
CORROSION PREVENTION

MATERIALS SELECTION**6-1 Metals and Alloys**

The most common method of preventing corrosion is the selection of the proper metal or alloy for a particular corrosive service. Since this is the most important method of preventing or reducing corrosion damage, Chaps. 5, 7, 8, and 11 are also devoted to this topic, and only brief mention of some general rules will be presented here. One of the most popular misconceptions to those not familiar with metallurgy or corrosion engineering concerns the uses and characteristics of stainless steel. Stainless steel is not stainless, it is not the most corrosion-resistant material, and it is not a specific alloy. Stainless steel is the generic name for a series of more than 30 different alloys containing from 11.5 to 30% chromium and 0 to 22% nickel, together with other alloy additions. Stainless steels have widespread application in resisting corrosion, but it should be remembered that they do not resist all corrosives. In fact, under certain conditions, such as chloride-containing mediums and stressed structures, stainless steels are less resistant than ordinary structural steel. Stainless alloys are more susceptible to localized corrosion such as intergranular corrosion, stress-corrosion cracking, and pitting attack than ordinary structural steels. Frequently, the quality of stainless steels is checked with a magnet. This is based on the belief that nonmagnetic stainless steels represent "good" alloys, and stainless steels that are magnetic are inferior. This test has no basis and, in fact, is misleading. Many stainless steel alloys are magnetic, and many of the cast austenitic stainless steels show some ferromagnetic properties. There is no correlation between magnetic sus-

ceptibility and corrosion resistance. Under certain conditions many of the magnetic stainless steels are superior to the nonmagnetic varieties. In summary, a large number of corrosion failures can be directly attributed to the indiscriminate selection of stainless steels for construction on the basis that they are the "best." Stainless steels represent a class of highly corrosion-resistant materials of relatively low cost that should be carefully used.

In alloy selection, there are several "natural" metal-corrosive combinations. These combinations of metal and corrosive usually represent the maximum amount of corrosion resistance for the least amount of money. Some of these natural combinations are as follows:

1. Stainless steels–nitric acid
2. Nickel and nickel alloys–caustic
3. Monel–hydrofluoric acid
4. Hastelloys (Chlorimets)–hot hydrochloric acid
5. Lead–dilute sulfuric acid
6. Aluminum–nonstaining atmospheric exposure
7. Tin–distilled water
8. Titanium–hot strong oxidizing solutions
9. Tantalum–ultimate resistance
10. Steel–concentrated sulfuric acid

The above list does not represent the only material-corrosive combinations. In many instances, cheaper materials or more resistant materials are available. For nitric acid service, the stainless steels are usually considered first, as these have excellent resistance to this medium under a wide range of exposure conditions. Tin or tin coatings are almost always chosen as a container or piping material for very pure distilled water. For many years, tantalum has been considered and used as an "ultimate" corrosion-resistant material. Tantalum is resistant to most acids at all concentrations and temperatures and is generally used under conditions where minimal corrosion is required, such as implants in the human body. An interesting feature about tantalum is that it almost exactly parallels the corrosion resistance of glass. Both glass and tantalum are resistant to virtually all mediums except hydrofluoric acid and caustic solutions. For this reason, manufacturers of glass-lined equipment use tantalum plugs to seal defects since this material matches the resistance of glass.

There are some general, but usually accurate, rules that may be applied to the resistance of metals and alloys. For reducing or nonoxidizing environments, such as air-free acids and aqueous solutions, nickel, copper, and their alloys are frequently employed. For oxidizing conditions, chromium-containing alloys are used. For extremely powerful oxidizing conditions, titanium and its alloys have shown superior resistance. This generalized rule is demonstrated in Chaps. 7 and 8.

6-2 Metal Purification

The corrosion resistance of a pure metal is usually better than that of one containing impurities or small amounts of other elements. However, pure metals are usually expensive and are relatively soft and weak. In general, this category is used in relatively few cases which are more or less special.

Aluminum is a good example because it is not expensive in a fairly pure state—99.5% plus. The commercially pure metal is used for handling hydrogen peroxide, where the presence of other elements may cause decomposition because of catalytic effects. In another case, localized attack of aluminum equipment occurred because of segregation of impurity iron in the alloy. Reduction of the maximum iron content, agreeable to both producer and user, eliminated the localized attack and satisfactory performance of the equipment was obtained without added cost of material.

Another example is arc-melted zirconium, which is more corrosion resistant than induction-melted zirconium because of more impurities in the latter. This is a special case in an atomic-energy application where a little corrosion is too much.

6-3 Nonmetallics

This category involves integral or solid nonmetallic construction (mainly self-supporting) and also sheet linings or coverings of substantial thickness (to differentiate from paint coatings). The five general classes of nonmetallics are (1) rubbers, natural and synthetic; (2) plastics; (3) ceramics; (4) carbon and graphite; and (5) wood. Their mechanical properties and corrosion resistance are described in Chap. 5.

In general, rubbers and plastics, as compared with metals and alloys, are much weaker, softer, more resistant to chloride ions and hydrochloric acid, less resistant to strong sulfuric acid and oxidizing acids such as nitric, less resistant to solvents, and have relatively low temperature limitations (170 to 200°F for most). Ceramics possess excellent corrosion and high-temperature resistance, with the main disadvantages being brittleness and lower tensile strength. Carbons show good corrosion resistance, electric and heat conductivity, but they are fragile. Wood is attacked by aggressive environments.

Materials Technology Institute Manual No. 7, *Practical Guide to the Use of Elastomeric Linings* (May 1983), covers rubber linings for tanks, lines, fans, filters, scrubbers, etc. This manual contains sections on rubbers used, selection, testing, design, fabrication, preparation of equipment to be lined, processing, inspection, acceptance, maintenance, chemical resistance, and cost factors. Good and bad practices are described. Hard and soft natural rubbers, polychloroprene and butyl rubbers are included.

ALTERATION OF ENVIRONMENT

6-4 Changing Mediums

Altering the environment provides a versatile means for reducing corrosion. Typical changes in the medium that are often employed are (1) lowering temperature, (2) decreasing velocity, (3) removing oxygen or oxidizers, and (4) changing concentration. In many cases, these changes can significantly reduce corrosion, but they must be done with care. The effects produced by these changes vary depending on the particular system, as discussed in Chap. 2.

Lowering temperature This usually causes a pronounced decrease in corrosion rate. However, under some conditions, temperature changes have little effect on corrosion rate (see Sec. 2-8). In other cases, increasing temperature decreases attack. This phenomenon occurs as hot, fresh or salt water is raised to the boiling point and is the result of the decrease in oxygen solubility with temperature. Boiling seawater is therefore less corrosive than hot seawater (e.g., 150°F).

Decreasing velocity This is often used as a practical method of corrosion control. As discussed in Sec. 2-7, velocity generally increases corrosive attack, although there are some important exceptions. Metals and alloys that passivate, such as stainless steels, generally have better resistance to flowing mediums than stagnant solutions. Very high velocities should be always avoided where possible, because of erosion-corrosion effects (Chap. 3).

Removing oxygen or oxidizers This is a very old corrosion control technique. Boiler feedwater was deaerated by passing it through a large mass of scrap steel. In modern practice this is accomplished by vacuum treatment, inert gas sparging, or through the use of oxygen scavengers (see Sec. 6-5). Hydrochloric acid that has contacted steel during its manufacture or storage contains ferric chloride as an oxidizer impurity. This impure acid, termed *muratic acid* in commerce, rapidly corrodes nickel-molybdenum alloys (Hastelloy B, Chlorimet 2), whereas these materials possess excellent resistance in pure hydrochloric acid (Chap. 7). Although deaeration finds widespread application, it is not recommended for active-passive metals or alloys. These materials require oxidizers to form and maintain their protective films and usually possess poor resistance to reducing or non-oxidizing environments. For additional discussion of the effects of oxidizers, see Sec. 2-6.

Changing concentration This and its effect on corrosion have been described (Sec. 2-9). Decreasing corrosive concentration is usually effective. In many

processes, the presence of a corrosive is accidental. For example, corrosion by the water coolant in nuclear reactors is reduced by eliminating chloride ions. Many acids such as sulfuric and phosphoric are virtually inert at high concentrations at moderate temperatures. In these cases, corrosion can be reduced by *increasing* acid concentration.

No discussion of corrosion control would be complete without mentioning the *magic devices* or *water-conditioning gadgets* that have been and continue to be widely sold for purposes of controlling water corrosion. These gadgets are usually promoted on the basis that they will "stop corrosion," "prevent scaling," "destroy bacteria," "improve taste and odor," or "reduce water hardness." Some manufacturers make all of the above claims for their product! In every case, the device is based on some pseudoscientific principle, is simply constructed, quite expensive, and totally worthless. Several of them consist merely of a pipe coupling that looks identical to those available in any hardware store. Surprisingly, large numbers of these gadgets are installed each year by trained engineers.

Magic devices should not be confused with the water-softening, water-treating and cathodic protection apparatus and systems sold by reputable manufacturers. The worthless device is easily spotted by a number of clues: (1) It is based on a questionable or a "secret" new principle. (2) The advertising contains an excessive number of testimonials (usually from untrained persons). (3) The promotion makes no mention of any limitations—the device will work in any kind of water and protect any size system. (4) The device is always sold with a complete guarantee.*

6-5 Inhibitors

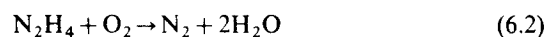
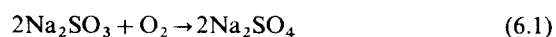
An inhibitor is a substance that, when added in small concentrations to an environment, decreases the corrosion rate. In a sense, an inhibitor can be considered as a retarding catalyst. There are numerous inhibitor types and compositions. Most inhibitors have been developed by empirical experimentation, and many inhibitors are proprietary in nature and thus their composition is not disclosed. Inhibition is not completely understood because of these reasons, but it is possible to classify inhibitors according to their mechanism and composition.

Adsorption-type inhibitors These represent the largest class of inhibiting substances. In general, these are organic compounds which adsorb on the metal surface and suppress metal dissolution and reduction reactions. In most cases, it appears that adsorption inhibitors affect both the anodic and cathodic processes, although in many cases the effect is unequal. Typical of this class of inhibitors are the organic amines.

*For an excellent survey of magic devices including a historical tabulation of those sold since 1865, see B. Q. Welder and E. P. Partridge, *Ind. Eng. Chem.*, **46**:954 (1954).

Hydrogen-evolution poisons These substances, such as arsenic and antimony ions, specifically retard the hydrogen-evolution reaction. As a consequence, these substances are very effective in acid solutions but are ineffective in environments where other reduction processes such as oxygen reduction are the controlling cathodic reactions.

Scavengers These substances act by removing corrosive reagents from solution. Examples of this type of inhibitor are sodium sulfite and hydrazine, which remove dissolved oxygen from aqueous solutions as indicated in Eqs. (6.1) and (6.2) below:



It is apparent that such inhibitors will work very effectively in solutions where oxygen reduction is the controlling corrosion cathodic reaction but will not be effective in strong acid solutions.

Oxidizers Such substances as chromate, nitrate, and ferric salts also act as inhibitors in many systems. In general, they are primarily used to inhibit the corrosion of metals and alloys that demonstrate active-passive transitions, such as iron and its alloys and stainless steels.

Vapor-phase inhibitors These are very similar to the organic adsorption-type inhibitors and possess a very high vapor pressure. As a consequence, these materials can be used to inhibit atmospheric corrosion of metals without being placed in direct contact with the metal surface. In use, such inhibitors are placed in the vicinity of the metal to be protected, and they are transferred by sublimation and condensation to the metal surface. The vapor-phase inhibitors are usually only effective if used in closed spaces such as inside packages or on the interior of machinery during shipment.

Table 6-1 lists some important inhibitors, their applications, and their sources. Examples of all the above-mentioned types of inhibitors appear in this table. It is important to remember that inhibitors are specific in terms of metal, environment, temperature, and concentration range. As mentioned above, the concentration and type of inhibitor to be used in a specific corrosive is usually determined by empirical testing, and this information is usually available from manufacturers. It is important to use enough inhibitor, since many inhibiting agents accelerate corrosion, particularly localized attack such as pitting, when present in small concentrations. Hence, too little inhibitor is less desirable than none at all. To avoid this possibility, inhibitors should be added in excess and their concentration checked periodically. When two or more inhibiting substances are added to a corrosive system, the inhibiting effect is sometimes greater than that which

Table 6-1 Corrosion inhibitor reference list

Metal	Environment	Inhibitor	Reference
Admiralty	Ammonia, 5%	0.5% hydrofluoric acid	54
Admiralty	Sodium hydroxide, 4% Be	0.6 moles H ₂ S per mole NaOH	71
Aluminum	Acid hydrochloric, 1N	0.003M α phenylacridine, β naphthoquinone, acridine, thiourea or 2-phenylquinoline	39
Aluminum	Acid nitric, 2-5%	0.05% hexamethylene tetramine	22
Aluminum	Acid nitric, 10%	0.1% hexamethylene tetramine	22
Aluminum	Acid nitric, 10%	0.1% alkali chromate	16
Aluminum	Acid nitric, 20%	0.5 hexamethylene tetramine	22
Aluminum	Acid phosphoric	Alkali chromates	52
Aluminum	Acid phosphoric, 20%	0.5% sodium chromate	16, 60
Aluminum	Acid phosphoric, 20-80%	1.0% sodium chromate	16, 60
Aluminum	Acid sulphuric, conc.	5.0% sodium chromate	45
Aluminum	Alcohol anti-freeze	Sodium nitrite and sodium molybdate	6
Aluminum	Bromine water	Sodium silicate	10
Aluminum	Bromoform	Amines	44
Aluminum	Carbon tetrachloride	0.05% formamide	55
Aluminum	Chlorinated aromatics	0.1-2.0% nitrochlorobenzene	21
Aluminum	Chlorine water	Sodium silicate	10
Aluminum	Calcium chloride, sat	Alkali silicates	59
Aluminum	Ethanol, hot	Potassium dichromate	52
Aluminum	Ethanol, commercial	0.03% alkali carbonates, lactates, acetates or borates	50
Aluminum	Ethylene glycol	Sodium tungstate or sodium molybdate	41
Aluminum	Ethylene glycol	Alkali borates and phosphates	52
Aluminum	Ethylene glycol	0.01-1.0% sodium nitrate	7
Aluminum	Hydrogen peroxide, alkaline	Sodium silicate	75
Aluminum	Hydrogen peroxide	Alkali metal nitrates	20
Aluminum	Hydrogen peroxide	Sodium metasilicate	59
Aluminum	Methyl alcohol	Sodium chlorate plus sodium nitrite	42
Aluminum	Methyl chloride	Water	72
Aluminum	Polyoxyalkene glycol fluids	2% Emery's dimer acid (dilinoleic acid), 1.25% N(CHMe ₂) ₃ , 0.05-0.2% mercaptobenzothiazole	43
Aluminum	Seawater	0.75% sec. amyl stearate	5
Aluminum	Sodium carbonate, dilute	Sodium fluosilicate	67
Aluminum	Sodium hydroxide, 1%	Alkali silicates	59
Aluminum	Sodium hydroxide, 1%	3-4% potassium permanganate	17
Aluminum	Sodium hydroxide, 4%	18% glucose	57
Aluminum	Sodium hypochlorite contained in bleaches	Sodium silicate	58
Aluminum	Sodium acetate	Alkali silicates	59
Aluminum	Sodium chloride, 3.5%	1% sodium chromate	22
Aluminum	Sodium carbonate, 1%	0.2% sodium silicate	28

(continued)

Table 6-1 Corrosion inhibitor reference list (continued)

Metal	Environment	Inhibitor	Reference
Aluminum	Sodium carbonate, 10%	0.05% sodium silicate	28
Aluminum	Sodium sulfide	Sulfur	46
Aluminum	Sodium sulfide	1% sodium metasilicate	59
Aluminum	50% sodium trichloracetate soln.	0.5% sodium dichromate	1
Aluminum	Tetrahydrofurfuryl alcohol	1% sodium nitrate or 0.3% sodium chromate	15
Aluminum	Triethanolamine	1% sodium metasilicate	22
Brass	Carbon tetrachloride, wet	0.001–0.1 aniline	53
Brass	Furfural	0.1% mercaptobenzothiazole	36
Brass	Polyoxyalkene glycol fluids	2.0% Emery's acid (dilinoleic acid), 1.25% N(CHMe ₂) ₃ , 0.05–0.2% mercaptobenzothiazole	43
Brass	50% sodium trichloracetate soln.	0.5% sodium dichromate	1
Cadium plated steel	55/45 ethylene glycol—water	1% sodium fluorophosphate	12
Copper	Fatty acids as acetic	H ₂ SO ₄ , (COOH) ₂ or H ₂ SiF ₆	63
Copper	Hydrocarbons containing sulfur	P-hydroxybenzophenone	61
Copper	Polyoxyalkene glycol fluids	2% Emery's acid (dilinoleic acid), 1.25% N(CHMe ₂) ₃ , 0.05–0.2% mercaptobenzothiazole	43
Copper & brass	Acid sulfuric, dil	Benzyl thiocyanate	68
Copper & brass	Ethylene glycol	Alkali borates & phosphates	22
Copper & brass	Polyhydric alcohol anti-freeze	0.4–1.6% Na ₃ PO ₄ plus 0.3–0.6 sodium silicate plus 0.2–0.6% sodium mercaptobenzothiazole	62
Copper & brass	Rapeseed soil	Succinic acid	9
Copper & brass	Sulfur in benzene solution	0.2% 9, 10 anthraquinone	29
Copper & brass	Tetrahydrofurfuryl alcohol	1% sodium nitrate or 0.3% sodium chromate	15
Copper & brass	Water-alcohol	0.25% benzoic acid, or 0.25% sodium benzoate at a pH of 7.5–10	23
Galvanized iron	Distilled water	15 ppm. mixture calcium and zinc metaphosphate	77
Galvanized iron	55/45 ethylene glycol—water	0.025% trisodium phosphate	12
Iron	Nitroarylamines	Dibenzylaniline	19
Lead	Carbon tetrachloride, wet	0.001–0.1% aniline	53
Magnesium	Alcohol	Alkaline metal sulfides	16
Magnesium	Alcohol, methyl	1% oleic or stearic acid neutralized with ammonia	13
Magnesium	Alcohols, polyhydric	Soluble fluorides at pH 8–10	26
Magnesium	Glycerine	Alkaline metal sulfides	16

(continued)

Table 6-1 Corrosion inhibitor reference list (continued)

Metal	Environment	Inhibitor	Reference
Magnesium	Glycol	Alkaline metal sulfides	16
Magnesium	Trichlorethylene	0.05% formamide	55
Magnesium	Water	1% potassium dichromate	8
Monel	Carbon tetrachloride, wet	0.001–0.1% aniline	53
Monel	Sodium chloride, 0.1%	0.1% sodium nitrite	72
Monel	Tap water	0.1% sodium nitrite	72
Nickel & silver	Sodium hypochlorite contained in bleaches	Sodium silicate	58
Stainless steel	Acid sulfuric, 2.5%	5–20 ppm. CaSO ₄ ·5H ₂ O	35
Stainless steel	Cyanamide	50–500 ppm. ammonium phosphate	65
Stainless steel, 18–8	Potassium permanganate contained in bleaches	Sodium silicate	58
Stainless steel, 18–8	Sodium chloride, 4%	0.8% sodium hydroxide	49
Steel	Acid citric	Cadmium salts	37
Steel	Acid sulfuric, dil	Aromatic amines	51
Steel	Acid sulfuric, 60–70%	Arsenic	74
Steel	Acid sulfuric, 80%	2% boron trifluoride	4
Steel	Aluminum chloride— hydrocarbon complexes formed during isomerization	0.2–2.0% iodine, hydriodic acid or hydrocarbon iodide	30
Steel	Ammoniacal ammonium nitrate	0.2% thiourea	40
Steel	Ammonium nitrate—urea solns.	0.05–0.10% ammonia 0.1% ammonium thiocyanate	18
Steel	Brine containing oxygen	0.001–3.0 methyl, ethyl or propyl substituted dithiocarbamates	48
Steel	Carbon tetrachloride, wet	0.001–0.1% aniline	53
Steel	Caustic—cresylate solution as in regeneration of refinery caustic wash solutions, 240–260F	0.1–1.0% trisodium phosphate	3
Steel	Ethyl alcohol, aqueous or pure	0.03% ethylamine or diethylamine	25
Steel	55/45 ethylene glycol—water	0.025% trisodium phosphate	12
Steel	Ethylene glycol	Alkali borates & phosphates	22
Steel	Ethylene glycol	Guanidine or guanidine carbonate	
Steel	Ethyl alcohol, 70%	0.15% ammonium carbonate plus 1% ammonium hydroxide	56
Steel	Furfural	0.1% mercaptobenzothiazole	36
Steel	Halogenated dielectric fluids	0.05–4% (γC ₄ H ₃ S) ₄ Sn γ(C ₄ H ₃) ₂ Sn or γC ₄ H ₃ S SnPh ₃	24

(continued)

Metal	Environment	Inhibitor	Reference
Steel	Halogenated organic insulating materials as chlorinated diphenyl	0.1% 2, 4(NH ₂) ₂ C ₆ H ₃ NHPh, <i>o</i> -MeH ₄ NH ₂ or <i>p</i> -NO ₂ C ₆ H ₄ NH ₂	31
Steel	Herbicides as 2, 4 dinitro-6-alkyl phenols in aromatic oils	1.0-1.5% furfural	32
Steel	Isopropanol, 30%	0.03% sodium nitrite plus 0.015% oleic acid	72
Steel	1:4 methanol-water	To 4 l. water and 1 l. methanol add 1 g. pyridine and 0.05 g. pyragallo	66
Steel	Nitrogen fertilizer solutions	0.1% ammonium thiocyanate	2
Steel	Phosphoric acid, conc.	0.01-0.5% dodecylamine or 2 amino bicyclohexyl and 0.001% potassium iodide, potassium iodate or iodacetic acid	47
Steel	Polyoxyalkylene glycol fluids	2% Emery's acid (dilinoleic acid) 1.25% N(CHMe ₂) ₃ 0.05-0.2% mercaptobenzothiazole	43
Steel	Sodium chloride, 0.05%	0.2% sodium nitrite	72
Steel	50% sodium trichloracetate soln.	0.5% sodium dichromate	1
Steel	Sulfide containing brine	Formaldehyde	14
Steel	Tetrahydrofurfuryl alcohol	1% sodium nitrate or 0.3% sodium chromate	15
Steel	Water	Benzoic acid	70
Steel	Water for flooding operations	Rosin amine	38
Steel	Water saturated hydrocarbons	Sodium nitrite	73
Steel	Water, distilled	Aerosol (an ionic wetting agent)	27
Tin	Carbon tetrachloride, wet	0.001-0.1% aniline	53
Tin	Chlorinated aromatics	0.1-2.0% nitrochlorobenzene	21
Tinned copper	Sodium hypochlorite contained bleaches	Sodium silicate	58
Tin plate	Alkali cleaning agents as trisodium phosphate, sodium carbonate, etc.	Diethylene diaminocobaltic nitrate	34
Tin plate	Alkaline soap	0.1% sodium nitrite	64
Tin plate	Carbon tetrachloride	2% mesityl oxide, 0.001% diphenylamine	76
Tin plate	Sodium chloride, 0.05%	0.2% sodium nitrite	72
Titanium	Hydrochloric acid	Oxidizing agents as chromic acid or copper sulfate	33
Titanium	Sulfuric acid	Oxidizing agents or inorganic sulfates	33
Zinc	Distilled water	15 ppm. mixture calcium and metaphosphates	77

Source: Maxey Brooke, Corrosion Inhibitor Checklist, *Chem. Eng.*, 230-234 (Dec. 1954).

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would be achieved by either of the two (or more) substances alone. This is called a *synergistic* effect. Many of the inhibitors listed in Table 6-1 are synergistic combinations of two or more inhibiting agents. At present, the mechanism of the synergistic effect is not completely understood.

Although inhibitors can be used to great advantage to suppress the corrosion of metals in many environments, there are certain limitations of this type of corrosion prevention which should be recognized. First, it may not be possible to add inhibitors to all corrosive systems because they may contaminate the environment. Further, many inhibitors are toxic, and their application is limited to those mediums that will not be used directly or indirectly in the preparation of food or other products that will come in contact with humans. Arsenic salts, which exert a powerful inhibiting effect in strong acids, have limited application for this reason. Inhibitors are primarily used in closed systems where the corrosive environment is either contained for long periods or recirculated. Inhibitors are usually not practical in "once-through" systems. Finally, inhibitors generally rapidly lose their effectiveness as the concentration and temperature of the environment increase.

Additional *general* information including *theoretical* aspects and also other examples of *applications* of various types of inhibitors are discussed here.

Rosenfeld* in his NACE Whitney Award Lecture 1981 presents a theoretical discussion and also the use of quantum chemistry calculations, x-ray photoelectron spectroscopy, radioactive tracers (i.e., ^{36}Cl), and chemical polarization as "tools" for studying inhibition. Inhibition can be caused by both adsorption and phase layers on the metal surface. He shows that adsorption inhibition prevents pitting of stainless steels. Protection is related to the adsorption displacement of activator (Cl^-) from the surface by passivating ions. It is related to this displacement power and not the oxidizing power of the anion. NO_3^- is more effective than CrO_4^{2-} , although the latter is a stronger oxidizer. He indicates that protection of steel from corrosion by hydrogen sulfide is due to the emergence of phase films containing iron, sulfur, and inhibitor components on the steel surface. He also shows that only a small part (in one case 4%) of the surface needs to be covered by the adsorbed inhibitor to stop corrosion. Adsorption in some cases has a chemical nature. Rosenfeld's main point "is that the inhibitor mechanism, irrespective of the amount adsorbed by the surface, consists in changing the electrophysical properties of surface atoms by the donor-acceptor inhibitor/metal reaction, rather than in screening the metal surface from the corrosive environment."

*I. L. Rosenfeld, New Data on the Mechanism of Metals Protection with Inhibitors, *Corrosion*, 37:371-377 (July 1981).

An International Conference on Corrosion Inhibition was held during May 1983. Evidence presented during recent years indicates that many organic and inorganic inhibitors become effective through interaction with one of several corrosion products to form a new protective phase rather than by absorption on the metal surface. The conference focuses on distinction between *interface* and *interphase* inhibitors. The Proceedings of this Conference (about 30 papers) will be published by NACE in 1984.

One commercial inhibitor and rust remover known as KO-99 is claimed to be of the interphase type.

Greene* discusses mechanisms, applications, and limitations of oxidizing inhibitors. They must be used with extreme caution in the presence of halides and other ions associated with localized corrosion.

A review paper that gives 161 literature references is by G. Trabanelli and V. Carassiti, "Mechanism and Phenomenology of Organic Inhibitors," in *Advances in Corrosion Science and Technology*, vol. 1, pp. 147-228, Plenum Press, New York, 1970. Structural formulas of organic inhibitors are included and are helpful.

An important cause of corrosion in overhead streams in oil refineries is attack by hydrogen sulfide and hydrochloric acid. Film-forming inhibitors are suggested by Nathan and Perugini.† Case histories are described. Inhibitors are also helpful in reducing hydrogen blistering.

Environmental considerations have focused attention on nonheavy metal inhibitors (i.e., chromates are banned). A paper by Breske‡ contains information on testing and field experience with these inhibitors for corrosion by waters. Fouling (deposition) is also discussed. Brunn¶ replaced chromate with a triazole inhibitor. See also Chapter 8 under cooling waters.

Vukasovich and Sullivan§ studied combined and separate effects of molybdate, phosphate, and borate used with nitrate and tolyltriazole for cooling water in auto engines and describe test procedures.

Addition of 0.2% water to anhydrous ammonia has stopped attack on steel. Inhibitors are also discussed in Chapter 8 under the appropriate environments and in Chapter 3 as well.

*N. D. Greene, Mechanism and Application of Oxidizing Inhibitors, *Materials Performance*, 21:20-22 (Mar. 1982).

†C. C. Nathan and J. J. Perugini, Prevention of Corrosion in Refinery Overhead Streams by Use of Neutralizing and Film-Forming Inhibitors, *Materials Performance*, 13:29-33 (Sept. 1974).

‡T. C. Breske, Testing and Field Experience with Nonheavy Corrosion Inhibitors, *Materials Performance*, 16:17-24 (Feb. 1977).

¶A. F. Brunn, Jr., Chromate Inhibitor Successfully Replaced in Copper-Nickel Plant Cooling Tower, *Materials Performance* 22:13-16 (June 1983).

§M. S. Vukasovich and F. J. Sullivan, Evaluation of Molybdate as an Inhibitor in Automotive Engine Coolants, *Materials Performance* 22: 25-33 (Aug. 1983).

DESIGN

The design of a structure is frequently as important as the choice of materials of construction. Design should consider mechanical and strength requirements together with an allowance for corrosion. In all cases, the mechanical design of a component should be based on the material of construction. This is important to recognize, since materials of construction used for corrosion resistance vary widely in their mechanical characteristics.

6-6 Wall Thickness

Since corrosion is a penetrating action, it is necessary to make allowances for this reduction in thickness in designing pipes, tanks, and other components. In general, wall thickness is usually made twice the thickness that would give the desired life. If a 10-year life is required for a given tank, and the best estimate of corrosion rate is $\frac{1}{8}$ in. in 10 years (corrosion rate about 12 mpy), the tank would be designed with a wall thickness of $\frac{1}{4}$ in. Such a design factor allows for some variation in the depth of penetration during uniform corrosion, which in most cases is not completely uniform. Of course, the wall thickness must meet mechanical requirements such as pressure, weight, and stress considerations.

This general rule may not apply where *reliable* corrosion data and *effective* monitoring are involved. Wallace and Webb* present an interesting discussion on realistic corrosion allowances. They ask the question, "Are you lining your vessels with cold, hard cash?" In other words, excessive corrosion allowances add weight and costs. They also suggest, for example, different corrosion allowances in the upper and lower zones of a tall vertical vessel. The upper portion could be subject to less corrosion than the lower half. I used this idea over 40 years ago when specifying heavier top portions of steel tank cars for shipping sulfuric acid—the upper area corroded many times faster than the lower.

6-7 Design Rules

There are many design rules which should be followed for best corrosion resistance. When I started working for the Du Pont Co. in 1934 I had to write a report every month and state the dollars saved because of my efforts. After one year or so we convinced the design people that "preventive medicine" was cost effective. In other words, "design corrosion out" of the system instead of waiting until the equipment *fails* in service. (It costs much less to change some lines on a drawing.) This resulted in close communication between designers and corrosion engineers and all major

*A. E. Wallace and W. P. Webb, Cut Vessel Costs with Realistic Corrosion Allowances, *Chem. Eng.*, 123-126 (Aug. 24, 1981).

projects included funds for utilization of corrosion engineers. I firmly believe the corrosion engineer should "sign off" on equipment drawings and not only the design engineer.

Some of the design rules that should be followed are listed below. It would be helpful if the designer had a good background in corrosion but unfortunately this is usually not the case.

1. Weld rather than rivet tanks and other containers. Riveted joints provide sites for crevice corrosion (see Chap. 3).
2. Design tanks and other containers for easy draining and easy cleaning. Tank bottoms should be sloped toward drain holes so that liquids cannot collect after the tank is emptied. Concentrated sulfuric acid is only negligibly corrosive toward steel. However, if a steel sulfuric acid tank is incompletely drained and the remaining liquid is exposed to the air, the acid tends to absorb moisture, resulting in dilution, and rapid attack occurs.
3. Design systems for the easy replacement of components that are expected to fail rapidly in service. Frequently, pumps in chemical plants are designed so that they can be readily removed from a piping system.
4. Avoid excessive mechanical stresses and stress concentrations in components exposed to corrosive mediums. Mechanical or residual stresses are one of the requirements for stress-corrosion cracking (see Chap. 3). This rule should be followed especially when using materials susceptible to stress-corrosion cracking.
5. Avoid electrical contact between dissimilar metals to prevent galvanic corrosion (see Chap. 3). If possible, use similar materials throughout the entire structure, or insulate different materials from one another.
6. Avoid sharp bends in piping systems when high velocities and/or solids in suspension are involved (erosion corrosion).
7. Provide thicker structures to take care of impingement effects.
8. Make sure materials are properly selected.
9. List complete specifications for all materials of construction and provide instructions to be sure the specs are followed all the way through to final inspection. Specify quality control procedures if relevant.
10. Be sure all relevant codes and standards are met.
11. Set realistic and scheduled dates for delivery of equipment.
12. Specify procedures for testing and storage of parts and equipment. For example, after hydraulic testing do not let the equipment sit full or partially full of water for any extended period of time. This could result in microbial corrosion, pitting, and stress corrosion. With regard to storage, spare stainless steel tubing showed stress-corrosion cracking when stored near the seacoast.
13. Specify operating and maintenance procedures (i.e., scheduled shut-downs).

14. Properly design against excessive vibration, not only for rotating parts but also, for example, for heat exchanger tubes.
15. Provide for "blanketing" with dry air or inert gas if vessels "inhale" moist marine atmosphere while being emptied.
16. Select plant site upwind from other "polluting" plants or atmosphere if relevant and/or feasible.
17. Avoid hot spots during heat-transfer operations. Heat exchangers and other heat-transfer devices should be designed to ensure uniform temperature gradients. Uneven temperature distribution leads to local heating and high corrosion rates. Further, hot spots tend to produce stresses that may produce stress-corrosion cracking failures.
18. Design to exclude air. Oxygen reduction is one of the most common cathodic reactions during corrosion, and if oxygen is eliminated, corrosion can often be reduced or prevented. In designing chemical plant equipment, particular attention should be paid to agitators, liquid inlets, and other points where air entrainment is a possibility. Exceptions to this rule are active-passive metals and alloys. Titanium and stainless steels are more resistant to acids containing dissolved air or other oxidizers.
19. The most general rule for design is: *avoid heterogeneity*. Dissimilar metals, vapor spaces, uneven heat and stress distributions, and other differences between points in the system lead to corrosion damage. Hence, in design, attempt to make all conditions as uniform as possible throughout the entire system.

CATHODIC AND ANODIC PROTECTION

6-8 Cathodic Protection

Cathodic protection was employed before the science of electrochemistry had been developed. Humphrey Davy used cathodic protection on British naval ships in 1824. The principles of cathodic protection may be explained by considering the corrosion of a typical metal M in an acid environment. Electrochemical reactions occurring are the dissolution of the metal and the evolution of hydrogen gas; for example,



Cathodic protection is achieved by supplying electrons to the metal structure to be protected. Examination of Eqs. (6.3) and (6.4) indicates that the addition of electrons to the structure will tend to suppress metal dissolution and increase the rate of hydrogen evolution. If current is considered to flow from (+) to (-), as in conventional electrical theory, then a structure

is protected if current enters it from the electrolyte. Conversely, accelerated corrosion occurs if current passes from the metal to the electrolyte. This current convention has been adopted in cathodic protection technology and is used here for consistency.

There are two ways to cathodically protect a structure: (1) by an external power supply or, (2) by appropriate galvanic coupling. Figure 6-1 illustrates cathodic protection by impressed current. Here, an external dc power supply is connected to an underground tank. The negative terminal of the power supply is connected to the tank, and the positive to an inert anode such as graphite or Duriron. The electric leads to the tank and the inert electrode are carefully insulated to prevent current leakage. The anode is usually surrounded by backfill consisting of coke breeze, gypsum, or bentonite, which improves electric contact between the anode and the surrounding soil. As shown in Fig. 6-1, current passes to the metallic structure, and corrosion is suppressed.

Cathodic protection by galvanic coupling to magnesium is shown in Fig. 6-2. As discussed in Chap. 3, magnesium is anodic with respect to steel

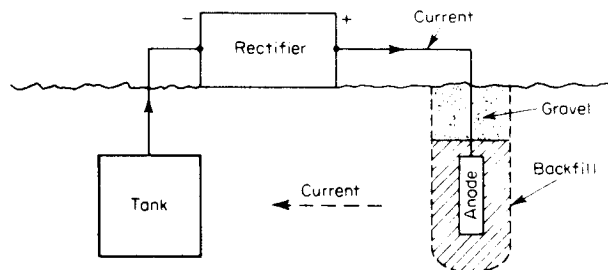


Figure 6-1 Cathodic protection of an underground tank using impressed currents.

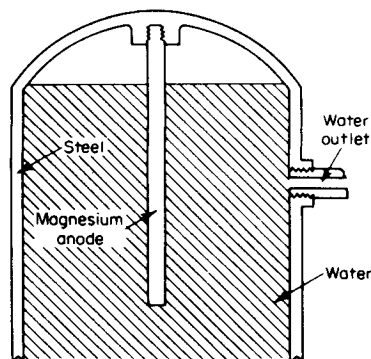


Figure 6-2 Cathodic protection of a domestic hot-water tank using a sacrificial anode.

and corrodes preferentially when galvanically coupled. The anode in this case is called a sacrificial anode since it is consumed during the protection of the steel structure. Cathodic protection using sacrificial anodes can also be used to protect buried pipelines, as shown in Fig. 6-3. The anodes are spaced along the pipe to ensure uniform current distribution.

Protective currents are usually determined empirically, and some typical values are listed in Table 6-2. Aggressive corrosives such as hot acids require prohibitively high currents, whereas much lower currents are needed to protect steel in less severe environments (concrete). Table 6-2 indicates typical average values of protective currents. Specific applications can deviate from these values. For example, in certain very acidic soils, 10 to 15 mA is often needed to reduce the corrosion of steel structures to tolerable levels. Also, pipes with organic coatings require much lower currents since the only areas requiring protection are defects or "holidays" in the protective layer. In such cases, trial-and-error adjustments of anode size or applied current can be made until satisfactory protection is achieved. A more accurate and less time-consuming approach is to measure the potential of the protected structure with a suitable reference electrode.

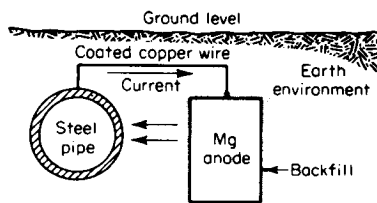


Figure 6-3 Protection of an underground pipeline with a magnesium anode.

Table 6-2 Typical current requirements for cathodic protection of steel

Structure	Environment	Conditions	Current density, mA/ft ²
Tank	Hot H ₂ SO ₄	Static	50,000
Pipelines and storage tanks	Underground (soil)	Static	1-3
Pipelines	Fresh water	Flowing	5-10
Water heaters	Hot, fresh water	Slow flow	1-3
Pilings	Seawater	Tidal motion	6-8
Reinforcing rods	Concrete	Static	0.1-0.5

Source: Some data taken from M. Stern, Principles of Cathodic Protection, *Symposium on Corrosion Fundamentals*, p. 84, University of Tennessee Press, 1956.

Steel structures exposed to soils, fresh and brackish water, and seawater are protected if they are polarized to a potential of -0.85 volt versus a copper/copper sulfate reference electrode. Figure 6-4 shows such an electrode designed for cathodic-protection surveys. This electrode has the advantages of low cost, good accuracy, and ruggedness. The potential of a structure is determined with a high-resistance voltmeter as shown in Fig. 6-5. During this measurement, the reference electrode is placed in the ground or on a sponge soaked in brine to make electrical contact. The cathodic current density necessary to polarize the pipe to -0.85 volt can be readily determined. In cases where sacrificial anodes (e.g., magnesium) are used, this same measurement is used to indicate the number and size of anodes needed for full protection. On long pipes or large, complex structures, reference-electrode surveying is utilized to determine uniformity of applied currents.

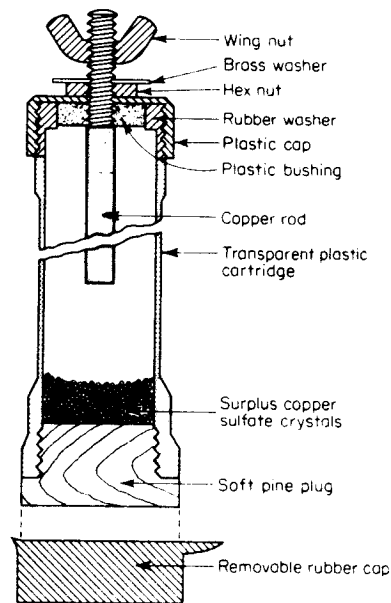


Figure 6-4 Copper-copper sulfate reference electrode.

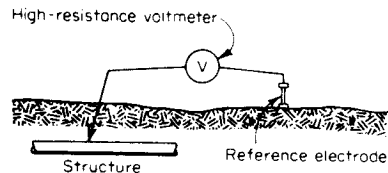


Figure 6-5 Pipe potential measurements with a reference electrode.

Anode selection for cathodic protection is based on engineering and economic considerations. Table 6-3 compares several types of sacrificial and impressed-current anodes. Of the sacrificial anodes, magnesium is the most widely used. Although its efficiency is low (about 50%), this is more than offset by its very negative potential, which provides high current output.

There is a considerable variety of impressed-current anodes ranging from low-cost scrap steel, which suffers relatively large losses, to the inert platinized titanium which is both efficient and expensive. Steel, graphite, and silicon-iron are the most widely used anode materials, with lead and platinized titanium finding increased applications in marine environments.

Stray-current effects are often encountered in cathodic-protection systems. The term *stray current* refers to extraneous direct currents in the earth. If a metallic object is placed in a strong current field, a potential difference develops across it and accelerated corrosion occurs at points where current leaves the object and enters the soil. Stray-current problems were quite common in previous years due to current leakage from trolley

Table 6-3 Comparisons of sacrificial and impressed-current anodes for cathodic protection

Sacrificial anodes			
	Magnesium	Zinc	Aluminum-tin
Theoretical consumption, lb/ampere-year	9	23	6.5
Actual consumption, lb/ampere-year	18	25	16-20
Potential vs. Cu/CuSO ₄	-1.7	-1.15	-1.3
Impressed-current anodes			
Material	Typical applications	Typical loss, lb/ampere-year	
Scrap steel	Soil, fresh- and sea-water	20	
Aluminum	Soil, fresh- and sea-water	10-12	
Graphite	Soil and fresh water	0.25-5.0	
High-silicon iron and Si-Cr iron	Soil, fresh water, and seawater	0.25-1.0	
Lead	Seawater	0.1-0.25	
Platinized titanium	Seawater	nil	

Source: Modified from J. H. Morgan, *Cathodic Protection*, The Macmillan Company, New York, 1960.

tracks. Pipelines and tanks under tracks were rapidly corroded. However, since this type of transportation is now obsolete, stray currents from this source are no longer a problem. A more common source of stray currents is from cathodic-protection systems. This is especially pronounced in densely populated oil production fields and within industrial complexes containing numerous buried pipelines.

Figure 6-6 illustrates stray currents resulting from a cathodic-protection system. The owner of the buried tank installed cathodic protection. He did not know of the nearby pipeline that failed rapidly due to the stray-current field. If the owner of the pipeline applies cathodic protection, it is possible to prevent stray-current attack of his pipe, but it will produce stray-current attack of the buried tank. It is easy to see how stray-current corrosion tends to escalate. As each owner adds or increases protective currents to his structures, he increases the current requirements on other adjacent structures. In one industrial area containing a high density of protected underground structures, protective current requirements rapidly rose to 20 mA/ft² in several areas! The solution to this problem is cooperation between operators. For example, the stray-current problem shown in Fig. 6-6 could be prevented by electrically connecting the tank and pipe by a bus connector and rearranging anodes as shown in Fig. 6-7. Here, both pipe and tank are protected without stray-current effects, with the owners sharing the cost of installation and operation.

Cathodic protection involving impressed current anodes to reduce highway and other bridge maintenance costs is being done and substantial savings realized. Corrosion of the reinforcing steel is reduced. Solar panels to supply current for bridges in rural areas has been suggested.

Cathodic protection is still more of an art than a science, and past experience is the best basis for judgment. This remark was made by a corrosion engineer who retired after 30 years of experience, mostly on cathodic

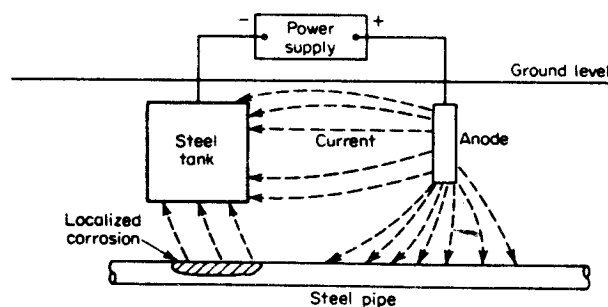


Figure 6-6 Stray currents resulting from cathodic protection.

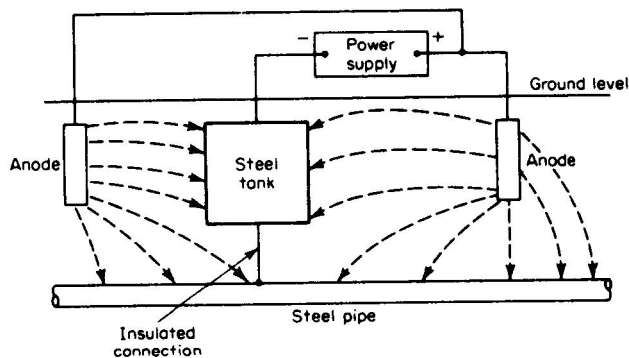


Figure 6-7 Prevention of stray-current corrosion by proper design.

protection of pipelines. There are many firms in the cathodic-protection business, and they should be consulted if you have a major project.

One of the most extensive bibliographies on any subject is on underground corrosion and Part I appeared in *Materials Performance*, pp. 41-43 (Jan. 1982). A total of 10 parts was published in consecutive issues. This bibliography contains 1172 English-language journal articles. Subjects include underground and soil corrosion, bacterial corrosion, cathodic protection and protective coatings.

6-9 Anodic Protection

In contrast to cathodic protection, anodic protection is relatively new; it was first suggested by Edleanu in 1954. This technique was developed using electrode kinetics principles and is somewhat difficult to describe without introducing advanced concepts of electrochemical theory. Simply, anodic protection is based on the formation of a protective film on metals by externally applied anodic currents. Considering Eqs. (6.3) and (6.4), it appears that the application of anodic current to a structure should tend to increase the dissolution rate of a metal and decrease the rate of hydrogen evolution. This usually does occur except for metals with active-passive transitions such as nickel, iron, chromium, titanium, and their alloys. If carefully controlled anodic currents are applied to these materials, they are passivated and the rate of metal dissolution is decreased. To anodically protect a structure, a device called a *potentiostat* is required. A potentiostat is an electronic device that maintains a metal at a constant potential with respect to a reference electrode. The anodic protection of a steel tank containing sulfuric acid is illustrated in Fig. 6-8. The potentiostat has three terminals, one connected to the tank, another to an auxiliary cathode

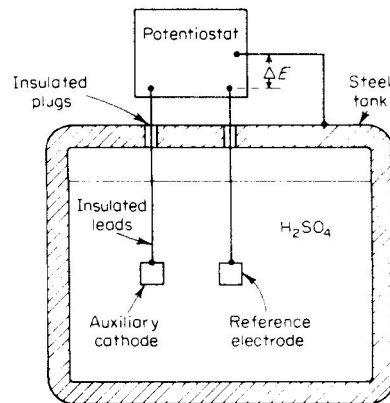


Figure 6-8 Anodic protection of a steel storage tank containing sulfuric acid.

(a platinum or platinum-clad electrode), and the third to a reference electrode (e.g., calomel cell). In operation, the potentiostat maintains a constant potential between the tank and the reference electrode. The optimum potential for protection is determined by electrochemical measurements.

Anodic protection can decrease corrosion rate substantially. Table 6-4 lists the corrosion rates of austenitic stainless steel in sulfuric acid solutions containing chloride ions with and without anodic protection. Examination of the table shows that anodic protection causes a 100,000-fold decrease in corrosive attack in some systems. Although anodic protection is limited to passive metals and alloys, most structural materials of modern technology contain these elements. Thus, this restriction is not as important as it first might seem. Table 6-5 lists several systems where anodic protection has been

Table 6-4 Anodic protection of austenitic stainless steel at 30°C

Protected at 0.500 volt vs. saturated calomel electrode

Alloy type	Environment (air exposed)	Corrosion rate, mpy	
		Unprotected	Anodically protected
304 (19Cr-9Ni)	$N H_2SO_4 + 10^{-5} M NaCl$	14	0.025
	$N H_2SO_4 + 10^{-3} M NaCl$	2.9	0.045
	$N H_2SO_4 + 10^{-1} M NaCl$	3.2	0.20
	$10N H_2SO_4 + 10^{-5} M NaCl$	1930	0.016
	$10N H_2SO_4 + 10^{-3} M NaCl$	1125	0.04
	$10N H_2SO_4 + 10^{-1} M NaCl$	77	0.21

Source: S. J. Acello and N. D. Greene, *Corrosion*, 18:286t (1962).

Table 6-5 Current requirements for anodic protection

Fluid and concentration	Temperature, °F	Metal	Current density, mA/ft ²	
			To passivate	To maintain
H₂SO₄				
1 molar	75	316SS	2100	11
15%	75	304	390	67
30%	75	304	500	22
45%	150	304	165,000	830
67%	75	304	4700	3.6
67%	75	316	470	0.09
67%	75	Carpenter 20	400	0.8
93%	75	Mild steel	260	21
Oleum	75	Mild steel	4400	11
H₃PO₄				
75%	75	Mild steel	38,000	19,000
115%	180	304SS	0.03	0.00014
NaOH				
20%	75	304SS	4400	9.4

Source: C. E. Locke et al., *Chem. Eng. Progr.*, **56**:50 (1960).

applied successfully. The primary advantages of anodic protection are its applicability in extremely corrosive environments and its low current requirements. (For additional information concerning the principles and mechanism of anodic protection, see Chap. 10.)

An interesting and economical application of anodic protection is the use of type 316 stainless pipes for cooling acid in sulfuric acid plants. The pipes have anodic protection. This arrangement replaces the old thick-wall cast-iron heat exchangers.

The reader is referred to an excellent book, *Anodic Protection—Theory and Practice in the Prevention of Corrosion*, by O. L. Riggs and C. E. Locke, Plenum Press, New York (1981). This extensively covers *all phases* of this subject.

6-10 Comparison of Anodic and Cathodic Protection

Some of the important differences between anodic and cathodic protection are listed in Table 6-6. Each method has advantages and disadvantages, and anodic and cathodic protection tend to complement one another. Anodic protection can be utilized in corrosives ranging from weak to very aggressive, while cathodic protection is restricted to moderately corrosive conditions because of its high current requirement, which increases as the corrosivity of the environment increases. (Compare steel in H₂SO₄ in Tables 6-2 and 6-5.) Hence, it is not practical to cathodically protect metals in

Table 6-6 Comparison of anodic and cathodic protection

	Anodic protection	Cathodic protection
Applicability		
Metals	Active-passive metals only	All metals
Corrosives	Weak to aggressive	Weak to moderate
Relative cost		
Installation	High	Low
Operation	Very low	Mediums to high
Throwing power	Very high	Low
Significance of applied current	Often a direct measure of protected corrosion rate	Complex—does not indicate corrosion rate
Operating conditions	Can be accurately and rapidly determined by electrochemical measurements	Must usually be determined by empirical testing

very aggressive mediums. Anodic protection, on the other hand, uses very small applied currents, and it can be utilized in strong corrosive mediums.

The installation of a cathodic-protection system is relatively inexpensive since the components are simple and easily installed. Anodic protection requires complex instrumentation including a potentiostat and reference electrode, and its installation cost is high. The operating costs of the two systems differ because of the difference in current requirements noted above. Throwing power, or the uniformity of current-density distribution, varies between the two types of protection. The throwing power of cathodic protection is generally low, which requires numerous closely spaced electrodes to achieve uniform protection. Anodic-protection systems have throwing power, and consequently, a single auxiliary cathode can be utilized to protect long lengths of pipe.

Anodic protection possesses two unique advantages. First, the applied current is usually equal to the corrosion rate of the protected system. Thus, anodic protection not only protects but offers a means for monitoring instantaneous corrosion rate. Secondly, operating conditions for anodic protection can be precisely established by laboratory polarization measurements. In contrast, the operating limits for cathodic protection are usually established by empirical trial-and-error tests. Although various rapid evaluation methods for estimating the current requirements for cathodic protection have been suggested, all of these have proved to be unreliable to a greater or lesser degree, and the final choice is usually based on past experience.

The concept of anodic protection is based on sound scientific principles, as discussed in Chap. 10, and has been successfully applied to industrial

corrosion problems. However, the incorporation of anodic protection into corrosion engineering practice has occurred very slowly since its introduction. The reluctance of corrosion engineers to utilize this new method of preventing corrosion is probably due in large measure to their personal corrosion experiences and to classic corrosion literature. The disastrous effects that are produced if a cathodic-protection system is connected with reverse polarity, the rapid deterioration of an anode in a galvanic couple, and the generalized rule of classic corrosion literature, which states that impressed anodic currents accelerate corrosion, all tend to suppress the introduction of this protection technique. In essence, anodic protection represents an exception to the general rule that impressed anodic current or the removal of electrons from a metal accelerates corrosion. In the future, anodic protection will probably revolutionize many current practices of corrosion engineering. Utilizing this technique, it is possible to reduce the alloy requirements for a particular corrosion service. Anodic protection can be classed as one of the most significant advances in the entire history of corrosion science.

COATINGS

6-11 Metallic and Other Inorganic Coatings

Relatively thin coatings of metallic and inorganic materials can provide a satisfactory barrier between metal and its environment. The chief function of such coatings is (aside from sacrificial coatings such as zinc) to provide an effective barrier. Metal coatings are applied by electrodeposition, flame spraying, cladding, hot dipping, and vapor deposition. Inorganics are applied or formed by spraying, diffusion, or chemical conversion. Spraying is usually followed by baking or firing at elevated temperatures. Metal coatings usually exhibit some formability, whereas the inorganics are brittle. In both cases a complete barrier must be provided. Porosity or other defects can result in accelerated localized attack on the basic metal because of two-metal effects.

Examples of metal-coated articles are automobile bumpers and trim, household appliances and fixtures, silverware, galvanized steel, and tin cans. Bathtubs and "glassed" steel tanks are representative of ceramic coatings. Examples of conversion and diffusion coatings are anodized aluminum and chromized steel, respectively.

Electrodeposition This process, also called electroplating, consists of immersing a part to be coated in a solution of the metal to be plated and passing direct current between the part and another electrode. The character of the deposit depends on many factors including temperature,

current density, time, and composition of the bath. These variables can be adjusted to produce coatings that are thick (say 20 mils) or thin (thousandths of a mil in the case of some tin plate), dull or bright, soft (lead) or hard (chromium), and ductile or brittle. Hard platings are utilized to combat erosion corrosion. The electroplate can be a single metal, layers of several metals, or even an alloy composition (e.g., brass). For example, an automobile bumper has an inner flash plate of copper (for good adhesion), an intermediate layer of nickel (for corrosion protection), and a thin top layer of chromium (primarily for appearance). Zinc, nickel, tin, and cadmium, in that order, are plated on the largest tonnage basis. Gold, silver, and platinum plates are common. The majority of the metals can be applied by electro-deposition.

Flame spraying This process, also called metallizing, consists of feeding a metal wire or powder through a melting flame so that the metal, in finely divided liquid particles, is blown onto the surface to be protected. Oxygen and acetylene or propane are commonly used for the melting flame. The coatings are usually porous and are not protective under severe wet corrosive conditions. Generally the porosity decreases with the melting point of the metal—zinc, tin, and lead are better from this standpoint than steel or stainless steel. The surface to be sprayed must be roughened (sandblasted) to obtain a mechanical bond. Sometimes a paint coating is applied over the sprayed metal to fill the voids and provide a better barrier. The porous metal makes a good base for the paint and a good bond is obtained. Flame spraying is an economical way of building up worn surfaces on parts such as shafting. High-melting metals may be deposited by plasma-jet spraying.

Flame-sprayed applications include tank cars and vessels of all kinds, bridges, ship hulls and superstructures, refrigeration equipment, and many fabricated steel products. Exhaust stacks sprayed with aluminum and sealed with a silicone-aluminum-organic coating are protected up to 900 F. Sprayed stainless (18-8) steels covered with sprayed aluminum gives protection in air up to 1500 F. Average costs for a 5-mil coating are 6¢/ft² for aluminum and 12¢/ft² for zinc.

Cladding This involves a surface layer of sheet metal usually put on by rolling two sheets of metal together. For example, a nickel and a steel sheet are hot-rolled together to produce a composite sheet with, say, $\frac{1}{8}$ in. of nickel and 1 in. of steel. The cladding is usually thin in relation to the other material. High-strength aluminum alloys are often clad with a commercially pure aluminum skin to provide the corrosion barrier because the alloy is susceptible to stress corrosion.

Sometimes a thin liner is spot-welded to the walls of a steel tank. Nickel, aluminum, copper, titanium, aluminum, stainless steels, and other materials are often used as cladding for steel.

Development of the very-low-carbon stainless steels (type 304L) has increased the utilization of clad vessels. A stainless clad steel tank cannot be quench-annealed. A higher alloy rod is necessary for welding clad parts to avoid dilution of the weld deposit and loss of corrosion resistance. For example, type 310 stainless steel weld rod is used to join type 304L clad steel plate.

Cladding presents a great economic advantage in that the corrosion barrier or expensive material is relatively thin and is backed up by inexpensive steel. A good example is a high-pressure vessel that could have a $\frac{1}{8}$ - or $\frac{1}{4}$ -in. clad on 3 in. of steel. Costs might be astronomical if the entire wall were made of highly corrosion-resistant material.

Hot dipping Hot dip coatings are applied to metals by immersing them in a molten metal bath of low-melting-point metals, chiefly zinc, tin, lead, and aluminum. Hot dipping is one of the oldest methods for coating with metal. Galvanized steel is a popular example. Thickness of the coating is much greater than electroplates because very thin dip coatings are difficult to produce. Coated parts can be heat-treated to form an alloy bond between the coating and the substrate.

Vapor deposition This is accomplished in a high-vacuum chamber. The coating metal is vaporized by heating electrically, and the vapor deposits on the parts to be coated. This method is more expensive than others and generally limited to "critical" parts, for example, high-strength parts for missiles and rockets. The exception to this statement is a new process (U.S. Steel Corporation) for depositing aluminum on steel on a production basis.

Diffusion Diffusion coatings involve heat treatment to cause alloy formation by diffusion of one metal into the other. For this reason the process is also termed "surface alloying." Parts to be coated are packed in solid materials or exposed to gaseous environments containing the metal that forms the coating. Sherardizing (zinc), chromizing (chromium) and aluminizing (aluminum) are examples. In the latter, a protective layer of Al_2O_3 forms over the iron-aluminum alloyed surface. Carbon steel, low-alloy steels, and stainless steel are aluminized. This provides the strength of the treated metal and good corrosion resistance to air and sulfur gases at high temperatures ($\sim 1650^\circ\text{F}$). These aluminum-treated steels are used in the petroleum and chemical industries (e.g., production of sulfuric acid) as heat exchangers and other hot surfaces. This process is not generally recommended for aqueous environments.

Aluminized steels are used on a competitive basis, but they would be utilized extensively as substitutes in the event of a shortage of chromium.

Chemical conversion Coatings from chemical conversion are produced by "corroding" the metal surface to form an adherent and protective corrosion product. *Anodizing* consists of anodic oxidation in an acid bath to build up an oxide layer. The best-known product is anodized aluminum, wherein the protective film is Al_2O_3 . Great improvement in corrosion resistance is not obtained, so anodized aluminum should not be used where untreated aluminum would show rapid attack. The surface layer is porous and provides good adherence for paints. The anodized surface can be "sealed" by exposing to boiling water. Anodized aluminum is used for many architectural purposes (e.g., building wall panels) and others where a pleasing appearance is of prime importance. In other words, anodized aluminum could be considered as "controlled weathering" to produce a uniform surface.

Additional examples are Bonderizing and Parkerizing (*phosphatizing* in a phosphoric acid bath), *chromatizing* (exposure to chromic acid and dichromates), and *oxide* or heat coatings for steel. Automobile bodies are the best known example of phosphatizing. Here the treatment provides a good base for the paint and also provides some time before rusting occurs if the finish is damaged. Chromate treatments are applied to magnesium and zinc parts and offer some measure of corrosion resistance, although the parts are normally painted. Oxide coatings are produced on steel by heating in air or by exposing to a hot liquid. These coatings must be treated with a petroleum product to avoid rusting—the colored oxide is present primarily for appearance. The author "blues" his guns by immersing them in a hot caustic solution and then rubbing the oxidized metal with raw linseed oil while it is still hot.

Surface modification Surface treatments involving directed energy beams are receiving increasing attention. Eventually these treatments may be desirable when alloying elements such as chromium may not be readily available.

Laser surface alloying is described in an excellent review paper by C. W. Draper.* Techniques, basic considerations, and results are described. CO_2 lasers are most popular. An AIME book† covers the effects of directed beam processing and resultant behavior of various alloys of steel, aluminum and copper (Fe-Al bronze). McCafferty et al.‡ show that laser treatment improves resistance to uniform corrosion in hydrochloric acid and citrate solutions, and has no effect on pitting potential in 0.1M NaCl for this 3003

*C. W. Draper, Laser Surface Alloying: The State of the Art, *J. Metals*, **34**(6):24-32 (June 1982).

†C. R. Clayton and C. M. Preece, eds, *Corrosion of Metals Processed by Directed Energy Beams*, Metals Society of AIME, New York (1982).

‡E. McCafferty, P. G. Moore, and G. T. Pease, Effect of Laser Surface Melting on the Electrochemical Behavior of an Al-1% Mn Alloy, *J. Electrochem. Soc.* **129**:9-17 (Jan. 1982).

aluminum alloy. Moore and McCafferty* show passivation for steel alloyed with 5, 20, and 80% chromium. Lasers are also used to impregnate metals with hard particles (i.e., WC and TiC) for improved wear resistance.

Ion implantation Application of ion beams to modify surfaces is another method that may eventually have practical application. Potter et al.† in a review paper describe beneficial results on corrosion resistance.

Glassed steel or glass-lined steel is an important material of construction for the process industries and also in the home,—in hot-water tanks, for example. The smooth surface is an advantage when ease of cleaning is a requirement or sticky materials, such as latex, are being handled. Glassed



Figure 6-9 Glassed steel vessel and internals. (*Pfaunder Co.*)

*P. G. Moore and E. McCafferty, Passivation of Fe-Cr Alloys Prepared by Laser Surface Alloying, *J. Electrochem. Soc.* **128**(6):1391-1393 (June 1981).

†D. I. Potter, M. Ahmed, and S. Lamond, Metallurgical Surfaces Produced by Ion Implantation, *J. Metals*, 17-22 (Aug. 1983).

steel is widely used in the drug industry, in pilot plants, in wine, brewery, and food plants, and in many others where severe corrosives or contamination of product are involved. Figure 6-9 shows glassed-steel equipment.

Concrete is utilized for many corrosion applications. Examples are encasing structural steel (also for fireproofing), concrete-lined pipe, and concrete vessels.

6-12 Organic Coatings

These involve a relatively thin barrier between substrate material and the environment. Paints, varnishes, lacquers, and similar coatings doubtless protect more metal on a tonnage basis than any other method for combating corrosion. Exterior surfaces are most familiar, but inner coatings or linings are also widely utilized. Approximately 2 billion dollars per year are expended in the United States on organic coatings. A myriad of types and products are involved, and some are accompanied by outlandish claims. Substantial knowledge of this complex field is required for successful performance. The best procedure for the uninitiated is to consult with a reputable producer of organic coatings. As a general rule, these coatings should not be used where the environment would rapidly attack the substrate material. For example, a paint would not be used to line the inside of a tank car for shipping hydrochloric acid. One defect or a small area of exposed metal would result in rapid perforation. An evaluation test program is also recommended.

Aside from proper application, the three main factors to consider for organic coatings, listed in order of importance, are (1) surface preparation, (2) selection of primer or priming coat, and (3) selection of top coat or coats. If the metal surface is not properly prepared, the paint may peel off because of poor bonding. If the primer does not have good adherence or is not compatible with the top coat, early failure occurs. If the first two factors are wrong, the system will fail regardless of the top coat used. Poor paint performance is, in most cases, due to poor application and surface preparation.

Surface preparation involves surface roughening to obtain mechanical bonding ("teeth") as well as removal of dirt, rust, mill scale, oil, grease, welding flux, crayon marks, wax, and other impurities. In other words a clean, rough surface is needed. The best method is to grit-blast or sandblast the steel surface. Other methods are pickling and other types of chemical treatments, scraping, wire brushing, flame cleaning (heat with torch and scrape off dirt and scale), chiseling, and chipping. A study of surface preparation on paint life showed 10.3 years for sandblasting, 9.6 years for pickling, and 2.3 years for weathering and then hand cleaning. Pinholes in welds and sharp edges should be ground out to ensure contact between the paint and the metal. Other chemical methods are solvent degreasing, hot or

cold alkali treatments, phosphatizing, chromate treatment, and electrochemical treatments such as anodizing and cathodic cleaning.

In addition to economic considerations, the selection of surface preparation method depends upon the metal to be painted; the shape, size and accessibility of the structure; the coating system; and the service conditions.

Primers can contain rust-inhibitive pigments such as zinc chromate and zinc dust and thereby provide another function in addition to acting as barriers. Wettability is needed so that crevices and other surface defects will be filled rather than bridged. Short drying times are advantageous to preclude contamination before the top coats are applied, particularly in field applications.

Top-coat selection is important. Use of cheap paints is false economy because the majority of the cost of a paint system is in application. Many times paint is applied primarily for appearance—it might be cheaper to provide corrosion allowance by making the steel thicker in the first place. However, who wants a rusty tank on their property? An important point here is that good appearance and good corrosion protection, even in severe atmospheres, can be obtained at very little *extra* cost (a fraction of a cent per square foot per year) by selecting a good top-coat material.

The coating thickness must be such that no bare metal is exposed. It is almost impossible to apply one coat of a paint and have it completely free of pinholes or other defects (“holidays” in the trade). Multiple coats are needed so that a pinhole in one coat will be covered by a complete film of another. Thickness is important also because paint deteriorates or weathers with time.

Various methods are available to reduce maintenance painting costs. One is to institute a touch-up program (you should do this to your car) to cover bad spots early instead of waiting until the coating is so bad that a repaint job is required. It would be a rare case where a coating system fails all over at the same time. Another method is to apply the paint by a hot-spray method. In this case the higher temperature permits higher solids content (with less thinner) and good sprayability, which means a thicker film per coat. Another method consists of applying tape on edges so that the edge is protected; edges are of course the hardest to protect. Another method is to design the structure such that minimum surface area and edges are presented (use a channel or pipe instead of an I beam).

Many companies let all of their paint jobs to outside contractors on a bid basis. This may result in low first cost, but it is usually more costly in the long run. If a plant has sufficient work, it should hire and train its own painters. One company made this change and as a result saved many thousands of dollars per year.

To sum up, a good paint job consists of proper surface preparation, proper coating selection, and proper application. A tremendous variety of paints are available, but it is beyond the scope of this book to go into detail.