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Corrosion Control and Tactics

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Introduction

Corrosion in its several forms is a well-known problem that occurs in many applications. The associated costs are many and widespread in scope. These corrosion-induced costs may include customer dissatisfaction with deteriorated appearance or function of consumer products, serious personnel injury due to material failures, large financial losses from litigation that may follow personnel injuries or fatalities or extended shutdowns of continuous operating manufacturing plants due to corrosion. In the latter case the cost of repair or replacement of the specific corroded equipment often is minor compared to the cost of lost production caused by the shutdown. It has been estimated that the direct cost of corrosion across all U.S. industries in 1998 was \$276 billion (that's billion with a B), or more than 3% of the country's gross domestic product in that year, Reference 1.

Many research and development efforts have been and are in progress in universities and industries to combat corrosion by various approaches. This work includes gaining more complete basic understanding of the several specific mechanisms of corrosion through their electrochemical and metallurgical aspects; developing and adequately testing new metallic alloys that combine good resistance and other needed characteristics; applying nanotechnology to anticorrosion coatings, developing fundamentally different and reliable corrosion sensors; etc. All these efforts are justified and potentially can provide big payoffs.

While R&D concerning new approaches to control corrosion is proceeding there are many methods and tactics that are well established and effective those, unfortunately, are not always used. Often this may be because the probability of corrosion was overlooked or misunderstood by the responsible individual or engineering team during the design of the product or system. Corrosion and its control are not topics given much attention in most engineering curriculums. It may also be that management mandates the decision to omit some method of corrosion control based on the rationale that it will not be effective in the given application or, more frequently, the initial cost is prohibitive.

The objective of this course is to show that there can be many ways to lessen and control corrosion in a given application. Some of these can be relatively easy and inexpensive to apply – especially when compared to the human and financial costs that may be incurred by omitting them. The main point is simply to be aware of what parameters cause or accelerate corrosion and what actions, if taken early in the planning phases of engineering, can be helpful in avoiding major corrosion effects.

Before discussing the classic corrosion control methods and specific tactics that may be used in different applications, some fundamental information may be useful. This will include certain aspects of electrochemistry, brief descriptions of the various forms of attack and a discussion of some important environmental and application parameters that affect corrosion rates.



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Some Electrochemical Aspects of Corrosion

Aqueous corrosion of metals has both electrical and chemical aspects. Therefore some basic ideas from electrochemistry are essential in understanding and in seeking to control those processes. Non-metals such as polymers (plastics), ceramics (e.g., glasses and refractories) and composite materials (combinations of two or more classes of materials) also can deteriorate and fail due to exposure to specific environmental or mechanical conditions but, in general, those failure mechanisms are not electrochemical.

When metals corrode two types of simultaneous, electrochemical reactions always occur. These reactions are oxidation and reduction (redox reactions). Oxidation reactions produce electrons while reduction reactions consume electrons. The areas of the metal surface where the oxidation reaction occurs are known as anodes and the areas where reduction occurs are known as cathodes. Oxidation is the conversion of stable, electrically neutral metal atoms into electrically charged ions of that metal (or into an insoluble compound with nonmetallic elements) as electrons are released. These electrons from the anodic reaction sites flow through and below the surface of the exposed metal to the cathodic reduction sites. Ions generated at the anodic sites conduct electrical current through the corrosive medium – known as the electrolyte - away from the exposed surface in an opposite direction to that of the electron flow. Oxidation at the anodic sites results in chemical dissolution and penetration of the metal. At the same time, at the cathodic reduction sites, the electrons generated by the oxidation reaction are consumed in the process of producing other chemical species that are released into the electrolyte.

In general corrosion the anodic and cathodic regions on the metal continually change and switch locations so that the attack and penetration is approximately uniform at most areas across the exposed surface. In the many forms of localized corrosion, e.g., pitting or stress-corrosion cracking, the anodic oxidation reaction is concentrated and remains at a specific location. The attack is essentially confined in a specific area, e.g., at the bottom of pits or at the tip of a growing crack. Thus the rates and effects of localized forms of corrosion are typically more detrimental than general corrosion.

There is only one possible type of anodic, oxidation reaction and that is the conversion of the uncharged atomic form of the given metal into charged ions of that metal while releasing electrons into the metal. These ions then may either go directly into the electrolyte or they may react further to generate insoluble compounds. By comparison there are several possible cathodic or reduction reactions possible dependent on the corrosive medium present. One very common cathodic reaction is the reduction of molecular oxygen dissolved in water to produce hydroxide ions while consuming electrons. Another common cathodic reaction is the reduction of hydrogen ions in an acid to produce molecular hydrogen gas while consuming electrons. Multiple cathodic reduction reactions can be active simultaneously. If an acid that contains air (oxygen) or chemical species that are readily reduced, e.g., ferric or cupric ions, is exposed to a susceptible metal, both hydrogen ion reduction to generate hydrogen gas and oxygen reduction (or reduction of other oxidizing species) can occur at the cathodic sites on the metal.



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A fundamental concept in the electrochemistry of corrosion is that oxidation and reduction reactions occur simultaneously and each must occur at the same rate. This has significant practical importance. For example, if the oxygen reduction cathodic reaction applies in a given situation then the rate of the overall corrosion that occurs can be retarded or accelerated depending largely on how efficiently dissolved oxygen in the water reaches the exposed metal surface. Specific application parameters determine the availability of the oxygen as will be discussed later. Another example applies to chemical corrosion inhibitors. When these are added to electrolytes they can limit the rate of corrosion by slowing the oxidation reaction or the reduction reaction or, in many cases, both reactions.

Not all liquids are electrolytes and thus not all liquids support corrosion. An electrolyte must be able to permit the efficient transport of electrically charged ions. This characteristic is the electrical conductivity of the liquid medium. Electrolytes may include a great variety of substances, for example - normal fresh and saltwater or acid solutions with or without added chemical species. Specific additional constituents can result in the electrolyte becoming either more or less corrosive. Certain “pure” liquids such as demineralized water and hydrocarbons like gasoline, lubrication oils and alcohols cannot support corrosion because they do not ionize or only ionize slightly and thus their conductivity is very poor. However, a mixture of a “pure” liquid such as gasoline plus a small amount of fresh water becomes an electrolyte because of the added water.

Both thermodynamic and kinetic relationships govern the incidence of corrosion. Energy relationships from thermodynamics determine which combinations of metals or alloys and specific environmental conditions may or may not result in corrosion. For those combinations in which corrosion may occur, the practical issue then becomes how fast the reactions will take place. That’s when kinetic relationships take over. Most practical engineering alloys are thermodynamically unstable, i.e., they are subject to corrosion, when exposed to a variety of electrolytes. Even so corrosion scientists make valuable use of thermodynamic relationships in their studies. However, for this course normally used engineering alloys will be assumed and thus corrosion can and will occur with them in practical usage. The important question then becomes what can be done to affect the kinetics and decrease the rate of attack.

Any given metal exposed to a specific electrolyte has a unique potential – measured in volts – known as its electrode potential. These potentials are not measured independently but, instead, must be measured with respect to another very stable metallic electrode known as a reference electrode. There are different types of reference electrodes for laboratory and for field usage.

When corrosion of a metal electrode begins there is a net flow of electric current and a change in electrode potential from its thermodynamic equilibrium state. As the corrosion rate increases the metal changes its potential and becomes more positive. This change is anodic polarization. The magnitude of the resulting anodic potential is directly related to the propensity for oxidation to occur on the given metal and application conditions. The terms anodic potential and oxidizing power are often used interchangeably. Every electrode potential value has an associated level of current flow. It is important to



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understand that the magnitude of each current (or current density) measured is directly proportional to the rate of corrosion occurring at a given electrode potential. See Figure 1 to follow. This corrosion current can be measured in laboratory tests and in many field applications.

The magnitude of the flowing anodic current, and therefore the corrosion rate, is measured in amps (or microamps). A small change in potential often has a much larger change in current and, therefore, in the resulting corrosion rate. Typically corrosion current is represented on laboratory data plots as a current density. This derived value is the ratio of the corrosion current at a given potential to the exposed area of the metallic sample being evaluated. A high value of current density indicates a high rate of corrosion for a given sample size.

In addition to anodic polarization, cathodic polarization of a laboratory sample electrode or a metallic surface in field service applications can be accomplished. This causes the potential of the metal to become more negative as the rate of anodic oxidation (corrosion) is reduced. The resulting anodic corrosion current and thus the rate of corrosion is greatly reduced (but not stopped completely) as the potential is made more negative. This is the basis for the widely used method of corrosion control – cathodic protection.

During corrosion the rate of reduction that occurs during polarization is controlled by one of two possible mechanisms. Sometimes polarization occurs by a combination of the two. These mechanisms are activation and concentration polarization. Each includes a rate-controlling step or aspect of their mechanism that governs how fast the reduction reaction can occur and, therefore, what the overall corrosion rate can be. In contrast to the reduction reaction, the anodic oxidation portion of the corrosion process generally occurs readily and does not present a restraint on the overall corrosion rate. These two reduction polarization mechanisms are important because common application variables such as temperature, pH, concentration and velocity have different effects on corrosion rates according to which mechanism is active. These variables are discussed later.

Activation polarization is predominant in certain corrosive media. It involves the multiple steps that occur at the interface of the exposed metal and the electrolyte to accomplish the reduction reaction. Hydrogen reduction with generation of hydrogen gas bubbles in an acid is a typical example. Here the activation steps include first an adsorption of hydrogen ions from the acid onto the metal surface; these ions then must join with electrons that came through the metal from the anodic sites to form single hydrogen atoms at the metal surface; these atoms must then join together on the metal surface to form hydrogen molecules and finally these molecules must join together to form bubbles of hydrogen gas that leave the surface. One of these steps will be the slowest in the series and it will govern the rate of reduction that can occur.

Concentration polarization predominates in certain corrosive applications when there is a limited quantity of specific chemical species in the bulk electrolyte that is needed to support the reduction reaction on the metal surface. An example of this situation might include a dilute, relatively high pH acid, e.g., pH of about 5.5, without any oxygen or



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other oxidizing species present so that there would be few hydrogen ions available in the bulk solution to be reduced. (Note - Remember from basic chemistry that the concentration of hydrogen ions in an acid is inversely proportional to its pH and that oxygen and other oxidizing chemical species are reduced while reducing species are oxidized.) Another example where concentration polarization applies is water that contains little dissolved oxygen or other oxidizing species (such as ferric, cupric or chromate ions) so that the available oxidizing species at the metal surface are severely limited. The possible rate of reduction often is restrained in each of these examples.

The critical, rate-controlling factor in concentration polarization is the rate of diffusion possible in the given situation. That is the ability of limited quantities of reducible agents, i.e., oxidizing species, present to move from the bulk electrolyte through the diffusion layer on the metal surface, contact the metal surface and react. This diffusion layer contains less reducible species than the bulk electrolyte. Rates of diffusion through the diffusion layer depend on several of the application variables mentioned earlier.

Several metals and their alloys are known as active-passive metals. These materials experience distinctly different rates of corrosion at different potentials, i.e., from higher to very small rates as potentials increase. The idealized anodic polarization plot in Figure 1 illustrates this behavior. The figure shows a range of corrosion potential values versus the logarithm of corresponding values of current density. The plot shows polarization above the equilibrium potential, i.e., E_q , the minimum potential represented. Increasing corrosion potentials on the vertical axis are said to become more noble or anodic (both terms are used). By comparison, decreasing values of potential on the vertical axis are said to become more active.

As indicated in Figure 1, three separate regions exist for active-passive materials. The active anodic corrosion region involves a steady increase in corrosion current and thus increasing corrosion rates as the potential becomes more noble. At the top end of the active region, there are two important values - the primary passive potential, E_{pp} , and the corresponding critical anodic current density for passivity, I_p . The corrosion current drastically decreases and the passive state initiates when these values are attained. Then corrosion rates in the fully passive region are stable and remain very low for a range of increasing anodic potentials. Finally, when the potential exceeds a specific noble value, i.e., E_{loc} , the current again increases as potential increases. This region is known as the transpassive area. Localized attack occurs above E_{loc} .

Active-passive materials include iron, chromium, nickel, titanium and alloys of these metals. This is fortunate because alloys that contain these elements also often have mechanical properties that allow them to be practical engineering materials in many applications. The classic example is the group of austenitic stainless steels. These and other active-passive materials often provide reduced corrosion rates when passive that are less than their rates in the active range by factors of 10,000 to 1,000,000.

It should be clearly understood that active-passive behavior for a given alloy can occur in one electrolyte but not in another. This also applies to other variable service conditions. The effects of variable service conditions are discussed later.

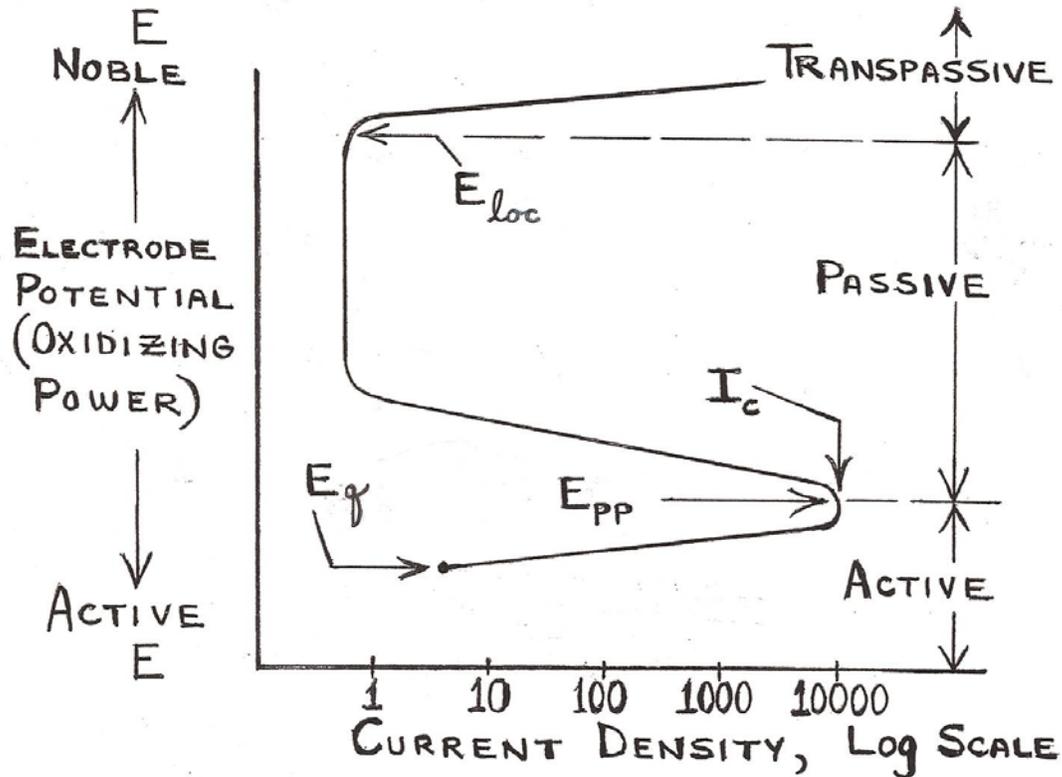


Figure 1. Active-Passive Polarization (from Ref. 2, page 321)

As mentioned above, localized forms of corrosion, e.g., pitting, crevice corrosion and stress-corrosion cracking, are not seen in the passive region but begin and accelerate whenever the potential at the start of the transpassive region, i.e., shown in Figure 1 as E_{loc} , is exceeded. This minimum potential value is more commonly known as the protection potential or breakdown potential. When all other conditions are equivalent, crevice corrosion will typically initiate on a given alloy at a less noble breakdown potential than the potential at which pitting starts on that same alloy without a crevice being present.

The specific mechanisms by which various active-passive alloys form the passive condition are not well understood. However, it is clear that a film forms on the metal surface – typically an oxide layer - and this provides a barrier between the electrolyte and the metal below. These films are extremely thin – on the order of 30 angstroms or less in thickness - and they can be fragile. General corrosion can initiate when there is overall



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breakdown of an entire passive film but frequently there is only localized rupture of the film at specific spots on a metal surface. One of the localized forms of corrosion may then begin at that failure site in the film.

The relative sizes of the active and the passive regions plus the values of the E_{pp} potential, the E_{loc} protection (or breakdown) potential and the ability of an alloy to quickly repair its passive film when local film rupture occurs are all important to its corrosion resistance. These results depend on a combination of the specific electrolyte, the chemical composition of the given alloy and several service factors.

Types of Corrosion –

General (or uniform) corrosion occurs when there is attack in a fairly consistent pattern at all wetted areas on a metal. This happens because anodic and cathodic microscopic areas continually switch with time and no one area suffers extra, localized penetration. Typically this form of attack occurs on plain carbon steel (mild steel) that does not form a robust passive film like alloyed active-passive materials such as stainless steels.

In most applications it's easier to control general corrosion compared to the many types of localized attack such as pitting or stress-corrosion cracking. Traditional control methods such as using a coating can be effective. It is much easier to reliably detect and monitor attack by general corrosion because the metal loss is uniform. Therefore effective inspection intervals can be planned. Added metal thickness – above the thickness needed for mechanical strength alone – can be used as a corrosion allowance as a means of preventing failure by general corrosion but this may not be useful in detecting or preventing localized forms of attack at some spots but not all. Much information is available on the general corrosion rates of several metals for a variety of corrosive media so that the metal thickness necessary for a given service life often can be effectively estimated.

Atmospheric corrosion has characteristics in common with traditional general corrosion. It accounts for a major category of corrosion cost across many applications. Typically carbon steel is the material affected. Low-alloy steels offer better resistance than plain carbon steels. The nature of the attack from atmospheric corrosion depends on whether or not moisture is retained or drained from the metal surface, the presence and concentration of certain chemical species that exist in atmospheric air and the availability of oxygen. The latter is necessary for the very common oxygen reduction cathodic reaction. Sulfur dioxide and chloride ions in the air are the critical chemical species most important to the level of attack that occurs. Both accelerate corrosion.

Galvanic corrosion is well known as the result of electrical contact between dissimilar metals when both are wetted by an electrolyte. The metal in the couple that is the most active, i.e., most likely to corrode in the given corrosive medium, will suffer accelerated corrosion whereas the other metal will experience decreased corrosion rates. These are the anodic and the cathodic metals, respectively, in the galvanic couple. The more anodic (or active) metal corrodes and sacrifices itself and in the process provides protection



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against corrosion of the more cathodic (or noble) metal. This process is the basis for the sacrificial anode type of cathodic protection.

Combating galvanic corrosion is often addressed by avoiding galvanic couples of dissimilar metals or alloys that are far apart in a standard galvanic series. The materials in such a series are listed according to their unique electrode potentials in seawater at room temperature. These electrode potentials are thermodynamic parameters and thus the standard series does not consider kinetic effects. Its use is not always reliable for predicting attack. For example, whether a stainless steel is in its active or its passive state for the actual application conditions needs to be established before using a traditional galvanic series to make predictions on the rate of galvanic attack that is likely.

The area ratio of anodic to cathodic metals in a galvanic couple is very important. Maximum rates occur with a small anode area and a large cathode area. Thus a large anodic metal area relative to the area of the cathodic metal is most desirable.

Pitting corrosion is a localized form of attack in which there is a breakdown of the passive protective film at very specific spots on the metal surface followed by concentrated metal dissolution and penetration into the surface at those spots. The anodic oxidation reaction occurs in the pits while the cathodic reduction reaction occurs on the area surrounding each pit. Like many forms of corrosion there is an initiation phase and, once started, a propagation phase in which the pit penetration increases rapidly. The initiation phase generally lasts a long period in comparison to the propagation phase.

Pitting is a much more difficult problem to deal with than general corrosion. This is because its initiation can be triggered by a range of very local conditions that may not be obvious. These might include a scratch on the metal surface, a metallurgical irregularity at the surface, e.g., a sulfide inclusion in the alloy, or a high local concentration of aggressive ions that breakdown the passive film at a small area. Because of its localized nature, inspection for corrosion damage due to pitting is much more problematic than general corrosion and thus pitting can be much more of a threat.

Pitting is most common on active-passive alloys such as stainless steels and nickel alloys plus aluminum alloys when severe application conditions exist. Pitting can also occur on carbon steel but it is less common. That is because a passive film that forms on plain carbon steel is more susceptible to being damaged due to conditions compared to alloys with more robust films. Carbon steel is more likely to experience general corrosion.

Crevice corrosion is a form of localized attack that occurs in the wetted portions of several types of closely confined, but not completely closed-off areas on a metal. Such areas could include the gasket surfaces of a pipe flange, overlapping plates or plates that butt up to one another but are not sealed at the interface, the free space between the threads on a bolt and the threads inside the nut it is fastened to, under countersunk screw heads, etc. The creviced or partially closed region does not require that two *metals* be in



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close contact. Attack can and often does start under sand, dirt or debris collected on a wetted metal surface.

Similar to pitting, in crevice corrosion the anodic oxidation reaction occurs inside the creviced area while the necessary cathodic reaction occurs just outside on the nearby freely exposed area. There is an initiation phase in which the passive film on the metal breaks down inside the creviced area and accelerated corrosion begins and propagates while the reduction reaction occurs outside. The time necessary for the process to begin is dependent on all the various factors that can accelerate or retard all corrosion mechanisms but there is another factor unique to crevice attack. That is the geometry and dimension of the crevice opening. If it is open enough to let the electrolyte freely move in and out or if it is completely closed off (as with a properly sealed crevice) then no attack will occur. However, crevice attack occurs when the interface opening is very small but still open enough for the electrolyte to get in but too small for it to freely circulate. Once started crevice attack is often rapid like pitting.

In general, crevice corrosion presents a greater practical problem than pitting. When all other conditions are equivalent, a given alloy in a given corrosive medium will have crevice corrosion initiate in any susceptible crevices present before pitting will start on a freely exposed area of that metal surface. As stated earlier the protection (breakdown) potential for pitting is more noble than that for crevice corrosion when all other conditions are equal. Another practical issue is created by the fact that it is often very difficult to design and/or fabricate a variety of equipment and that omits all potential creviced areas. The more creviced areas that exist in a given application the greater is the probability of crevice attack.

Stress-corrosion cracking (SCC) is a one of the localized forms of attack that combines a corrosion process and a mechanical cracking process to make the result worse than either mechanism acting alone. SCC requires a specific corrosive medium and alloy combination, tensile stress and varying time periods (depending on specific levels of aggressiveness of the causative factors) for synergistic interaction of these factors. Even though there are several susceptible combinations – see Table 1 that follows – SCC is unique in that particular alloys crack in particular corrosive media but not in others. For example, carbon steel is subject to SCC in certain sodium hydroxide (caustic) solutions but not in seawater whereas austenitic stainless steels will not crack in caustic but may crack in many chloride-containing media such as seawater if other conditions permit.

The stress that causes SCC is constant or static – unlike the stress in corrosion fatigue. It must be tensile stress and not compressive. The application direction of tensile stress acts to further open a crack and to expose “fresh” metal to the corrosive medium. This two-step, mechanical and corrosion process continues as the crack advances. Propagation is most rapid when the primary stress component acts perpendicular to the primary crack path. The tensile stress can be applied stress or, very frequently, it is residual stress. Residual tensile stresses can be caused by a variety of manufacturing processes such as welding, cold working or heat treatment. These residual stresses can be most dangerous in causing SCC because they are often overlooked.



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Time of interaction of the causative factors is an important parameter in the incidence of SCC. If the given combination of alloy and corrosive medium are susceptible, other

Table 1. Known Combinations of Alloys and Corrosive Media Subject to SCC [or HE] (from Ref. 3, page 831)

Carbon steels – Nitrate, hydroxide, carbonate/bicarbonate, acidified cyanide and amine aqueous solutions; anhydrous ammonia; gaseous hydrogen at high temperature and pressure

Low alloy steels – Aqueous solutions with hydrogen sulfide and/or halide ions; gaseous chlorine, hydrochloric & hydrobromic acids; gaseous hydrogen or gaseous hydrogen sulfide (each at ambient temperature); sulfide impurities in aqueous solutions; arsenic, antimony or bismuth ions in aqueous solutions at ambient temperature. HE is most common.

Austenitic stainless steels – Hot solutions with chloride and other halide ions; fluoride ions in aqueous solutions at ambient temperature if steel is sensitized; oxygen dissolved in liquid water at temperatures above 570 F if steel is sensitized; hydroxide solutions if temperature is above 210 F; polythionic acid at ambient temperature if the steel is sensitized.

Nickel alloys – Inconel 600 alloys in polythionic acids at ambient temperature if sensitized and in hot NaOH; Inconel 600 alloys in the very high temperature, dilute chloride conditions in nuclear reactors; Alloys 400 and B-3 in hydrofluoric acid.

Copper alloys – Aerated aqueous ammonia solutions; amines in aqueous solutions; nitrogen oxides with moisture; sulfur dioxide gas with moisture.

Aluminum alloys – Halide ions in aqueous solutions at ambient temperature for high strength alloys; fuming nitric acid (that is acid at concentrations above about 85%) at temperatures above 210 F for high strength alloys.

Titanium alloys – (For industrial alloys Grades 1,2,9,12 & 28) – Nitrogen tetroxide, fuming nitric acid; anhydrous methanol. (Higher strength, aerospace alloy grades may also be susceptible to these same media plus aqueous halide solutions and certain organic compounds with halide ions.)

overall conditions for producing corrosion are severe and the tensile stress level is high, then initiation and propagation of SCC can be very rapid. However, if the susceptible combination of alloy and corrosive still exists but one or more of the other factors is greatly reduced in intensity then the cracking process can take an extended period.



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SCC can be minimized by several means that influence one or more of the factors that act together to cause the process or by other control measures to be reviewed later.

Hydrogen embrittlement (HE) should not be confused with SCC. HE is a metallurgical and mechanical process without a corrosion component. HE is caused by the entry of atomic hydrogen (H^0) into susceptible metals. This hydrogen “charging” greatly lowers the ductility of the affected alloy and can make it fracture with little or no prior plastic deformation. HE is not reduced or controlled by the several ways employed to control corrosion. This mechanism often causes lowered ductility without fracture in lower strength plain carbon steel but it can cause complete brittle fracture in high strength steels. The strength of a steel is indicated by its metallurgical hardness. It has been found that ASTM A-193, Grade B-7 bolts don’t crack due to HE if their hardness on the Rockwell C scale is 22 (HRC 22) or less (Reference 8, page 140). There have been many proposals that atomic hydrogen effects can combine with and accelerate SCC that is occurring. This is most likely to occur in high strength steels when atomic hydrogen can be changed into the material and conditions for the occurrence of SCC also exist.

Corrosion Fatigue is a widespread form of localized attack that, like SCC, results from the combined effects of a corrosion process and tensile mechanical stress. Unlike SCC the stress in corrosion fatigue is cyclic and often fluctuates irregularly with time. This form of attack is so widespread because fatigue itself - without the added effect of corrosion - is a (if not the) major factor in producing failures in a variety of dynamic mechanical equipment and in other situations where cyclic tensile stresses act. A corrosive environment adds to the incidence of failure by lowering the level of tensile stress or the number of stress cycles necessary for failure. Failure is typically initiated on the surface of the exposed metal and propagates as a growing crack through the cross-section until too little material remains to withstand the load.

Very aggressive corrosive applications are not required for corrosion fatigue. It has been shown for some alloys that this form of attack occurs sooner when exposed to plain water as compared to the same alloys exposed to “pure” mechanical fatigue (without the water) for identical fatigue parameters. The probability of pitting on a particular alloy in a given electrolyte is often a prime indicator of its susceptibility to corrosion fatigue in that same medium. This is because pits concentrate whatever level of tensile stress is acting and thus initiation of fatigue cracking is accelerated.

Most of the classic corrosion control measures apply to corrosion fatigue and these are the first line of defense against this form of attack. In the mechanical area the best preventative measures are to minimize all tensile stresses at or near the surface of the metal. Just as in SCC this applies to both applied and residual tensile stresses. Some applications that induce cyclic tensile stresses include rotating shafting, reciprocating components, temperature changes that produce thermal stresses and flow-induced vibrations. The effect of the frequency of the acting cyclic stresses is different in corrosion fatigue versus fatigue without a significant corrosive component. In the latter the frequency of the stresses has little or no effect on how soon failure occurs. However, in corrosion fatigue a lower frequency of the cycles is more detrimental and causes quicker failure. This is because the advancing crack remains open and exposed to the



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corrosive medium for longer periods when the frequency of the cyclic stresses is low.

Erosion-corrosion (E-C) is a combination of flow-induced abrasive wear and corrosion. It produces more metal damage than either process acting alone. Often the normally protective passive film on the metal surface is damaged by high velocity or turbulent flow of the process steam and this permits accelerated corrosion.

E-C frequently is found in very localized areas on a metal surface where velocities and/or turbulence are the highest. The abrasive degradation portion of E-C is enhanced if there are hard solid particles, e.g. as a slurry, in the flowing fluid. While the metal's abrasion resistance plays a role in its resistance to E-C, it has been found that a more important factor in overall resistance is the metal's corrosion resistance in the specific electrolyte.

Most metals and alloys have a critical velocity. Above this value, E-C begins and significantly increases in the given electrolyte. If the critical value must be exceeded for a specific application, it is necessary to use either a more corrosion resistant alloy or to use a suitable coating on the less resistant alloy.

The occurrence of E-C is directly affected from an electrochemical perspective dependent on whether the rate of corrosion is controlled by a concentration or by activation polarization mechanism. This is discussed later.

Intergranular attack (IGA) is preferential corrosion in the regions surrounding the metallurgical grain boundaries of susceptible alloys with little or no attack of the grains. Susceptibility occurs when certain alloys are exposed to specific temperatures for sufficient time periods and precipitation of a portion of the normal constituents in the alloys move to grain boundary areas. This critical temperature range often occurs during cooling after welding the material or during incorrect heat treatment. The critical temperature exposure may also occur in service. The distinct segregation and heterogeneous condition caused by the precipitation process makes the affected alloys much more susceptible to accelerated corrosion near the grain boundaries. Attack around the entire circumference of some grains can cause whole grains to fall completely out of the alloy's matrix. Corrosion rates determined by post-exposure weight loss measurements then indicate rapidly increasing rates with time of exposure to the electrolyte.

An alloy that has become subject to IGA through temperature and time exposure is said to have become sensitized. Stainless steels and nickel-based alloys plus aluminum alloys are subject to this form of corrosion. If tensile stresses are acting in a sensitized alloy, frequently intergranular SCC will occur in which the advancing crack travels between the grains of the material. Generally the crack is perpendicular to the direction of the primary tensile stress. Many types of electrolytes can cause IGA in sensitized alloys, e.g., austenitic stainless steels can experience IGA in several types of inorganic and organic acids and in seawater.

The most common example of IGA occurs in the frequently used wrought austenitic stainless steels, i.e., Types 304 and 316. When these alloys are exposed to temperatures



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in the range of approximately 900 to 1500 degrees F they can be sensitized. The carbon present in these alloys has a high affinity for joining with chromium and in this temperature range it combines with chrome to form chromium carbides that precipitate to grain boundary areas. The result is that the percentage of chromium in the alloys adjacent to the grain boundaries is significantly reduced below its pre-sensitized level. Chromium is the major element in stainless steels (and to a lesser extent in nickel alloys) that allows them to develop a passive, corrosion-resistant state. The minimum chromium concentration in stainless alloys to achieve this passive state is about 12%. After significant chromium carbide precipitation has occurred the chromium content immediately adjacent to grains can be far less than 12%.

IGA can also be a problem in cast stainless steel alloys due to the same mechanism as in the wrought alloys. These cast alloys are often used for pump casings and valves in the chemical and petrochemical industries and IGA often is a problem.

Chromium carbide precipitation and, specifically, the percentage of carbon present in an alloy are directly connected to IGA of nickel-based alloys just as in stainless steels. However, in nickel alloys the mechanism is more complicated and the temperature ranges necessary for sensitization differ somewhat from those that apply to stainless steels. Inconel 600 is one nickel-base alloy that has been widely used in nuclear reactors that has experienced failures due to IGA and/or intergranular SCC. These failures occur in high temperature reactor water containing low concentrations of chloride ions.

IGA failures can occur in certain high strength aluminum alloys that contain copper, magnesium, zinc or manganese. Unlike stainless steels and nickel alloys, here carbon does not play a role but instead copper, magnesium, zinc or manganese compounds precipitate to grain boundaries and create electrochemical differences with the nearby grains. These potential differences promote IGA. Susceptible aluminum alloys are those in the 2XXX, 7XXX and 5XXX classes.

The possible solutions to IGA include either making specific material selections initially to avoid the problem or, where possible, using a post-sensitization heat treatment to regain the original homogeneous metallurgical composition that can resist attack. Alternative material choices are discussed later.

Dealloying (or selective leaching) **corrosion** occurs when one element in an alloy is preferentially attacked. The remaining material is generally left with essentially the same original shape and dimensions but the mechanical properties of the alloy are severely diminished. Currently there is no general agreement on the specific causes.

The two most common examples of dealloying are preferential attack of zinc in certain brass alloys (dezincification) and the preferential attack of the iron in gray cast iron (graphitic corrosion). The amount of zinc and/or certain other elements present in brass



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alloys determine whether or not they suffer dezincification. Graphitic corrosion often occurs only after many years of service and is most often seen in older underground utility piping.

Alternative material selections are generally the most practical approach to controlling these forms of attack.

Microbiological influenced corrosion (MIC) – is a form of corrosion produced by the results of the life processes of certain microorganisms or simply by their presence on a metallic surface. Different microorganisms can produce a variety of effects that lead to accelerated corrosion. These include formation of black iron sulfide deposits that create corrosion cells on carbon steel; production of either mineral or organic acids and the resulting lowered pH; formation of hydrogen sulfide and the associated corrosive condition in oil and natural gas applications; driving the electrode potential of stainless steels more anodic and out of their passive state into the pitting range plus generating hydrogen so that high strength steels are made more susceptible to HE or SCC. Microorganisms often form a slime deposit on metallic surfaces called biofilms. The presence of these films alone – without the added other effects of different microorganisms – can often cause crevice corrosion.

Most all alloys are subject to MIC although titanium alloys can offer resistance. Carbon steels and cast irons are the materials where MIC is most often encountered. These materials most often suffer general corrosion while stainless steels and aluminum alloys experience pitting and crevice attack due to MIC.

The microbes involved with MIC require three essentials. These are water, some type of nutrient, e.g., a source of hydrocarbons, nitrogen or phosphorus, and some source of energy. The latter can be supplied by sunlight or by the redox (oxidation and reduction) chemical reactions that occur in all corrosion. Some microbes are anaerobic such as the very common sulfate reducing bacteria (SRB) and need an oxygen-free environment to live and grow while others require oxygen to do the same. Many types of microbes can survive over a wide range of temperatures – from subzero levels up to maximum of about 200 degrees F. They cannot live at very high temperatures. Submerged colonies of microbes attach to metal surfaces and grow quickest when exposed to stagnant or low velocity liquids. They can survive over a wide range of pH.

MIC may occur in several types of applications. Industrial water-handling systems are probably the most common. Others include the exterior of underground pipelines, in fire sprinkler systems and on marine piers and other structures exposed to seawater. MIC has also been a significant problem on aluminum in the lower sections of commercial aircraft below galleys and restrooms when adequate constraints on liquid spills are missing. Stainless steels are particularly susceptible to MIC at welds.

Control methods for MIC include using biocides to kill the microbes and adding chemical corrosion inhibitors to retard corrosion. Coatings as well as design changes may be useful. Specific knowledge is needed to effectively analyze and control MIC problems.



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Effects of Environmental and Application Variables –

This section will discuss the primary in-service variables, besides the many different electrolytes, that affect corrosion rates. These factors include the following:

- Temperature
- pH
- Concentration of certain chemical species in the electrolyte
- Flow velocity (or the static condition)
- Heterogeneous conditions

Temperature of the Electrolyte -

Corrosion is, in part, a chemical reaction process and thus the rate of the reaction is generally increased as the temperature of the electrolyte increases. In acidic conditions the rate or kinetics of the corrosion reaction will typically double for every 18 degrees F increase. In these situations the rate-controlling cathodic reaction is the reduction of hydrogen ions to produce the evolution of molecular hydrogen gas. In near neutral or in alkaline pH electrolytes the governing cathodic reaction very often is the reduction of oxygen in water to form hydroxide ions. In this case the rate of corrosion generally doubles for about every 55 degrees F increase in temperature.

Corrosion rates do not always increase as temperature increases. The classic example of this occurs in a comparison of recirculating, closed, steel water piping system and a recirculating, open-to-the-atmosphere steel water system. In both types of water systems the typical rate-controlling corrosion reaction is the reduction of dissolved oxygen. This assumes no other oxidizing species or acids are present in the water to support another type of reduction reaction. In this closed system the overall rate of corrosion continually increases as the temperature increases. This is because the oxygen in the air required for the reduction reaction cannot escape the system.

In the open system the same relationship applies initially. However, at about 176 degrees F the solubility of oxygen begins to decrease significantly and since the system is open it can escape. The rate of corrosion then begins to decrease because the cathodic reduction reaction is being restrained. By the time the boiling point of the water is reached the corrosion reaction is essentially shutdown because the necessary oxygen is no longer available. The difference in corrosion rates of the two systems is shown in Figure 2.

This relationship between water temperature, solubility of oxygen in the water and the resulting corrosion rate is important because it occurs so frequently. Higher corrosion rates are not always associated with higher temperatures but they often are. This serves to make the point that there are very few general rules that always apply in analyzing corrosion rates.



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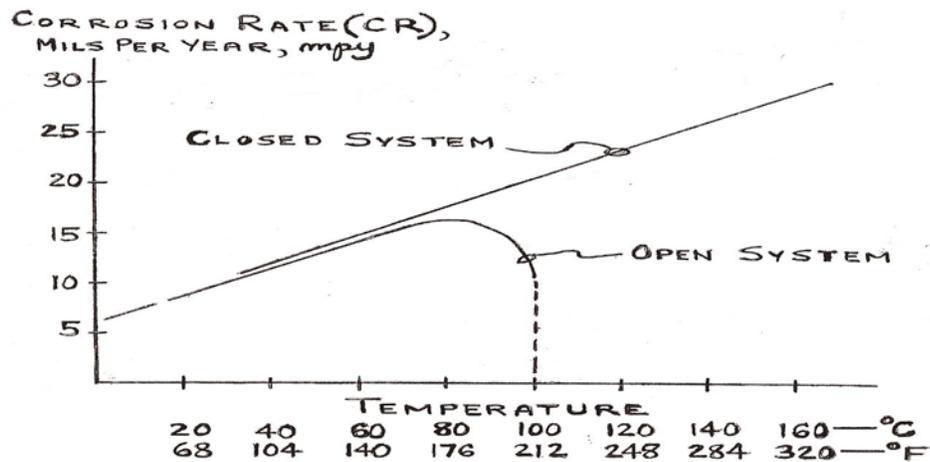


Figure 2. Effect of Temperature on the Corrosion Rate (CR) of Iron or Carbon Steel in Water Containing Dissolved Oxygen (after Ref. 4, page 98)

Another effect of temperature occurs with certain metals in galvanic contact. At normal ambient temperature, in a galvanic couple between zinc and carbon steel the zinc is the anode and it is preferentially corroded while the steel is the cathode that is protected by the zinc. The corrosion rate of the steel is then greatly diminished compared to its rate when uncoupled in the same electrolyte. However, starting at about 140 degrees F and at higher temperature the roles are reversed and the steel becomes the anode that is preferentially attacked while the zinc is protected.

Temperature, along with certain other environmental variables, has important effects on anodic polarization, i.e., the plot shown schematically in Figure 1, of active-passive alloys. These changes affect the potential and associated current at which there is a switch from active to passive behavior and the potential range over which passivity is maintained.

pH of the Electrolyte -

The corrosion rates of many alloys are generally independent of pH over mid-range values of approximately 5 to 9 when assessing this variable alone. Changes in rates – either higher or lower – occur outside of this range depending on the specific alloy as well as other conditions. The “other conditions” are very important because applicable variables all work together synergistically to generate a specific result for the given alloy. Besides pH the other conditions can include temperature, availability of dissolved oxygen (commonly affected by electrolyte velocity), the presence or absence of tensile stresses in the metal, other chemical species in the electrolyte, etc.



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First consider the effects of pH changes on iron, plain carbon steels and low-alloyed steels. These materials all experience very similar corrosion rates in aerated, soft water at ambient temperature as a function of pH. Figure 3 shows the results of a series of tests of iron completed in ambient, soft water at different pH values. To generate these data sodium hydroxide or hydrochloric acid was added to the water to produce higher or lower pH values, respectively.

Corrosion rates (here indicated by CR) for pH values over the range of 10 down to 4 are stable for the stated conditions. Corrosion in that range is controlled by the rate of oxygen reduction where oxygen is readily available in the aerated water. Over that range a protective barrier of hydrated ferrous oxide forms and is maintained on the metal surface. At higher, more alkaline pH values the corrosion rates decrease because the metal is shifted into its passive range for the stated conditions. At the other extreme of pH values, lower than 4, the hydrated ferrous oxide barrier is dissolved; corrosion rates increase significantly and are controlled by the reduction of the readily available hydrogen ions.

It should be emphasized that the results in Figure 3 apply only for the stated conditions of ambient temperature, soft water, readily available oxygen, and (although not stated) it is implied that there are no significant tensile stresses in the metal tested. Variations from these conditions would likely produce different results.

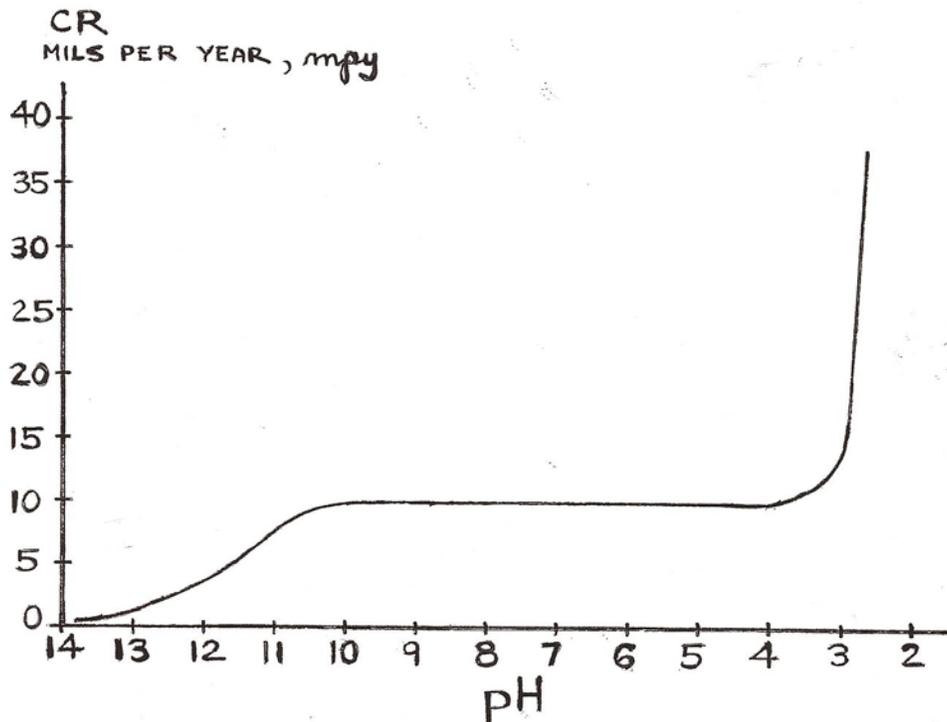


Figure 3. Effect of pH on the Corrosion Rate (CR) of Iron (and Carbon Steel) in Aerated, Soft Water at Room Temperature (after Ref. 4, page 99)



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The general role of temperature in its affect on corrosion has already been discussed. The use of soft water is important because unlike hard water it has little or no minerals that can precipitate out of solution and form protective scales (if uniformly distributed) made up of compounds such as carbonates on the metal surface. Thus this soft water would be expected to show a smaller range of pH values with stable, non-increasing corrosion rates compared to the use of hard water.

The use of aerated water for the Figure 3 tests is important because it confirms that sufficient oxygen was available so that cathodic oxygen reduction was not limited – and thus the overall corrosion rate was not limited in the mid-pH range – as would be the case if there had been a deficit of oxygen. Also, while not stated, it is implied that other oxidizing agents such as ferric or cupric ions were not added to the water to add possible cathodic reduction reactions. It is also implied that effective chemical corrosion inhibitors were not present in the soft water.

It indicated in Table 1 that SCC can occur in carbon steels in sodium hydroxide solutions if tensile stresses are present and if the temperature is sufficiently high. Sodium hydroxide was added to the soft water to create the very alkaline pH values seen in Figure 3. Neither high temperature nor tensile stresses in the metal were factors in producing the data shown.

As mentioned in the previous section on temperature, the value of pH of an electrolyte along with its temperature and the concentration of certain aggressive ions present all have significant influences on the electrochemical behavior of active-passive alloys. Figure 4 illustrates these effects. This shows generic effects of these three variables as a family of anodic polarization curves for a typical active-passive alloy.

As pH decreases, i.e., as the concentration of hydrogen ions increase, the “nose” of the polarization moves to the right and becomes slightly more noble. At the same time the protection or breakdown potential becomes more active. These effects also occur due to increasing temperature of the electrolyte. In addition, the same effects are particularly seen with stainless steels as the concentration of chloride ions in the electrolyte increase.

There are consequences of the effects seen in Figure 4. First the extent of the active corrosion zone for this typical active-passive alloy increases as the “nose” moves to the right. Thus the maximum current density, i.e., the critical current density for passivity, I_p , increases and the switch from high active rates to the drastically lower rates in the passive region is delayed. Secondly the potential range over which the alloy is passive is decreased as the primary potential for passivity, E_{pp} , becomes more noble as the breakdown potential, E_{loc} , decreases. The alloy's susceptibilities to either active corrosion or one of the forms of localized attack is then increased. If just one of these changes occurs – lower pH, increasing temperature or increasing chloride concentration - the effect on corrosion rates is negative and when more than one occurs simultaneously the synergistic negative effects are intensified.

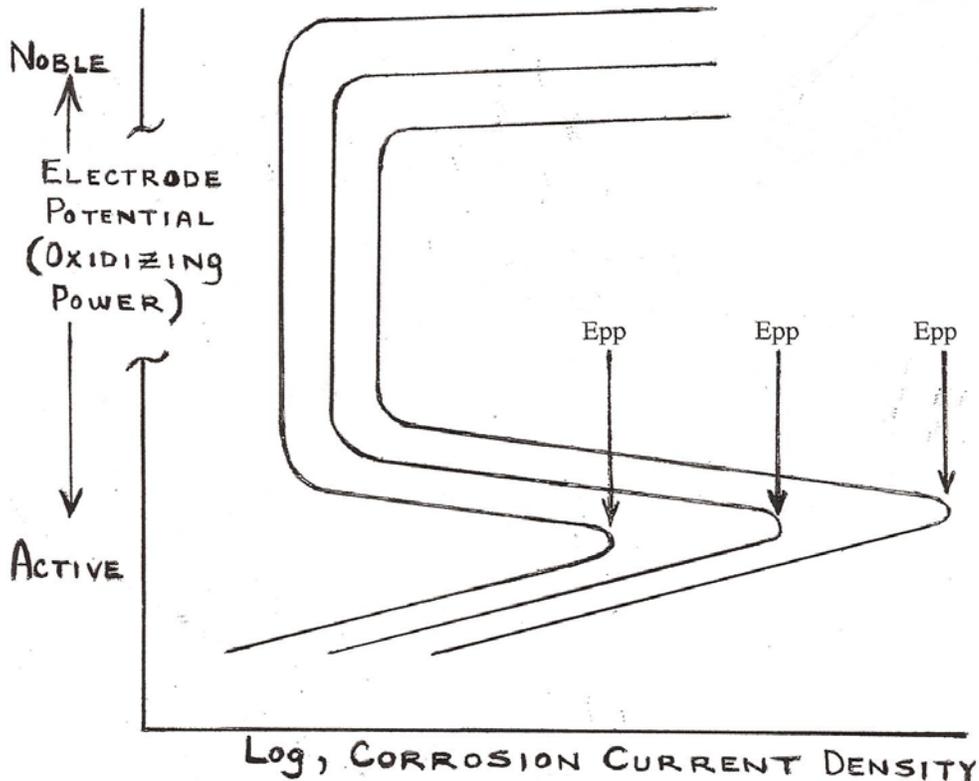


Figure 4. Anodic Polarization in Active-Passive Materials Due to Increasing Temperature or Chloride Ion Concentration or Hydrogen Ion Concentration (i.e., decreasing pH). Increasing Variables Shown by Curves \rightarrow Left to Right.

(after Ref. 2, page 322)

The resistance of stainless steels to general corrosion is typically good for high pH values even at raised temperatures up to about 200 degrees F. Their resistance to acidic pH values also depends on several factors including temperature, the composition of the alloy, the specific acid and its concentration, the degree of aeration and the presence and concentration of chloride ions. Choosing stainless steel alloys will be discussed further in the Material Selection section on control methods.

For a given set of conditions, specific types of alloys respond to pH as a variable in different ways. Nickel alloys are noted for being very resistant to high pH values (except when caused by ammonia or its compounds or when oxidizing conditions also exist in the electrolyte) and, depending on their specific alloyed composition, they can be useful in low pH conditions. Copper and copper-based alloys are generally resistant to all acidic pH conditions as long as no oxidizing agents, i.e., oxygen itself; oxidizing acids such as nitric or very concentrated sulfuric or chromic acids; or oxidizing ions such as ferric or cupric ions are also present. Copper and copper alloys are typically resistant to mildly alkaline conditions other than those caused by ammonia and ammonia-like compounds. It



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is well known that copper and its alloys are susceptible to SCC in ammonia. Zinc and lead experience a sharp increase in corrosion rates at high pH values. Aluminum alloys are generally useful in a mid-pH range of about 7 to 9 but they can experience significant corrosion rates in both more acidic and more alkaline pH ranges. Aluminum can provide excellent general corrosion resistance but depending on the specific alloy and other conditions may be subject to one of the localized forms of attack.

Concentration of Specific Chemical Species in the Electrolyte –

As discussed, the concentration of oxygen in the electrolyte is frequently a factor in the rate of corrosion that occurs. This is also true due to the presence of one of the oxidizing ions or an oxidizing acid. A common example of the effect of an oxidizing agent is the rate of corrosion on bare steel in a marine environment when part of the metal is above and part is below the water level. The portion of the metal at and just above the high tide water level – called the splash zone – corrodes much quicker than the metal that is well below the low tide water level. This is partly because oxygen is readily available at and above the splash zone to support corrosion but its concentration is likely much more limited well below the low tide level. Alternate wetting and drying in the splash zone also accelerates attack.

Still another example of this oxygen effect is that most corrosion typically occurs at the air-to-soil interface on a partially buried steel or iron object. There is usually much less attack well below the ground level because it is more difficult for oxygen to diffuse through the soil and reach the buried portions of the metal.

As shown in Figure 4, the concentration of chloride ions in an electrolyte often is important in the degree of corrosion that occurs on metals that have an active-passive behavior. The corrosion of carbon steel in aerated water is directly proportional to the concentration of chloride ions present up to about 6,000 ppm (0.6 %). Above this level the solubility of oxygen starts decreasing and then that factor becomes rate controlling, Reference 6, page 187. The effect of one variable on corrosion cannot be evaluated in isolation.

Typically the initiation and propagation of pitting, crevice attack plus SCC or corrosion fatigue (if sufficient stresses are present in the latter two cases) will increase for stainless steels as the concentration of chloride ions increase. This occurs when the chloride ions cause local breakdown in the normal passive film at spots where their concentrations are the highest. The effect is strongest when the electrolyte has an acidic pH. The effect is less pronounced when the electrolyte has a neutral pH and oxygen is present.

Unless a given active-passive material is able to resist the concentration of chlorides present or quickly repair its passive film at a break in the film local corrosion can begin. Nickel alloys have similar behavior to stainless steels but usually, depending on their composition, have greater resistance to the effects of chlorides. Although they do not have an active-passive behavior, aluminum alloys behave similar to stainless steels. As mentioned, chlorides have a deleterious effect on carbon steels but their passive films are much inferior and less robust than higher alloyed materials. On carbon steels when their



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relatively weak passive films are broken much of the entire surface is affected, film repair does not occur and general rather than a localized form of corrosion typically starts.

Sometimes a feature of the application can increase the concentration of chloride ions at specific areas on the metal's surface that is well above the level that exists in the absence of that factor. For example, if a susceptible alloy is exposed to a marine atmospheric corrosion environment with high levels of airborne chlorides – and typically high humidity – it is important where the metal is located. Its nearness to the sea is important because close proximity will generate more attack. However, another feature is whether or not it is sheltered from rain. If it is in the open and exposed to rain then the chlorides from the sea air will be washed off the surface periodically and corrosion may be less severe. If it is exposed to the salt air but protected from the rain the chloride concentration can build with time and corrosion rates are likely to be high. Crevices on the metal make matters worse because they can collect and concentrate chlorides inside that cannot be easily washed away by rain.

Other chemical species besides oxygen or oxidizing species and chlorides can be important to the incidence and rate of corrosion. For example, fluoride ions in aqueous solutions and as fluorine gas cause high corrosion rates in titanium alloys whereas these alloys have a high resistance to chlorides in seawater. Sulfur compounds and sulfides often cause accelerated attack on copper and silver. These two metals are commonly used in electrical and electronic contacts because of their normal, low electrical resistance.

Atmospheric exposure of copper or silver to sulfides as from hydrogen sulfide gas produces a copper or silver tarnish that is very thin but sufficient to increase the electrical contact resistance so that many low-voltage electrical or electronic devices may not function reliably. Another example is sulfur dioxide produced by many industrial processes. This often causes accelerated atmospheric corrosion of carbon steel.

High concentrations of dissolved metal in an electrolyte when that metal or alloy is the material of construction can serve as indicators of accelerated, on-going corrosion. Chemical analyses of the electrolyte after different periods of exposure can be used to indicate approximate rates of corrosion. Specific inspections or maintenance can then be planned when the particular part or section of the system cannot be assessed by other means. For example, high concentrations of iron or zinc in a process liquid likely would indicate high rates of corrosion of carbon steel or galvanized components, respectively. This is true especially for general rather than localized corrosion with the associated greater corroding area and larger quantities of corroded metal dissolving in the electrolyte. It would also apply to localized forms of attack but the quantities of dissolved metal likely would be smaller for equivalent exposure periods.

Flow Velocity –

The influence of electrolyte velocity, or agitation, e.g., as in an agitated chemical reaction vessel, on corrosion rates can be complex. The effect of this parameter depends on the specific alloy, the electrolyte, whether the corrosion polarization is under activation or



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concentration control and the level of velocity acting. The form of corrosion can also be important. In many incidences increased velocities can be negative, in others velocity can have little or no effect and in some cases increased velocities can be beneficial.

Four of the common situations are illustrated by the schematic curves shown in Figure 5, Cases A - D. This information and illustrations were adopted from information in Reference 2, page 20. In the figure relative velocity (V) values are shown on the vertical axis and relative corrosion rates (CR) are on the horizontal axis for each case.

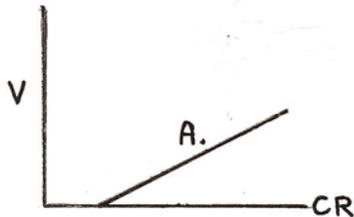
Case A in Figure 5 applies to carbon steel and low alloy carbon steels as well as copper exposed to water having limited quantities of dissolved oxygen. Corrosion rates are controlled by the speed of oxygen diffusion from the bulk electrolyte to the metal surface in order to supply the oxygen reduction reaction. The CR's are therefore under concentration polarization control. When the velocity increases the available bulk oxygen can more readily move through the diffusion layer next to the metal surface and reach the surface where it can be reduced. Therefore velocity and corrosion rates are directly proportional.

Unlike Case A., the alloys in Case B readily passivate. Initially the stainless steels and titanium in Case B behave like Case A but then they passivate, CR's drop significantly and remain essentially constant. While in the passive region, these alloys are unaffected by velocity increases. Like Case A, the CR's are under concentration control but the reducible species are now the oxidizing ions ferric or cupric. Initially greater velocities bring more of these ions to the metal surface but because of their oxidizing power (ability to shift to more noble potentials) the alloys passivate. In addition, the inherent properties of both stainless steels and titanium allow them to make the transition from the active to the passive state where this is not possible for the plain carbon steels and copper in Case A.

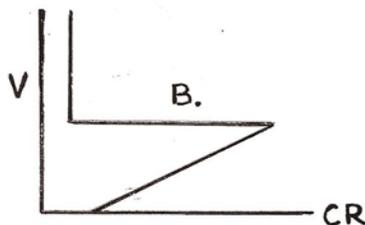
**Figure 5. - Relative Effects of Electrolyte Velocity (V)
 Changes on Corrosion Rates (CR)**

(Fe = plain carbon or low alloy steels; SS = common austenitic stainless alloys, e.g., Types 304 & 316)

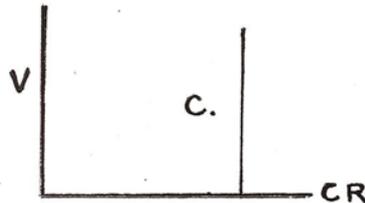
(after Ref. 2, page 20)



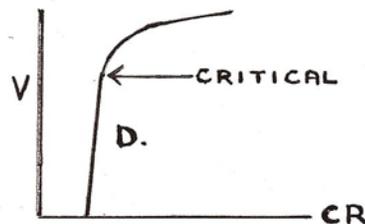
- Alloys whose corrosion rates increase with velocity and do not passivate
- CR control by concentration polarization
- Examples:
 Fe in water with limited dissolved oxygen
 Cu in water with limited dissolved oxygen



- Easily passivated alloys with oxidizing ions in the electrolyte
- CR control by concentration polarization
- Examples:
 SS in sulfuric acid with ferric ions
 Ti in hydrochloric acid with cupric ions



- Alloys that remain at relatively high CR's and are not affected by velocity changes
- CR control by activation polarization
- Examples:
 Fe in dilute hydrochloric acid
 SS in sulfuric acid



- Alloys whose CR's increase slowly until a critical velocity is attained
- CR control is by the formation of a thick, insoluble sulfate film
- Examples:
 Pb in dilute sulfuric acid
 Fe in concentrated sulfuric acid

Case C involves alloys that corrode at relatively high rates in specific acids. Plain carbon steels and low alloy steels experience very high CR's in hydrochloric acid and stainless steels show relatively high rates in sulfuric acid. In these situations the CR's are under activation polarization control because these strong acids can readily ionize and supply all the hydrogen ions needed for the cathodic reduction reactions. Increased velocity is not needed to bring more of the hydrogen ions to the metal surface to support corrosion and, therefore, CR's are independent of changes in velocity.



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Case D in Figure 5 illustrates two types of materials – lead in dilute sulfuric acid and plain carbon or low alloy steels – that form thick, insoluble sulfate films that provide barriers to corrosion as long as the films are intact. These films are relatively unstable compared to the very thin, tightly adherent passive films that form on stainless steels and other corrosion resistant active-passive alloys. There is generally little initial effect of increasing velocities in Case D. Then a critical high velocity is attained (unique to the given alloy) in which the sulfate film is removed by the mechanical shearing action of the increasing velocities. After exceeding the specific critical velocity, corrosion rates increase greatly. This last stage marks the beginning of erosion-corrosion.

The value of the critical velocity shown in Case D depends largely on which class of materials is being considered. Plain carbon steels and gray cast irons typically have the lowest values. Copper-based alloys offer some improvement, i.e., somewhat higher critical values. Typically the higher alloyed stainless steels as well as the nickel-based alloys and titanium alloys permit the highest allowable critical velocities before erosion-corrosion begins. Many alloys offer good resistance to a given corrosive medium when the electrolyte is static or has a very low velocity. However, they experience erosion-corrosion in that same medium when their critical velocity is exceeded. For this reason it is necessary when choosing a material to consider if it will ever be exposed to high velocities. If so then information must be obtained on its corrosion rate at expected velocities and not just for its rate based on static immersion in the given electrolyte.

Increased velocities can often have beneficial effects as long as the increase is not enough to cause erosion-corrosion. Case B in Figure 5 is an example of this. There the electrode potentials of easily passivated active-passive alloys are switched from the active corrosion region to the passive region by the action of the increased velocity that transports more of the oxidizing ferric and cupric ions to the metal surfaces.

Increased velocities are also helpful in minimizing the initiation of certain localized forms of corrosion. Pitting, crevice attack and MIC are each less likely in electrolytes that are not stagnant. Moving electrolytes tend to wash away sand, dirt and general debris that otherwise might collect on a metal surface and create crevice corrosion. Increased velocities can be helpful when using chemical corrosion inhibitors. The specified concentration of an inhibitor is critical in its effectiveness. Some minimum level of velocity helps to maintain the desired inhibitor concentration by continually bringing fresh treated solution to metal surfaces.

Heterogeneous Conditions in Applications –

Several circumstances may occur in applications in which dissimilar, non-uniform conditions increase the rate of corrosion. Very often this is because these conditions produce either macro or micro-scale electrochemical cells, i.e., anodes and cathodes, which do not generally exist in more homogeneous situations.

One of the most obvious of these circumstances occurs in the galvanic coupling of dissimilar metals. This macro-scale example results in accelerated corrosion of the more



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anodic member of the galvanic couple. Of course in most applications this result is undesirable. However, corrosion control by cathodic protection with a sacrificial anode material is a beneficial application of this idea. Accelerated corrosion of the zinc coating on galvanized steel that serves to protect the steel substrate is an example.

Crevices on a metal surface are another macro-scale example of the creation of heterogeneous conditions. Different chemical conditions are promoted inside versus outside crevices so that crevice attack is initiated and eventually propagated inside the partially closed-off areas. The anodic reaction occurs inside crevices while the cathodic reduction reaction occurs on the surrounding, freely exposed area. As stated previously, crevices can also concentrate aggressive ions inside and create a heterogeneous condition versus the much lower ion concentration on freely-exposed areas.

Typically metals that are commercially pure are more corrosion resistant than alloys of that metal. However, the “pure”, homogeneous metal usually does not have the necessary mechanical properties to be a practical engineering material. One solution is to use a cladding of commercially pure metal on an alloyed substrate of the metal. The cladding provides corrosion resistance while the substrate provides strength.

This is the basis for many Alclad-plus-another alloy combinations that have been used for years in aircraft and aerospace applications. Alclad cladding exposed to the corrosive is commercially pure aluminum, e.g., Alloy 1100, and has low strength while the thicker substrate is a heat treatable aluminum alloy such as Alloy 2024. The latter alloy has copper as its major alloying element. After heat treatment the copper in 2024 precipitates from the aluminum-copper, single phase solid solution to form a second phase of copper particulates. This precipitation greatly increases the strength of the 2024 but the presence of the second (different) phase of copper particulates, i.e., a micro-scale heterogeneous condition, also greatly lowers the alloy’s corrosion resistance.

For the Alclad combination described to function the electrode potentials of the cladding and the substrate alloys must be approximately equal in the electrolyte. This value for the non-heat treatable cladding is generally fixed. However, the several types of heat treatments, i.e., tempers, are possible with the substrate alloy and these produce different final potentials. There are other approaches to corrosion control in which it is desired for the Alclad to act as a sacrificial anode and thus provide cathodic protection to the substrate. In this case the Alclad and the substrate must have different potentials. This is accomplished by using a heat treatment for the substrate that results in it having a potential that is cathodic relative to that of the cladding.

Welds and the areas immediately adjacent to them, i.e., the heat affected zones (HAZ), often are particularly susceptible to corrosion but those same alloys without welds in the same electrolytes may be resistant. The heat from welding creates non-uniform, micro-scale metallurgical conditions such as different grain sizes or segregation of alloyed elements between the weld, HAZ and the unaffected portions of the parent metal. IGA is the possible result of the latter depending on the time the alloy spends in its sensitization range during cool down from welding temperature, its composition and whether or not it is then exposed to a corrosive medium that can cause IGA. The alloy is made susceptible



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to IGA because the area adjacent to grain boundaries has a different chemical composition than nearby homogeneous grains.

Welding also introduces stresses in the metal that remain as residual stresses around the weld area after the material cools. These areas are subject to greater corrosion than surrounding parent metal that does not have these stresses. Residual weld stresses are additive to applied stresses generated in service and are often overlooked. The total level of tensile stress present – residual plus applied – contributes to the probability of SCC or corrosion fatigue. It is important, often vital, in a variety of corrosive applications to apply a post-weld heat treatment, i.e., a stress relief annealing treatment, suitable for the given application to lessen the residual stress contribution to total stress.

Ambient-temperature, plastic deformation of an alloy during fabrication, i.e., cold working, also introduces residual stresses. These stresses are confined to certain areas of the material that has been cold worked such as at bends, at sheared edges or where the metal has been drawn through a die. Such areas are susceptible to accelerated corrosion where nearby areas that were not similarly worked are not. This effect is particularly severe in acidic environments. If practical, cold worked areas should be stress relief annealed after cold working and if this is not possible they should be viewed as susceptible regions for careful, periodic inspections once service begins.

In applications where there is circulation of the electrolyte there can be significant local differences in velocities and turbulence. The general effects of velocity can be complex and depend on the several factors previously discussed. However, if the critical velocity for the given situation is exceeded erosion-corrosion can start and corrosion rates will be greatly increased versus areas that are below that critical value. This is also true in areas where there is local turbulence such as at orifices, short radius piping elbows and across pressure let down valves. Like cold worked areas, all these areas deserve special attention during maintenance inspections.

Primary Methods of Corrosion Control –

It should be understood that the words “control” or “mitigation” are appropriate and “prevention” is generally not when discussing corrosion. Thermodynamics dictates that corrosion of practical engineering materials typically will occur. However, proper application of known control methods and tactics (often coupled with adequate corrosion monitoring and inspection) can reduce the frequent incidence and rates of corrosion of those materials to levels that will result in economic service.

The important roles of corrosion monitoring, inspection for corrosion and the value of completing root-cause failure analyses will be discussed in the section on tactics.

There are four traditional classes or methods used to mitigate corrosion:

- Use a coating or lining on the metal surface
- Select an alloy that has good resistance to the electrolyte and service conditions
- Apply cathodic protection
- Add a suitable chemical corrosion inhibitor to the electrolyte



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Coatings and Linings –

This category of corrosion control is generally the most widely used method and can take a wide range of forms. In most cases the coating or lining simply acts as a barrier between the alloy and the corrosive medium. In addition certain metallic coatings have an electrode potential that is anodic to the cathodic potential of the metal below it and thus the coating also protects the substrate by acting as a sacrificial anode, i.e., providing cathodic protection (CP).

The range of materials and applications in this category is extensive. It includes organic coatings (e.g., paints), polymeric linings and coatings, conversion coatings for steel and anodizing treatments for aluminum surfaces, galvanized and galvalume coatings on steel, cladding, weld overlays, electroplating, thermal sprays, chemical setting ceramic linings (e.g., acid bricks), porcelain enamels and glass linings. These many options mean that the optimal selection of a coating, lining or cladding for a given application can be very challenging. It is highly recommended that an objective, expert on coatings be consulted when making a selection and to assure proper implementation of the selection.

Organic coatings as paints on structural carbon steel are likely the most common form of corrosion control. Inorganic primers for steel that contain zinc to provide CP are often used with different varieties of topcoats in immersion services. Inorganic zinc (IOZ) is often used alone for atmospheric applications. Some common categories of organic coatings include alkyds, acrylics, epoxies, phenolics and polyurethanes.

The one general rule that is most important in effective use of paint coatings (and also in many other coating types) is the absolute need for good adhesion between the coating and the metal surface. Without the proper adhesion the best, most corrosion-resistant coating can disbond and fail to provide protection. This is primarily achieved by proper metal surface preparation. This means using and enforcing a clear specification for the level of surface preparation required in the given application. Some paint coatings are more tolerant of less-than-perfect surface preparation than others. Alkyd coatings are known as having a greater ability than other coating types to adhere to poorly prepared surfaces.

In the case of paint coatings, standardized surface preparation specifications are available from the Structural Steel Painting Council (SSPC). The National Association of Corrosion Engineers (NACE International) has similar standards. NACE also certifies coating inspectors. These persons are often essential to obtaining a quality coating system, i.e., the required surface preparation and specified coating characteristics.

Hot dipped galvanized steel is widely used. The thickness applied is directly proportional to corrosion resistance. Galvalume is a combination of zinc and aluminum applied to steel sheets. Its initial cost is more than galvanized steel but its corrosion resistance is considerably greater in atmospheric applications. Galvalume is often used as a roofing material for buildings.



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Natural or synthetic elastomers (rubber) are often used as linings inside chemical storage tanks. There are many material options in this category with various properties. Other polymers (plastics), especially fluoropolymers, are often used as linings or as coatings in steel pipe, in various piping components and on internal parts of pumps. They can provide excellent corrosion resistance to a variety of electrolytes. Some commonly used fluoropolymers are the oldest - polytetrafluoroethylene (PTFE, Teflon), fluorinated ethylene propylene (FEP), perfluoroalkoxy (PFA), ethylene tetrafluoro-ethylene (ETFE), ethylene chlorotrifluoroethylene (ECTFE) and polyvinylidene fluoride (PVDF). The fluoropolymers generally have a maximum service temperature limit of about 500 degrees F. They also differ in mechanical properties and in their ability to be fabricated into given configurations. Reference 5 provides a summary of these properties. Success with polymers depends on proper selection for the given use and the abilities of the application contractor.

Epoxy powder that is applied to metal surfaces by electrostatic spraying at high temperature has been used in two common applications. The resulting coatings are fusion bonded epoxy (FBE). One of these applications is for underground steel pipelines used in for oil and natural gas transmission. This is another example where a high quality surface preparation of the steel is essential in obtaining a good, long lasting coating.

Underground pipelines that transport hazardous materials must have both a coating and cathodic protection (CP) by federal regulations. The initial costs of FBE coatings are higher than other types of coatings for pipelines. However, the FBE has a significant advantage in that it minimizes or prevents cathodic shielding for the CP system. This is discussed in the CP section.

FBE is also frequently used to coat reinforcement bars (rebar) used in concrete. Bare rebar in concrete is subject to corrosion, e.g., as used in bridge decks or in concrete piers under marine-environment highways, due to moisture diffusion through the concrete and the effects of road deicing salts or seawater exposure. There has been much controversy about the effectiveness (and justification for the extra cost) of FBE rebar. Much of this has been caused by damage to the coating due to handling during construction. FBE coated rebar handled like bare rebar cannot be expected to remain free of defects.

Another widely used category of coatings is claddings. This entails metallurgically bonding a relatively thin layer of corrosion-resistant alloy to a thicker but corrosion-prone substrate that often is carbon steel but other alloys are also used. Thus corrosion resistance and mechanical strength are attained in the economic composite. The top, thinner layer may be a stainless steel, or a nickel, copper or aluminum metal or alloy. A related category of coatings is weld overlays. Here a thinner layer (compared to normal cladding) of the corrosion-resistant material over steel is attained by multiple welding passes using a suitably alloyed weld material. The welding parameters have to be carefully controlled to prevent the steel from diluting and thus diminishing the resistance of the overlay.



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Material Selection –

This class of corrosion control depends on choosing a given material that has the required corrosion resistance as well as other needed properties for the given application. The other properties might include strength, ductility, fracture toughness, strength-to-weight ratio, high temperature resistance, thermal or electrical conductivity, etc. Clearly all major classes of materials, i.e., metals, polymers, ceramics and composites, would be considered for a completely thorough evaluation but here the emphasis will be on metals and their alloys.

Before citing some potentially good corrosion-resistant material choices it is useful to categorize and give some typical examples of the different types of corrosive media:

While other constituents often are important, it is helpful to classify waters according to the approximate concentration of *chloride ions* they contain (Reference 6, page 189). There are four general types. These are fresh water (less than 1,000 parts per million, ppm); brackish water (1,000 to 10,000 ppm); seawater (25,000 to 35,000 ppm) and salt brine (above 35,000 ppm). Like all electrolytes, chemical analysis is often necessary to define the levels of these ions and others that can be important in a specific corrosion evaluation. Potable waters in the fresh water category may be hard or soft depending on whether or not they produce precipitated carbonate and magnesium scaling. In general scaling from hard water is protective if the scaling occurs on exposed surfaces.

Alkalies (higher pH electrolytes) might include sodium or potassium hydroxides; ammonia, amines (organic ammonia compounds); soda ash and hypochlorites (bleaches).

Acids can be either inorganic or organic. Generally the inorganic acids are more corrosive. The inorganic acids are classified as either oxidizing, e.g., nitric, sulfuric (at concentrations above 70%) and chromic or as reducing, e.g., sulfuric (at concentrations less than 70% but especially if below 20%); hydrochloric; hydrofluoric; phosphoric and carbonic. Two common organic acids are formic (the most aggressive of the organics) and acetic. Each is a reducing acid. The corrosive nature of contamination-free sulfuric acid in its reducing range can be altered significantly by the presence of contaminants such as ferric or cupric ions, chromates, nitrates, nitrites, hydrogen sulfide and, as is frequently true, chloride ions. See Reference 6.

Soil often is an electrolyte for underground metallic structures. Its aggressiveness depends on several factors including moisture content, electrical resistivity, and the presence and concentrations of specific ions, e.g., chlorides and sulfides, plus pH, the type of soil and the presence of microorganisms that can cause MIC. The American Water Works Association provides a standard, AWWA C105, that includes criteria that often are used to rank the relative corrosiveness of different soils. See also Reference 6, pages 210 –212.

Following are ***typically valid*** metallic material selections for several corrosive media and applications. In some cases comments on poor options for the given situation are provided. These are general recommendations. Often either mixtures of different



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electrolytes or trace contaminants occur such that general recommendations need to be modified. Also the common application variables previously discussed, e.g., temperature, velocity or heterogeneous conditions, have to be assessed to determine their effects in the specific situation.

Coated carbon steel (usually with a quality painting system or galvanization) for exposure to most atmospheric corrosion. Aluminum alloys are also widely used.

Bare weathering steel, e.g., A588 that contains about 0.30 % copper, to resist many atmospheric exposures except for high chloride, sulfide and sulfate atmospheres.

Coated carbon steel for underground service (quality applied FBE is often used) along with adequate cathodic protection specified for the particular local conditions.

Bare carbon steel for static storage of concentrated, i.e., 70% or more, sulfuric acid. Only very low velocities (about 3 feet/second is a maximum) are permitted.

Bare carbon steel for storage of ammonia or ammonium hydroxide water solutions if a small amount of iron contamination in the electrolyte is acceptable and certain provisions can be met. A minimum of about 2000 ppm (0.2%) of water must be present and no air should be present. Even so, post-weld stress relief of welds and low strength steels (not hardened, higher strength steels) are recommended. Without these provisions SCC in carbon steels is possible. If zero water is present, i.e., the electrolyte is anhydrous, SCC of carbon steel is possible. In the latter case, 304 stainless steel (SS) is recommended for temperatures up to approximately 212 degrees F.

If dissimilar metals or alloys must be used together in an application, select those that are closest together in a traditional galvanic series in seawater. However, be aware of the cautions mentioned in the galvanic corrosion section. Always use an insulator between dissimilar metals when possible. If this is not possible, obtain a favorable anode-to-cathode area ratio. That means avoid a small anode area galvanically coupled to a large cathode area.

304 stainless steel (SS) for exposure to nitric and other strongly oxidizing acids. Use 304L if the SS must be welded to avoid IGA. Note: 316 SS (and 316L) provide inferior service to 304 and 304L. The molybdenum in 316 & 316L causes accelerated attack in nitric and similar oxidizing acids compared to alloys without molybdenum.

SS's having high levels of molybdenum (Mo), chromium (Cr) and nitrogen (N) provide the best resistance to pitting and/or crevice corrosion in waters and other media that contain high levels of chlorides. The percentage of Mo present is particularly important. This role of Mo also applies to nickel-based alloys that contain chromium.

High purity ferritic SS's, e.g., alloys 29-4 or 29-4-2; austenitic SS's with high nickel contents, e.g., 20Cb-3; or nickel-based alloys, e.g., Alloy 200 or C-276, provide the best resistance to SCC in electrolytes with high levels of chlorides. Nickel (Ni) content in these alloys is the critical factor. Surprisingly, zero or a small percentage of Ni, as in 29-4



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and 29-4-2, or Ni percentages of about 20% as in 20Cb-3 or more as in Ni-based alloys provide the best resistance. The commonly used 300 series of austenitic SS's with 8 to 14% Ni are the most susceptible and they often experience SCC in chloride media.

Use lower carbon grades of 304 or 316 SS, i.e., 304L or 316L, where IGA is likely in a given service where 304 or 316 would otherwise be suitable. Post-sensitization heat treatment often is impractical. Current steel mill practice is to automatically supply these two standard grades of SS's in an "extra low carbon" or ELC version labeled as 304/304ELC or 316/316ELC. This practice permits limiting the carbon contents to a maximum of 0.03 % as in the older low carbon versions as a standard procedure.

Copper tubing and brass fittings for handling potable water. Velocities must be limited to prevent E-C.

Brasses with 15% or less zinc contents to prevent dealloying (dezincification) or, for more commonly used brasses with more than 15% zinc, use those that also have about 1% tin plus about 0.2 % of arsenic, antimony or phosphorus. Tin has the major positive effect in preventing dealloying but the minor elements enhance its role.

Commercially pure nickel (Alloy 200) for use in sodium hydroxide services. Nickel is not resistant to ammonia or its derivatives in the presence of air. Reference 6, page 140.

Cathodic Protection (CP) –

In this form of control DC electric current is supplied to the metal surface that is corroding to counteract the DC current generated at the anodic areas there by the corrosion process. By this action the electrode potential of the metal is polarized from an anodic to a cathodic potential. Corrosion is not stopped completely but its rate is greatly diminished so as to provide practical control.

The required level of applied CP current to achieve adequate protection depends primarily on the bare metal surface area exposed to the electrolyte. For this reason CP is commonly used with some type of coating on the metal to minimize the current required. However, no coating is perfect and different coatings will have various levels of small (or not so small) defects, known as holidays, which allow exposure of the substrate metal. The more current that is required for protection in a given application the lower, i.e., more negative or cathodic, the potential of the applied current source must be.

CP can be provided by two basic methods. The simplest is to use consumable current sources, i.e., sacrificial anodes, which are galvanically coupled to the metal to be protected. These anodes are more electrochemically active than the metal to which they are electrically attached and thus they preferentially corrode while cathodically polarizing the more noble metal and protecting it from corrosion. Typical sacrificial anode materials are zinc, magnesium or aluminum and most frequently one of these is coupled to steel to be protected. The other method of CP is impressed current CP (ICCP). Here a non-consumable, anodic material in the electrolyte is electrically connected to the positive terminal of an adjustable rectifier/transformer while the metal to be protected is



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connected to the negative terminal. The rectifier consumes AC electrical power, converts it to DC power and reduces the voltage (potential). This resulting DC current goes to the non-consumable anodic material where it is discharged to travel through the electrolyte to the metal to receive CP. Typical ICCP anode materials are graphite, cast iron or titanium wire coated with platinum.

Sacrificial anode CP systems have the advantages of being simple with less initial and operating costs. ICCP systems have higher initial and operating costs but they can be adjusted to deliver more current and thus they can protect more square feet of bare metal receiving CP compared to a sacrificial anode system. ICCP systems often cannot be used in remote locations where AC power to supply the rectifier is unavailable or too costly to bring to the area where the rectifier is located. It is essential in both types of systems to complete regular monitoring and maintenance to assure an adequate CP potential, and thus a proper level of current, is being delivered. Several matters can prevent successful operation. Persons qualified to monitor and, especially to troubleshoot and remedy problems, are needed to make CP function as intended. It is not an option to install a system, forget about required follow-up and expect good performance.

Cathodic shielding of CP current occurs when a coating on a buried pipeline receiving CP separates from the metal - commonly at a holiday – due to loss of adherence. This is coating disbondment. At an affected holiday the electrolyte can enter the entire disbonded area but applied CP current can penetrate only a short distance laterally there. The remainder of the disbonded region receives little or no protective current and thus corrosion is not mitigated. Shielded areas present problems because they cannot be detected by the standard monitoring procedure of measuring CP potentials between the pipe and a reference electrode placed in the soil at ground level at several spots along a buried pipeline route.

Fusion bonded epoxy (FBE) coatings on pipe sections are installed in the applicator's shop. If proper procedures and quality control are used then and if the finished pipe sections are handled carefully during transport and during setting in the ditch in the field, these coatings are noted for having high adherence and resistance to cathodic shielding problems. Some type of coating still has to be applied in the field to cover the circumferential field-completed welds that join the separate pipe sections. Shrinkable plastic sleeves are often successfully used over these weld areas. Some other types of pipeline coatings that are completely applied in the field, e.g., tapes, have been much less successful in attaining good adherence and resistance to cathodic shielding.

CP is used in several types of applications. A simplest form is the role of zinc deposited by hot dipping on structural steel or the use of certain Alcad on aluminum alloys as previously discussed. Each provides CP by sacrificial corrosion of the more active metal to protect the substrate. Attached sacrificial anodes have been used for many years to protect the steel hulls of ships and the underwater steel portions of offshore drilling rigs. Both sacrificial anode CP and ICCP are used for protection of buried pipelines, steel gasoline storage tanks and for the outer bottom surfaces of aboveground storage tanks. Often the inner surfaces of steel water tanks and steel tanks that hold corrosive chemicals



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are coated and an ICCP system is installed. Rebar in concrete is also protected using CP but, as is true all applications, regular monitoring is needed to attain long-term success.

Corrosion Inhibitors –

Inhibitors are chemical species added to electrolytes in small concentrations to reduce corrosion rates. They function either by adsorbing onto the metallic surfaces to be protected, and thus providing thin barriers to attack, or by otherwise affecting the electrochemistry of the given application to reduce rates. Most inhibitors are proprietary products from specialized chemical treatment providers. Some products act alone but in many applications two or more are specified to provide a greater beneficial effect due to their synergistic interaction.

Choosing and applying an effective inhibitor (or combination) depends on the specifics of the given application. This entails the metal to be protected, the electrolyte, service temperature, the required inhibitor concentration for the specific conditions and environmental regulations that may preclude a given type. The trade off between costs versus effectiveness always is a prime consideration. Similar to the situation for MIC, specialized expertise is needed to make the best technical recommendations.

There are many types of inhibitors and they may be classified in different ways. Some act to control the anodic corrosion reaction, some to control cathodic corrosion reactions and some affect both types. Some are effective when the primary cathodic reaction is oxygen reduction and others when that reaction is hydrogen reduction to produce hydrogen gas. Many exist as liquid additives for the electrolyte and some function because of their high vapor pressures and thus abilities to release inhibiting gases to nearby metals to be protected. The latter are used for equipment in closed storage and shipping containers.

Certain types of inhibitors must be used with great care. The specific concentration employed is the key factor. These inhibitors are designed to shift (and help maintain) the electrode potential of particular active-passive alloys from their active to their passive ranges (as shown in Figure 1) in a given electrolyte where this would not otherwise occur. They are known as passivators or oxidizing inhibitors. If the inhibitor concentration is too low for the specific service conditions the electrode potential of an alloy might be moved further out on the active corrosion portion of its anodic polarization curve but not far enough for it to shift back to its passive, low corrosion rate range. This results in a faster rate of corrosion than would occur if no inhibitor of this type were used.

This problem may also occur in local areas of a metallic system, e.g., a lengthy or complex piping system, if a sufficient concentration of the passivating inhibitor is not delivered to all regions of the system. Corrosion rates likely will be much higher in these deficient regions.

Some inhibitors cannot be used in certain applications because either they are chemically toxic or, while they are beneficial in controlling corrosion, their presence in the process stream interferes with desired chemical reactions. These results might be found in



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manufacturing systems handling food-quality substances or in chemical manufacturing plants.

Probably the most common applications of inhibitors are in recirculating cooling water systems or to minimize corrosion in oil field production systems. In water systems corrosion is just one of the considerations. The choice of inhibitor there must be compatible with other potential problems such as scaling or the presence of biofouling that may or may not affect corrosion but may influence effective heat transfer and cause higher pumping costs due to flow constrictions. Multiple considerations may also exist in oil field applications. As mentioned, vapor phase inhibitors are often effectively used inside shipping and short-term storage containers for metallic equipment. In these applications the selected inhibitor must not be harmful to any metals present or to any non-metallic materials included in the shipped or stored equipment.

Inhibitors are sometimes added to the mix water for concrete to help protect the enclosed rebar from corrosion in concrete structures such as bridge decks. One type commonly used is calcium nitrite. However, like many practical engineering problems, there are several interacting variables to be considered in choosing to use inhibitors. Some of these factors include the quality of the installed concrete, the desired service life of the reinforced structure, the depth of concrete cover over the top mat of rebar, the water-to-cement ratio that is used in mixing the concrete, the use of CP or not and the use of different rebar materials. Options in the latter area include bare carbon steel, epoxy-coated carbon steel, stainless steel or a newer steel, i.e., ASTM A 1035, with apparently excellent potential for these applications. Discounted, life-cycle costs of the various alternatives need to be determined to make the most rational decisions. See Reference 7, pages 559- 597 for discussions of the several interacting factors in this area of corrosion control.

Corrosion Control Tactics –

The following are tactical recommendations and ideas to consider in seeking corrosion control. Some will not be practical in particular situations. However, these items may serve as a checklist for the engineer to use so as not to overlook some of the various, possible approaches. The most promising ideas for the specific application should then be investigated in depth.

Overall Questions and Factors to Consider:

Is it possible to favorably alter the corrosive environment or operating variables? This might include the type or concentration of the electrolyte, the concentration of the aggressive ions in it, the temperature, pH, degree of aeration, electrode potential, velocity or stagnant conditions or various heterogeneous conditions.

Do application criteria permit the use of non-metals? Options might be solid polymeric materials such as PVC tubing, polyethylene (regular or high density, HDPE) pipe or polymeric coating and linings such as PTFE or rubber. Are any ceramics such as



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corrosion-resistant acid brick and mortar or glass linings for chemical reaction vessels possibilities? Are reinforced fiberglass piping, ducts or tanks potential options?

What design details can be changed to provide more inherent resistance? This should always include providing geometry, sloping and/or outlet sizes to provide for consistent, complete drainage of the electrolyte and to never allow a residue of it be retained in out-of-service facilities. Others might be to eliminate all possible crevices including providing for effective deposit or debris removal from metal surfaces; removing all possible small radii and other surface features that create stress concentrators and are difficult to effectively coat or specifying a quality surface finish on metals when corrosion fatigue is a possibility. Reference 8 provides other beneficial approaches the design engineer can use. Always configure the design for practical, regular inspections and maintenance. When other options are impossible, consider if designing for partial, periodic replacement of susceptible portions of the system without disturbing non-exposed portions is feasible.

Consider using the failure modes and effects analysis (FMEA) procedure early during the planning and design stages. This numerical procedure entails identifying all potential failure modes (not just corrosive types but also mechanical, electrical, etc.), assigning a probability and overall system consequence value to each and then using these values to form a simple, weighted product. These results allow a rank ordering of the degree of attention and justified funding for corrective actions according to the comparative importance of identified, potential failure modes. Reference 9 provides more details.

Provide a rational financial basis for alternative corrosion control expenditures by establishing the discounted, life-cycle cost of each option. Most engineering projects are intended to function for multiple years. Comparing only the initial costs of alternatives does not consider the total costs that may occur in the future over expected, long service lives. Several valid evaluation approaches for completing discounted, life-cycle cost analyses are presented in the engineering economics course taken by most engineers. These analyses often are completed in large organizations by cost engineering or financial or accounting groups when assessing large capital projects. However, the techniques are not difficult and may also deserve regular use by the individual engineer in determining the economic viability of smaller expenditures. Most managers “speak this language” and, hopefully, will welcome the input.

Factors Specific to the Types of Corrosion:

General attack – use a corrosion allowance in material thickness above that needed for mechanical strength; all four of the classic methods of corrosion control should be considered for use, i.e. coatings, materials selection, CP and inhibitors.

Galvanic attack – avoid dissimilar metals in contact if feasible; if this is not possible use an electrical insulator to separate them; if an insulator is not feasible use materials that are as close together as possible in a traditional galvanic series (but recognize the discussed shortcomings of this) *and* obtain a favorable anode-to-cathode area ratio. Another alternative is to coat, preferably, both metals but if that’s not possible coat the



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cathodic metal in the galvanic couple. No coating gives perfect coverage and if only the anodic material is coated there will be a very unfavorable anode/cathode area ratio created at each holiday in the coating on the anode while the large cathode is left bare.

Pitting and crevice attack – in stainless steels be aware of the importance of the alloying elements molybdenum (most important) plus chromium and nitrogen in selecting alloys to provide resistance in the very common cases of electrolytes with chlorides; realize that stagnant or very low velocity conditions promote attacks while moving liquids retard attack; if crevices cannot be eliminated open the entrances to them as much as possible to allow free exchange of the electrolyte in and out *or* use sealants to close them; all four of the classic methods of corrosion control should be considered for use.

SCC – recognize several situations that may induce or may help control SCC. These include which unique alloy and corrosive media combinations are susceptible when applied or residual tensile stresses also act. Identify residual stresses due to, for example, shrinkage after welding, cold working or surface machining of metals and seek to minimize them by stress relief heat treatment. Know the specific role of the alloyed element nickel in stainless and nickel alloys' susceptibility to SCC in chloride media. Consider the possibility of control by compressive stresses imparted to a metal surface by shot peening; recognize the possibility of attack on austenitic stainless steels under certain thermal insulation and use sodium silicate inhibitors in the insulation as a control measure. Know that carbon steel often provides more resistance to SCC than stainless steels if the carbon steel does not experience prohibited rates of general corrosion in the given medium. This idea can apply to the material used for the tubes in shell and tube heat exchangers in open, recirculating cooling water systems where the cooling medium is inhibited sea or brackish water. Reference 2, page 106.

Corrosion fatigue – eliminate all possible stress risers on the surfaces of dynamic equipment or structures subject to cyclic stresses; use surface (case) hardening techniques, e.g., nitriding or carburizing, to increase resistance; input helpful compressive stresses to the metal surface by shot peening; when there is a choice, use butt welds rather than fillet welds. Fillet welds are more susceptible, Reference 8 page 127. Recognize that relatively benign corrosives environments can change “pure” mechanical fatigue to the more dangerous corrosion fatigue form.

IGA – (if possible) avoid the sensitizing temperature range (this is approximately 900 to 1400 degrees F for stainless steels) due to welding, any type of heat treatment or in-service exposure; if sensitizing exposure cannot be avoided typically use an extra low carbon (ELC) grade of stainless steel; when an ELC stainless steel is welded also use compatible ELC welding electrodes or filler metal; if the stainless alloy must be exposed to the sensitizing temperature range for long periods (as in regular service) it may be better to use a stabilized grade of stainless, i.e., 321 or 347 that contains titanium or niobium, respectively, rather than an ELC grade. The titanium in 321 and the niobium in 347 have strong affinities for carbon and the carbides thus formed precipitate harmlessly to grain boundary regions after critical temperature exposure leaving protective chromium in place throughout the alloy's matrix as desired. Note – stainless grades 321 and 347 have no molybdenum so they offer inferior resistance to chloride pitting and



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crevice attack compared to 316L. In critical applications where the main concern is IGA, use the ASTM A 262, Practice C to confirm that a given stainless steel is resistant to IGA.

E-C – whenever possible minimize normal flow velocities and features that cause local turbulence; recognize that providing for corrosion resistance to the given electrolyte will provide more overall resistance to E-C than providing enhanced resistance to the abrasive wear portion of the mechanism; provide filters in the flow stream to remove solid particles that intensify attack; lessen turbulence by using a butterfly valve instead of a globe or gate valve; take large pressure reductions in multiple steps rather than a single one; seek to streamline flows rather than making abrupt direction changes in piping; where E-C is unavoidable – use local hard weld metal overlays or replaceable impingement plates.

Dealloying – recognize dezincification of brass as the most common type especially in stagnant water with high temperature and higher concentrations of chlorides, i.e., more than 500 ppm, and carbon dioxide; copper alloys with more than 15 % zinc are susceptible; if these are needed use alloys with tin plus phosphorus, arsenic or antimony in small amounts as inhibiting elements to resist attack. Recognize that loss of zinc in brass alloys is a major cause of SCC in them. Besides inhibited brasses other resistant alloys in order of increasing resistance are bronzes, aluminum bronzes, copper-nickel alloys and Alloy 400 (Monel). Gray cast iron can suffer selective attack on the iron and leave the graphite intact in soils especially those with sulfates or sulfate reducing bacteria (SRB). Cast iron attack frequency takes many years to develop; this may also occur in waters with low pH and in seawater; resistant alternatives to gray cast iron are ductile iron, white cast iron and cast iron with 2- 3% nickel.

MIC- recognize that all types of metals can be susceptible with the possible exception of titanium alloys, i.e., switching from carbon steel to stainless is not an effective control measure; stagnant water conditions and the presence of biofilms (slime) are well known to promote attack and if there is an option always use the cleanest source of water in cooling applications to minimize attack. Control measures include using coatings with CP (often with more negative {cathodic} potentials than typically used when MIC is not acting) for underground applications and chemical treatment with biocides in cooling water systems. Once a given water treatment plan is in use there must be competent, consistent long-term monitoring of the chemistry and corrosive action of the process stream to assure harmful microbes and corrosion rates are being controlled by the specific methods.

Along with the effective specific use of chemical corrosion inhibitors, analyzing and effectively controlling MIC problems include some of the most difficult issues in the corrosion field. It is recommended that specialized consultants or organizations that concentrate on MIC (or inhibitors or both) be employed for such tasks rather than persons or organizations that do not concentrate in these areas.



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Maintenance, Monitoring/Inspection and Post-Mortem Activities –

Note – Many of the following ideas are especially applicable to continuous operating facilities such as chemical plants, oil and petrochemical plants, pulp & paper processing plants or electric power generation plants. However, there are many other types of facilities and systems that may incur major costs or inconveniences for their owners or clients if corrosion failures cause interruption of intended operations. Consider if any of the following might have practical benefit in your specific application.

The most important potential costs of a corrosion failure relate to personnel or public safety issues and/or environmental releases and the resulting legal liabilities from each. Significant portions of the total life-cycle cost evaluation that (hopefully) is completed for each alternative control measure investigated will be the future costs of necessary maintenance and inspection activities as well as indicated replacements associated with the given alternative. Very large future costs could exist for facilities that must function on a 24/7 basis and, therefore, incur extremely high costs when there is an unplanned shutdown. In these situations the cost of unavailability due to a corrosion failure often will outweigh the initial cost of the most expensive corrosion control option. Thorough economic analyses of all costs are justified for these cases.

Understand that effective corrosion control must be an on going and not a one-time activity. Continually inspect for and monitor operational corrosion rates at susceptible areas and in the most critical operating equipment to detect significant changes so that timely corrections can be made. Suitable non-destructive evaluation (NDE) methods are regularly used in many industries. In addition effective monitoring can be accomplished by the use of weight-loss corrosion coupons to define average corrosion rates of alloys of concern or by using electrical corrosion sensors to obtain approximate, instantaneous corrosion rates. Another approach is to regularly take samples of the circulating electrolyte and chemically analyze them for changes in dissolved metal concentrations (caused by corrosion) or for other detrimental chemical changes. These sample analyses are mandatory when using corrosion inhibitors to confirm that the intended concentrations are being maintained at all locations in a system.

Make and maintain detailed records of the results of all inspections, monitoring and maintenance activities. Especially important to corrosion control are the magnitudes and timing of chemical changes in the process stream or changes in other operating variables. Electronic data storage and retrieval software make this activity much easier compared to manual methods used in the past. Corrosion rates and deleterious changes that are well documented can provide essential information for accomplishing planned, predictive maintenance work. The alternative of taking unplanned, emergency shutdowns when a failure occurs is always expensive. Being proactive in the future is usually easily justified after the actual costs of an emergency shutdown are experienced.

Establish a policy of completing, documenting and maintaining records of thorough, root-cause failure analyses for significant material failures. Failures may be found to have been produced by corrosion as well as other failure modes, e.g., “pure” mechanical fatigue, fracture, wear, etc. The analyses should define the true root cause(s) of failures



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such as a bad material selection, poor design details, unexpected changes in the service environment, material defects, fabrication defects, improper or lack of required maintenance, etc. The results of these analyses, if kept in an organized and readily available form like the on-going monitoring and inspection records, can become very valuable, locally applicable resources.

Continued implementation of the policies of making and keeping excellent records of all monitoring, maintenance and root-cause failure analyses is becoming essential in current industrial settings. In many industries a large percentage of experienced personnel are reaching retirement age and leaving their responsibilities to much less experienced persons. Access to thorough corrosion control maintenance and other “lessons learned” records can be a great help to the newer workers in preventing repetition of past mistakes.



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