **Search** window, click the **Find
   Results Containing Text** box and paste
   (Ctrl + V) the selected word into the text
   box.
6. Repeat steps 3 through 5 for each word
   you want to use and separate each pair of
   words in the **Find Results Containing
   Text** box with AND or OR.

Changing Search Preferences

You may need to change the default settings in the **Search Preferences** dialog box.

1. Choose *File*, *Preferences*, *Search*.
2. Change preferences in the dialog box as necessary.
3. Click *OK*.

Selecting Indexes to Search

If you use Acrobat Reader to view and search documents other than this CD-ROM, you will need to understand how **Indexes** work. Otherwise, each time you start a search while using this CD-ROM, the appropriate **Index** will automatically be installed. If the search function does not work or the Search button is grayed-out, read the following information about **Indexes**.

Choosing *Tools*, *Search*, *Indexes* lists the available indexes. On a Macintosh, the list may also include indexes on currently unavailable file server volumes or CD-ROMs.

To be searchable, an index must be in the search list and it must be selected. When you add an index to the list, it is automatically selected. You can deselect or reselect it for specific searches or remove it from the list altogether. You can view a description of any index in the list.

Add an Index to the Search List

1. Choose *Tools, Search, Indexes.* (If the Search window is open, click the *Indexes* button in it instead.)
2. Click on *Add.*
3. Locate and select the appropriate index for this CD-ROM (e.g., blackcd for The Metals Black Book - on CD-ROM, or redcd, bluecd, etc.). Acrobat index-definition filenames usually end with with the extension .pdx.
4. Double-click the name of the index you want to use.

The new index is added to the search list.

Select or Deselect an Index

In the **Index Selection** dialog box, click the box of any index whose status you want to change and click *OK*.

Remove an Index from the Search List

1. In the **Index Selection** dialog box, highlight the name of the index you want to remove.
2. Click on *Remove*.
3. Click *OK*.

View a Description of an Index

1. In the **Index Selection** dialog box, highlight the name of the index you want information about.
2. Click on *Info* to view the information.
3. Click OK.