

WASTE PACKAGE CORROSION CONSIDERATIONS

FOR ON-SITE STORAGE

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ABSTRACT

Waste package corrosion will diminish on-site storage safety. This paper is a primer on radwaste package corrosion. Eight forms of corrosion are characterized: uniform attack, localized attack, galvanic attack, velocity phenomena, fretting, intergranular attack, dealloying attack, and cracking phenomena. Site corrosion testing is reviewed, and general corrosion prevention schemes are presented.

INTRODUCTION

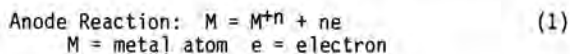
Nuclear power plant regulation continues to increase the complexity of managing radioactive waste (radwaste). With radwaste burial issues still unresolved, safe on-site storage becomes more important since radwaste may remain on-site for longer time periods in the future. Initially, on-site storage of low-level radwaste was considered a temporary problem. As soon as enough 55 gallon drums or boxes were full, radwaste was shipped to permanent storage sites and forgotten by chemistry and radiological personnel.

Waste package corrosion is one aspect of safe on-site storage requiring attention. If not recognized and treated, waste package corrosion will diminish storage safety due to leaks and other failures, and will require repackaging. This paper is a primer on radwaste package corrosion. Corrosion types are defined with characteristics and prevention information along with corrosion rate description. In addition, on-site corrosion testing is briefly reviewed. Finally, general corrosion prevention schemes are listed.

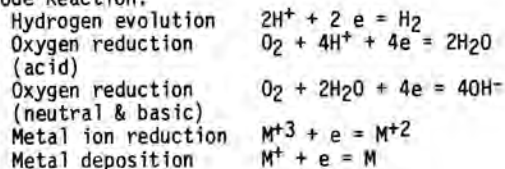
THE EIGHT CORROSION TYPES: CHARACTERISTICS & PREVENTION

The National Association of Corrosion Engineers (NACE)¹ have defined eight forms of corrosion: uniform attack, localized attack (pitting and crevice corrosion), galvanic attack, velocity phenomena, fretting, intergranular attack, dealloying attack, and cracking phenomena (stress corrosion cracking and cracking fatigue).

General chemical equations for corrosion are the following:



Cathode Reaction:



To remember where oxidation or reduction occurs, use CAR for Cathode Reduction and ANOX for ANode OXidation. From eq. 1, it's the anode reaction that causes concern about corrosion.

Uniform Attack

The entire surface experiences equal chemical attack. Thus, there are negligible surface differences. Water, salts, oxygen, acids, and a host of other chemicals contribute to uniform attack. Corrosion prevention for uniform attack includes neutralizing the environment by removing oxygen or corrosive chemicals, selecting alternate materials with greater corrosion resistance, using cathodic protection, and coating the surfaces. On-site storage tanks and 55 gallon drums will experience this form of corrosion.

Localized Attack

Metal loss or attack occurs in discrete areas. Two forms of corrosion belong to this group: pitting and crevice corrosion.

Pitting is an extreme form of localized corrosion. Generally, the pit will have a surface diameter as large as its depth. Pits usually grow in the direction of gravity. Although pits usually require an extended initiation time (months to years), pits, once started, grow at an increasing rate: pitting is autocatalytic. Rapid dissolution occurs in the pit while oxygen reduction takes place adjacent to the pit; thus, areas adjacent to the pit are protected. Chloride and hydrogen ions stimulate pit growth, although other halides will promote pitting (bromide and hypochloride). Fluoride and iodide are usually not as aggressive. Oxidizing

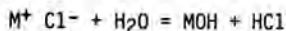
metal chlorides are aggressive pitting agents. Cupric, Cu^{+2} , ferric, Fe^{+3} , and mercuric, Hg^{+2} , halides are examples. Cupric and ferric chlorides do not need oxygen present since both serve as electron acceptors.

Surface conditions markedly affect pitting tendencies. Pitting is less likely on polished surfaces. However, when pits do occur on polished surfaces, the pits are usually larger than on other surfaces.

Prevention is similar to that used for uniform attack, with increased stress on neutralizing oxidizer and chloride ions. Solution agitation will eliminate or decrease pitting attack.

Crevice corrosion is a particular form of pitting usually occurring between faying surfaces where stagnant solutions form, e.g., flanged surfaces, gasket surfaces, bolt and rivet heads, and surface deposits like sand or dirt.

Initially, fluids enter a shielded area containing equal amounts of salts and oxygen similar to the liquid on the container. However, as corrosion progresses in the stagnant area, oxygen is used up within the crevice. Metal ions increase in concentration because oxygen is still available outside the crevice; thus, electrons have a place to reduce O_2 . The outside is protected since the area is cathodic. The metal ions promote chloride migration into the crevice where the metal-chloride complex encourages water decomposition by the following mechanism:



Thus, the crevice promotes a corrosive environment where oxide films and other protection fail.

The incubation period for crevice corrosion is six months to a year. Methods to avoid crevice corrosion include welds rather than bolts and rivets, minimum dirt or sand accumulation, and low oxygen concentration.

Galvanic Attack

Two dissimilar metals are required for galvanic attack to occur in the presence of an electrically conducting medium. The attack is greatest near the dissimilar metal junction and decreases as the distance from the junction increases. Table I shows the galvanic series of corrosion for common metals in sea water. The greater the distance between the metals, the greater the corrosion that will occur. Where the metals are bracketed, there is little difference in their potentials. Thus, couples of bracketed metals or alloys will not exhibit the galvanic effects. For example, if Chlorimet 3 is coupled with steel, the unit would fail on the steel side rapidly. However, Monel and cupronickel could be joined without galvanic attack corrosion. Fifty-five gallon drums, where the top is made of a different material than the drum, are candidates for galvanic attack.

Galvanic corrosion rates are influenced by areas of the anode and cathode by the following equation:

$$r = r_a (1 + A_c/A_a) \quad (2)$$

r = accelerated corrosion rate
 r_a = corrosion rate of anode metal when uncoupled
 A_c = Area of cathode
 A_a = Area of anode

From eq. 2, coupling a large cathode to a small anode would increase the corrosion rate. However, a large anode coupled to a small cathode would cause little difference in the corrosion rate.

If dissimilar metals must be joined, place an electrical insulator between the metals, e.g. rubber or polyethylene. Do not place storage containers on metal platforms without thinking about galvanic couples. Scrutinize container to metal contacts to avoid an accelerated corrosion problem.

TABLE I

Galvanic Series of Some Metals and Alloys in Seawater

| | |
|---|--|
| | Platinum |
| | Gold |
| | Graphite |
| | Titanium |
| | Silver |
| ▲ Noble | Chlorimet 3 (62% Ni, 18%Cr, 18%Mo) |
| | Hastelloy C (62% Ni, 17% Cr, 15% Mo) |
| | 18-8 Mo Stainless Steel (passive) |
| | 18-8 Stainless Steel (passive) |
| | Chromium Stainless Steel 11-30% Cr (passive) |
| | Inconel (passive) (80% Ni, 13% Cr, 7% Fe) |
| | Nickel (passive) |
| | Silver Solder |
| | Monel (70% Ni, 30% Cu) |
| | Cupronickels (60-90% Cu, 40-10% Ni) |
| ▼ Anodic | Bronzes (Cu-Sn) |
| | Copper |
| | Brasses (Cu-Zn) |
| | Chlorimet 2 (66% Ni, 32% Mo, 1% Fe) |
| | Hastelloy B (60% Ni, 30% Mo, 6% Fe, 1% Mn) |
| | Inconel (active) |
| | Nickel (active) |
| | Tin |
| | Lead |
| | Lead-tin solders |
| 18-8 Mo Stainless Steel (active) | |
| 18-8 Stainless Steel (active) | |
| Ni-resist (high Ni cast iron) | |
| Chromium Stainless Steel, 13% Cr (active) | |
| Cast Iron | |
| Steel or Iron | |
| 2024 Aluminum (4.5% Cu, 1.5% Mg, .6% Mn) | |
| Cadmium | |
| Commercially pure aluminum | |
| Zinc | |
| Magnesium or its alloys | |

Velocity Phenomena

Few radwaste containers will experience either form of velocity phenomena: erosion corrosion or cavitation erosion.

Erosion corrosion occurs when attack is initiated not only by chemical means, but also by mechanical means due to grit, metal filings, or corrosion products hitting surfaces at high velocities. Thus, one accelerates the corrosion process by wearing away protective oxide layers and substrate metal.

For radwaste personnel, trouble may occur when filling waste containers with a high velocity flow. Since the fill material will likely originate from volume reduction units, filtration/ion exchange waste tanks, or waste solidification systems, grit and corrosion product concentrations are likely to be high. In these cases, watch for erosion corrosion.

Cavitation erosion occurs when impeller blades pull a vacuum on a liquid. With vacuum, bubbles form on the blade of the impeller. These bubbles then collapse causing shock waves with pressures greater than 4×10^8 Pa (60,000 psi). This shock force deteriorates the impeller surface. Containers will not experience cavitation erosion, but volume reduction pumps may deteriorate due to this phenomenon.

Fretting

Fretting has two theories of attack: wear-oxidation and oxidation-wear. Fretting occurs when two objects rub together such as with vibration. The required distance of actual displacement is small, e.g. 10^{-8} cm. Yet, despite the small motion, fretting wear is extremely aggressive.

In wear-oxidation, two objects in very close contact experience motion. In addition, a corrosive environment is present. Surfaces of objects are rarely smooth. Upon magnification, one sees high and low spots throughout the entire surface. With motion, the high spots are carved off. This debris then corrodes. The corroded debris is often harder than the substrate metal causing more corrosion. Consequently, the fretting attack increases due to the presence of the corrosion product in the contact space of the two metals. In oxidation-wear, oxide or corrosion products become the high spots that are carved off during displacement and act as abrasives in the contact space.

There are prevention schemes for fretting. First, eliminate the motion. For some equipment, like motors and pumps, motion is required for operation. Therefore, more corrosion resistant and harder materials are used. Also, teflon, graphite, and lubricants are used. Furthermore, fretting will diminish if corrosion attack is minimized: remove oxygen, neutralize acids, and remove salts.

Intergranular Attack

Intergranular attack (IGA) occurs along grain boundaries when atoms within the substrate material are attacked preferentially due to initial fabrication methods or subsequent construction uses.

Weld decay is one example of IGA. This phenomena occurs when chromium (Cr) is depleted from a zone in the metal. Chromium diffuses through metals easily at high temperatures. While welding, Cr atoms diffuse from the area by the weld to the heat source and precipitate to form chromium carbide. Consequently, Cr is depleted from the area adjacent to the weld where corrosive attack subsequently occurs.

There are solutions to this problem. Heat treat the item to allow the Cr to diffuse into the depleted area. At the nuclear site, large heating compartments may not be available; thus, induction heating will achieve the same result. Barring use of heat, select alternative materials. For instance, low carbon steels (less than 0.03%) will prevent chromium carbide precipitation. In addition, metals with other agents (stabilizers) having greater affinity for carbon, e.g., columbium, titanium, and columbium plus tantalum, also prevent chromium carbide precipitation.

Exercise caution with low carbon steels; otherwise IGA will still occur. This attack is usually traced to poor handling by the welder. First, if the welder uses a greasy rag to wipe the

surface, carbon returns for Cr precipitation. Also, if the metal is shipped with a corrosion prevention organic coating, poor surface preparation will yield IGA after welding.

Dealloying Attack

Dealloying attack, selective leaching, or parting, represent the same phenomena. Dealloying attack preferentially leaches atoms from the substrate matrix. Resin containers where ion exchange media are still active are candidates for selective leaching.² Ion exchange materials at nuclear plants are used to remove corrosion products and other contaminants from systems. The process continues till the resin is deactivated. Therefore, to prevent dealloying attack, deactivate all ion exchange resins according to supplier directions. Even though a resin may appear exhausted due to its performance in radwaste cleaning systems, its exchange equilibrium may favor extracting metals from the storage container.

Cracking Phenomena

Cracking phenomena include both stress corrosion cracking and corrosion fatigue.

Stress corrosion cracking (SCC) has three components: environment, stress, and material. If one of these components is removed, SCC doesn't occur. The environment includes the presence of chlorides, oxygen, oxidizers (e.g., HNO_3), acids, caustic solutions, and water. The material will dictate which environment poses the most risk. For example, stainless steels experience SCC with chloride or caustic and resist SCC in sulfuric acid, nitric acid, and water. Yet, titanium experiences SCC when in the presence of nitric acid or seawater. Tensile stress, not compressive stress, is the third component of SCC. Tensile stresses may be applied, residual, thermal, or welding. Materials, as shown by the titanium-stainless steel example, react differently to different environments.

At the nuclear plant, much of the contamination removal equipment is there to remove chloride ion, hydroxide ion, and corrosion products. Consequently, final waste products for storage contain high concentrations of SCC promoting contaminants.

SCC prevention is best accomplished by changing one of the components. For instance, find out if the waste containers have residual stresses. Select different materials for different environments. Alter the environment by stabilizing the ions and corrosion products.

Corrosion fatigue is a synergistic effect caused by repeated stresses to a material exposed to a corrosive environment. Most materials have a fatigue limit, or measure of times that a material will allow a given stress level before the material will fail. All materials will fail sooner in a corrosive environment. For instance, 55 gallon drums that are moved frequently could experience corrosion fatigue. In addition, waste compactors may repeatedly induce stresses in the waste containers.

Due to the synergism, one need only remove the corrosive environment or stress inducer to decrease the corrosion rate. For example, apply less compactor pressure to the drums. Situate containers once. Prevent waste containers from bumping during shipping. Also, low cycle stress times and low stress favor corrosion fatigue: the lower cycle time

allows more corrosion processes to occur between cycles.

CORROSION RATES

Corrosion rate expressions range from simple weight loss without time considerations to penetration rates per time. To avoid decimals, most corrosion experts use mils per year (mpy). In SI units, this converts to meters per second (mps).

From weight loss data, mils per year are calculated from the following expression:

$$\text{mps} = W/(\text{DAT})$$

W = weight, Kg
D = density of material, kg/m³
A = area, M²
T = exposure time, seconds

$$\text{mpy} = 534W/(\text{DAT})$$

W = weight, gm
D = density of material, g/cm³
A = area, in²
T = exposure time, hr

CONTAINER INTEGRITY TESTING

Container integrity testing applies not only on-site but also during transportation and burial. On-site, a leaking container may contaminate previously uncontaminated area, necessitate personnel exposure for cleanup, and produce additional administrative burdens. Moreover, transportation and burial site personnel prohibit acceptance of leaking containers.

Testing

There are many non-destructive examination (NDE) tests available. Sheldon Strauss recently reviewed visual (fiber optic), liquid penetrant, magnetic particle, eddy current, radiography, ultrasonic, and acoustic emission.³ In addition, Strauss provides a quick reference chart for easy selection of the proper NDE technique. Other on-site tests include chip and pressure tests.

A chip test, suggested by Randy Parker of Humboldt Bay Power Plant,⁴ reveals corrosion processes and rates by exposing a chip of the waste container material to actual simulated process liquids (liquids with the same concentrations of ions but without the radioactivity). For example, suppose the site produces waste product containing electrolytes A, B, C, and D. Make up a solution, S, containing these same electrolytes. Take chips of the waste container materials, e.g. 5 cm X 5 cm, and expose the chips to solution S. Place solution S and the chips in the same environment where the waste containers will be stored. Periodically remove the chips and test for weight loss.

If the tests are performed properly, approximate corrosion rates for the waste containers will result. Consequently, an inspection schedule and potential failure times can be developed from the data for the plant's particular corrosion conditions. Actual containers could also be used to insure that area ratios and other parameters are matched.

There are many variables involved during testing. Variables include area ratios, oxygen concentrations, temperature effects, and so forth. NACE¹ provides information and courses on corrosion testing.

Leak tests include either pressure or vacuum tests. The pressure test requires pressurizing the waste container and watching the pressure drop with time. A vacuum test requires placing the container in a chamber where a vacuum is established. The chamber would have a pressure or an acoustic device to monitor escaping gas or sounds from the waste container.

From ALARA considerations, the chip tests seem most appropriate. In addition, ultrasonic measurements offer a fast thickness measurement process. Ultrasonic advantages include: accurate calibration since materials from similar containers are used for calibration; discontinuities in the material are shown for dirt and sand accumulation; and, fast, accurate measurements are possible.

Schedule

Unless corrosion test data are available for a particular application, monthly surveillance is required initially to monitor corrosion rates. One surveillance scheme would entail marking selected containers at specific locations on the containers for periodic thickness measurements. Typical corrosion sites for a 55 gal drum include bottoms, sides adjacent to the bottoms, sides adjacent to the tops, and the tops. If air is left in the drum, than the interface area between the contents and the air needs testing. Note this interface prior to placing a lid on the container.

For box containers, again bottoms and sides next to the bottom need inspection. The lid intersection with the container is the next point. Areas adjacent to corners or bends are next. Finally, random tests of selected sites on the flat surfaces are next.

Thickness measurements are then graphed with thickness versus time. Slope deviations from 0 slope would then alert personnel for potential problems.

When failures occur, examine the metal after decontamination for clues to the failure. Furthermore, for chronic or catastrophic problems, consult a corrosion expert who uses not only on-site examination data but also material surface science data obtained by using electron microscopy and other instrumentation.

PREVENTION

Eliminating corrosive attack may be an impossible task. However, minimizing the attack through careful material selection, proper environmental conditions, and appropriate material interface considerations will provide optimum corrosion prevention and container integrity.

Cathodic Protection

Cathodic protection (CP) uses the galvanic couple advantageously by providing a current source to the material (active CP) or allowing a more anodic material (called the sacrificial anode) to corrode (passive CP).

Active CP uses a current source to prevent attack. However, radwaste container protection using active CP seems inappropriate; therefore, active CP is not covered here: see Uhlig⁶, Fontanna and Greene⁷, Boyer⁵, or NACE¹ for specific information.

Passive cathodic protection (CP) allows a sacrificial anode to corrode preferentially. In passive CP, the more anodic material, shown by Table

I, is connected to the material that needs protection by an electrically conducting material. For example, waste containers could be attached to a sacrificial anode in one of the waste containers. Check the sacrificial anode occasionally to ensure that it has not corroded away. Once the sacrificial anode is depleted, the waste container that is most anodic due to its contents and materials will become the sacrificial anode. Passive CP offers inexpensive and reliable corrosion prevention for individual or groups of waste containers.

Alternate Materials

Polyethylene liners provide favorable barriers. The liners prevent interaction of the contents with the waste containers. In addition, the liners are inert to many chemicals. However, gamma rays are known to affect polyethylene. Effects of gamma rays include loss of strength, brittleness, and less chemical inertness. However, these effects are usually found in high gamma flux fields. Polyethylene waste containers also offer an excellent corrosion resistant alternative to metal containers.

Alternate metal selection will extend the life of some containers. For instance, waste containers containing higher concentrations of nickel would resist SCC better. However, higher costs are associated with some metal alternatives.

Coatings

Coatings offer protection for little additional cost. Coatings with excellent protection include polyurethanes, epoxies, and vinyl elastomers. There are other coatings, such as ionized metal sprays; however, their cost seems prohibitive for waste container use.

Coatings, if improperly applied, will accelerate attack. Repeat, thin coatings during application are preferred to one or two thick coats. One or two applications often lead to bubble formation: the bubbles then break and cause pinholes. Pinholes accelerate corrosion attack by concentrating the attack at the pinholes which are anodic. Thus, pits occur within months; the results are destructive. Consequently, if coatings are used, apply repeat, thin coats for more effective protection.

Oxygen and Moisture Control

Oxygen elimination offers one of the best defenses against corrosion. To control oxygen, airtight seals are required on waste containers. Also, inert gases could be used for void spaces in waste containers, e.g., place dry ice in the container. Furthermore, oxygen absorbants are available for use within the closed containers. In addition, polyethylene bags filled with inert gases, surrounding the waste container, could be used for containers experiencing rapid corrosion.

Unlike oxygen, moisture control is easier to apply. Good housekeeping, chemical absorbants, and protected storage will yield excellent moisture control. Furthermore, by maintaining dry clean conditions, dirt will not accumulate on containers and offer areas for corrosion processes to occur.

Chemical absorbants are especially effective in removing moisture. Furthermore, many of the absorbants are easily regenerated for repeated use.

CONCLUSION

Corrosion prevention requires planning to avoid such mistakes as galvanic couples or dealloying due to wrong material choices or improperly prepared waste container contents. This paper is by no means complete. Readers are encouraged to examine the references for more information.

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