

## CORROSION FAILURES

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Corrosion is the destruction of metals by chemical or electrochemical reaction with the environment. Annual cost of corrosion in the U.S.A. is 8 billion dollars. For example, estimates of automobile muffler corrosion alone range between 250 and 375 million dollars per year. Knowledge of a few basic essentials could avoid many failures.

A great majority of the corrosion costs are due to corrosion in electrolytes, which can be called wet corrosion. The basic requirements for electrochemical corrosion are that (1) anodes and cathodes must be present to form a cell, and (2) direct current must flow. The anodes and cathodes could be close together (local cells) or far apart. The current can be self-induced or it can be impressed on the system from an outside source.

The anode is the area where corrosion occurs and where the current leaves the metal. The cathode is the area where practically no corrosion occurs and where current enters the metal. Anodes and cathodes can form on a single piece of metal because of local differences in the metal or differences in the environment.

Figure 1 summarizes these requirements and can be considered as a basic diagram for corrosion. This figure indicates means of decreasing corrosion because anything that upsets this picture interferes. For example, a barrier coating would separate the metal from the environment. Also corrosion would be decreased or stopped if current entered the metal over its entire surface (cathodic protection).

Another very important factor is the area effect or ratio of cathodic to anodic areas. An unfavorable area ratio is a large cathode and a small anode. Corrosion of the anode may be 100 or 1000 times more than if the two areas are of the same magnitude. This is one reason why the stainless steels are susceptible to rapid pitting in some environments. Corrosion at one spot (the anode) progresses rapidly because it is surrounded by a large area of unattacked metal which acts as a cathodic area.

Both specimens shown in figure 2 were exposed to identical environments at the same time for 15 months. The specimen on the right has an unfavorable ratio, with steel rivets in copper plates. The steel rivets were corroded completely. The specimen on the left shows a more favorable area ratio. In this case the steel plates are corroded but a strong joint still exists. The rate of attack on steel is obviously much greater on the specimen with the large copper or cathodic area. Figure 2 is from the work at the test station of The International Nickel Co., Inc., Harbor Island, N. C.

Violation of these simple fundamentals often results in costly failures. For example, a plant installed several hundred large tanks in a major expansion program. Most of the older tanks were made of ordinary steel and completely coated on the inside with a baked phenolic paint. The solutions handled were only mildly corrosive to steel, but contamination of the product was a major consideration. The coating on the floor was often damaged also because of mechanical abuse, and some maintenance was required. To overcome this situation the bottoms of the new tanks were made of steel clad with 18-8 stainless steel. The tops and sides were of steel, with the sides welded to the stainless

clad bottoms as illustrated in figure 3. The steel was coated with the same phenolic paint with the coating covering only a small portion of the stainless steel below the weld.

A few months after start-up of the plant the tanks started failing because of perforation of the side walls. Most of the holes were located within a 2-inch band above the weld shown in figure 3. Some of the all-steel tanks had given essentially trouble-free life for periods as long as 10 to 20 years as far as side wall corrosion was concerned.

Small defects in the coating resulted in tiny steel anodes connected to the large stainless steel bottom. In other words, the area of the cathode to the anode was almost infinitely large!

A similar situation occurred wherein the noble metal exposed was a bronze manhole door in large coated steel tanks.

### EIGHT FORMS OF CORROSION

Corrosion can be classified by the eight forms in which it manifests itself, the basis for this classification being the appearance of the corroded metal. Each form can be identified by mere visual observation. In most cases the naked eye is sufficient, but some-times magnification is required. Valuable information for solving the problem can often be obtained through careful observation of the test specimen or failed equipment (that is, before cleaning). The eight forms are described as follows:

1. Uniform corrosion involves the general thinning of the metal over the entire exposed surface. Sometimes it is slow and sometimes very rapid. This form of corrosion is, of course, the one which we like to see. It is of least concern technically because in most cases it can be predicted by simple immersion tests. The other forms that are localized in nature often cause the headaches and plant shutdowns.

2. Galvanic or two-metal corrosion occurs when two dissimilar metals are in contact. Corrosion on the less resistant material is accelerated and the more noble metal is protected. Steel and copper in contact with aluminum have caused rapid failures of the aluminum parts.

Occasionally the general rule stated above, in connection with accelerating corrosion on the base metal, has exceptions. For example, in fuming nitric acid at 160°F aluminum by itself shows a corrosion rate of 30 mils per year and 18-8 stainless steel 150 mils. When these two materials are coupled, the corrosion rate of the stainless steel drops to 2 mils per year and that of aluminum increases to 600 mils per year.

3. Concentration cell corrosion is due to differences in the environment. It is also called gasket corrosion, deposit corrosion, and crevice corrosion. Figure 4 illustrates examples of ion cells and oxygen cells. This is one reason why welded joints are often preferred over riveted joints provided porosity or incomplete weld penetration do not exist. Whenever a liquid is stagnated under bolt heads, loose gaskets, deposits or other crevices, concentration cell corrosion is likely to occur. The stainless steels are particularly susceptible.

4. Pitting (holes) is one of the most vicious forms of corrosion because it is difficult to predict and because only a small weight loss is involved. Pitting is usually associated with deposits which form concentration cells. However, it can occur on

smooth surfaces, for example where "double valence" chlorides ( $\text{FeCl}_3$ ,  $\text{CuCl}_2$ ) are involved. The chloride ion is a bad pitting agent.

5. Selective leaching involves the removal of one element from an alloy. The classic example is dezincification of brass. Figure 5 shows uniform dezincification of a brass pipe in water service. The darker inner ring is copper colored. The outer ring is the unaffected yellow brass. Localized dezincification also occurs and this is the plug type. Another common example is the so-called graphitization of gray cast iron where the iron matrix dissolves leaving the graphitic network and some rust.

6. Intergranular corrosion is localized attack at the grain boundaries of a metal as shown by figure 6. The 18-8 steels are a classic example. When this material is heated in the range of approximately  $950^\circ$  to  $1400^\circ\text{F}$ , chromium carbide precipitates at the grain boundaries with resultant depletion of chromium in adjacent areas. Selective attack then occurs in these areas. This form of corrosion was christened "weld decay" because it was associated with welding. Resistance to intergranular corrosion can be achieved by (a) heat treatment to dissolve the carbides, (b) stabilization with columbium or titanium (tie up the carbon), and (c) use of very low carbon steel. Sometimes the stabilized stainless steels show intergranular corrosion in a narrow zone immediately adjacent to the weld. This has been christened knife-line attack. In this case the mechanism consists briefly of rapid cooling of this metal which is at a high temperature next to the molten weld metal; the columbium stays in solution and does not form carbides. When this metal is heated into the sensitizing or carbide precipitation zone, chromium carbide forms or the metal behaves as an unstabilized material.

7. Stress corrosion is the combined effect of stress and corrosion and failure is exhibited by cracking. The stresses in most cases are due to internal stresses because of cold working or locked-in stresses resulting from welding. If stresses are cyclic, this phenomenon is termed corrosion fatigue. This is an important factor in welded equipment because it can be assumed that stresses in the neighborhood of the yield point in metal are present after welding.

We have studied stress corrosion of stainless steels in our laboratories for many years. Hot chloride waters are good "crackers." "Vapor condensation" conditions are very bad in that stresses as low as 2,000 psi can cause cracking in an hour or so. Conditions that permit chloride concentration effects are destructive.

Recent work has shown that the wedging action of solid corrosion products in a crack is sufficient in itself to provide high stresses for crack propagation.

Some other bad cracking combinations are carbon steel in caustic and nitrates and copper alloys in ammonia or amines.

8. Erosion corrosion. Most metals and alloys depend upon a protective surface formation for corrosion resistance. When these surfaces are damaged by erosion we often obtain the destructive action which is called erosion corrosion. This often occurs in liquids at high velocity, solids in suspension, or when impingement is present. A common example involves corrosion of the first few inches of heat exchanger tubes where turbulence exists.



## EIGHT METHODS FOR COMBATTING CORROSION

1. Alloying or materials with better corrosion resistance is a very common method used for decreasing corrosion. For example, if steel corrodes we alloy it with chromium to make stainless steel. If stainless steel corrodes it may be necessary to use high silicon iron. Sometimes copper or aluminum are used where steel is unsatisfactory. This method includes proper heat treatment (and stress relief).

2. Cathodic protection is the protection of a structure by means of sacrificial anodes or by impressed currents. This is a very important method in the protection of underground pipe lines, in fact this form of transportation of commodities would not be economical were it not for decreased corrosion because of cathodic protection. Anodic protection involves passing a current the other way to form a protective surface (passivity).

3. Metallic coatings are often used and the most familiar example is the protection of automobile bumpers with nickel and chromium electroplates.

4. Examples of inorganic and organic coatings are glass linings and paints.

5. Alteration of the environment represents one of the oldest methods for combatting corrosion, namely de-aeration of water before feeding it into a steam boiler. Other examples are the so-called inhibitors and passivators. Reducing temperature, if possible, is very helpful.

6. Non-metallics, such as rubber, ceramics, plastics, and wood.

7. Metal purification represents the solution of special cases. For example, commercially pure aluminum is the most resistant aluminum material. Zirconium, arc melted, has better corrosion resistance than induction melted metal because of contamination. This method of combatting corrosion is special because in general the pure metals are expensive and are not as strong.

8. Design can often solve a corrosion problem. The term design means the use of the same material but a change in its physical or mechanical shape. A tank should be designed for proper draining and cleaning. Equipment can be designed so that parts are readily replaceable. Standard sizes are often desirable.

These are the methods a corrosion engineer uses to solve corrosion problems. Sometimes combinations of these are used. The decision is usually dictated by economics.

## EFFECT OF TEMPERATURE

Temperature is our worst enemy in our fight against corrosion. Figure 7 shows the rapid increase in corrosion with temperature particularly above the boiling point.

## FAILURES--CAUSES AND CURES

1. Cracking of welded steel tanks handling 35 percent caustic at 250°F. Eliminated by stress relieving after welding. Figure 8 shows the relation between temperature and concentration of caustic and their effect on cracking of as-welded steel. This information

was obtained by a committee of NACE and is based on actual service experience. It is particularly valuable in deciding whether or not field welded piping will crack.

2. Erosion corrosion of solid bowl centrifugal used for separating monohydrate ferrous sulfate solids from recovered sulfuric acid. Solved by adding cupric ion to the slurry. Figure 9 shows the data on which this decision was based.

3. Stress corrosion of large carbon steel autoclave. Crack shown in figure 10. Vessel was stress relieved but the member containing the slot was welded in place in the plant (this weld not stress relieved). Solution--weld this member in before stress relieving the vessel.

4. Failure of Type 304 stainless steel vessels and lines from the outside surface. Caused by rain soaking insulation, leaching out of chlorides from insulation, then drying out (chlorides concentrated). Solved by removing insulation and leaving it off. Where very high heat losses were involved, the entire vessel was cased in sheet metal (to keep the rain out). Failure of a vessel handling warm distilled water is shown in figure 11. Several cracks are on this outside surface. "Dy-Chek" was used for a color photograph but this picture is not clear in black and white.

5. Rapid corrosion of stainless steel autoclaves used for testing acids at temperatures up to 450°F. Solved by using a Teflon liner.

6. Automobile corrosion. Wash off salt frequently. Use plastic body (i.e. Corvette). Touch up spots exposed by chipped coating. Aluminized and zinc coatings. Wax frequently.

7. Cracking of Type 347 stainless steel exchangers from the cascading cooling water side in 5 months. Replaced with 5 percent Cr steel which has lasted over 10 years and still going.

8. "Catastrophic oxidation" of steel furnace tubes heated with vanadium-containing fuel oil. Stopped by keeping tube temperature below 1200°F.

9. "Ringworm corrosion" of oil well tubing and also in a chemical plant. Spheroidized pearlite attacked--normal pearlite not corroded. Solved by normalizing heat treatment to form lamellar pearlite.

10. One side of valve on electroplating tank badly corroded because of stray currents. Solved by insulating valve from tank.

11. Gasket corrosion of stainless steel flanges in contact with asbestos gaskets. Eliminated by using Teflon gaskets (no wick action).

12. Stress corrosion of 18-8 tubes just below top tube sheet of vertical condenser. Solved by venting the air space to keep tubes wet (submerged) over entire surface.

13. "Inlet tube" erosion corrosion on heat exchangers. Several such problems solved by one of the following: (a) "Ferrules" placed in tube ends, (b) install tubes 5 inches longer (extend into head), and (c) turn evaporator upside down.

14. Atmospheric corrosion of plant equipment. Good paint and paint maintenance or "let it rust." Increasing thickness of steel (corrosion allowance) cheaper than painting

but rust is unsightly and makes for poor public relations. Can obtain pleasing appearance and long life with proper selection of coat systems.

15. Many stress-corrosion problems involving 18-8 type steels solved by using Inconel which is very good in chloride-containing hot waters. Cast CF-8 alloys containing ferrite have higher strength and better resistance to stress corrosion than the completely austenitic material.

16. Dezincification of brass problems solved by using red brass (15% Zn) and cupro-nickels.

17. Corrosion of underground pipe lines, water tanks, etc. solved by using cathodic protection with impressed current anodes such as Duriron. See figure 12.

18. Corrosion of offshore platforms and "Texas towers" controlled by simultaneous use of five methods of combatting corrosion: (1) Monel sheathing in the splash zone, (2) cathodic protection for submerged portion, (3) coatings above the splash zone, (4) streamlining of design of structure to facilitate coating and coating repair, and (5) inhibitor in stagnant water between H beam pile and its outer casing.

19. Corrosion of gas well tubing caused by condensate and  $\text{CO}_2$ . Periodically treat well with organic inhibitor.

20. Old plant made of steel operated for many years. New and more efficient plant designed and built with an operating temperature of  $100^\circ\text{F}$  higher than old plant. High pressure pumps made of Type 410 failed in a short time because of erosion corrosion. Parts replaced by CD4MCu and worked fine. Failure next occurred in the heat exchangers because of inlet tube erosion corrosion. Controlled by making them into 2-pass instead of 4-pass to reduce velocity of flow. Really major problem developed when large steel lines corroded through. System lined by welding in nickel sheet.

21. Failure of plug valves because of attack on the lubricant and also because of poor maintenance lubrication. Many of these problems solved by use of F and G valves (figure 13) which contain a Teflon liner between the plug and body (no grease).

22. Durcon (epoxy) pipe, valves, and pumps used where corrosive too severe for metals, that is, hydrochloric acid containing amounts of  $\text{FeCl}_3$ . Durcon sinks (figure 14) are widely used.

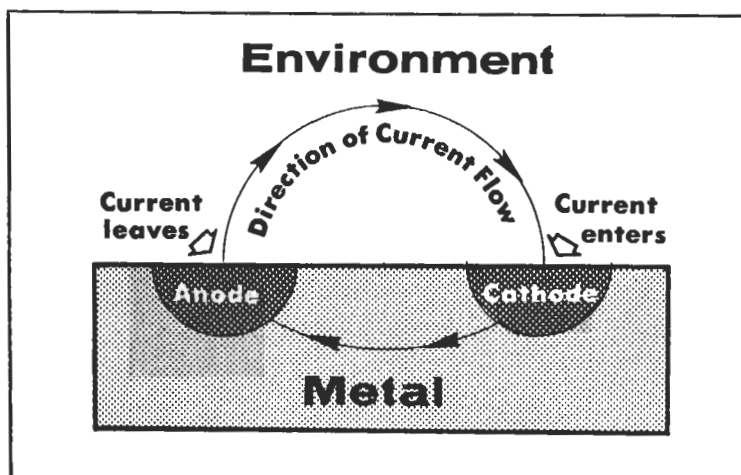
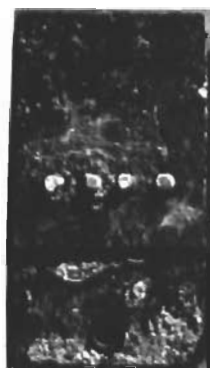
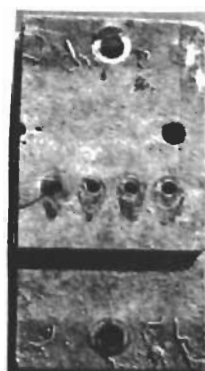


Figure 1. Basic Diagram Showing Requirements for the Corrosion of Metals by Electrolytes



COPPER RIVETS  
IN STEEL PLATE  
LARGE ANODE  
SMALL CATHODE



STEEL RIVETS  
IN COPPER PLATE  
LARGE CATHODE  
SMALL ANODE

Figure 2. Effect of Area Relationship on Corrosion of Rivets in Sea Water 15 Months

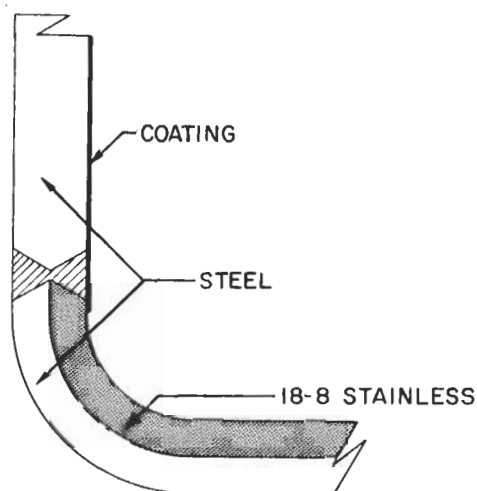


Figure 3. Detail of Welded Steel-Stainless Clad Steel Tank Construction



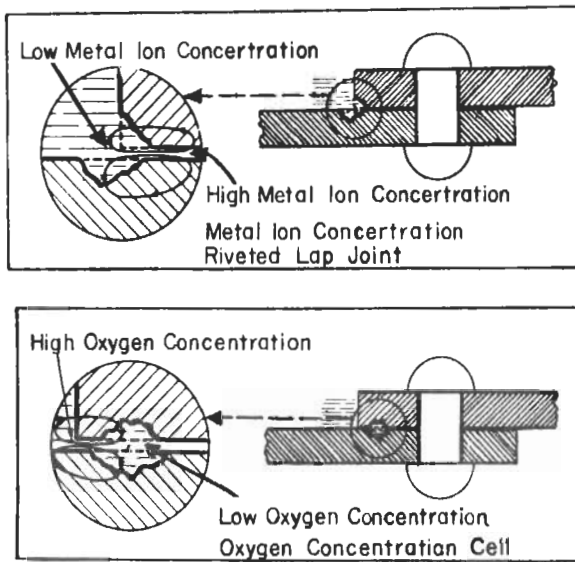


Figure 4. Concentration Cells

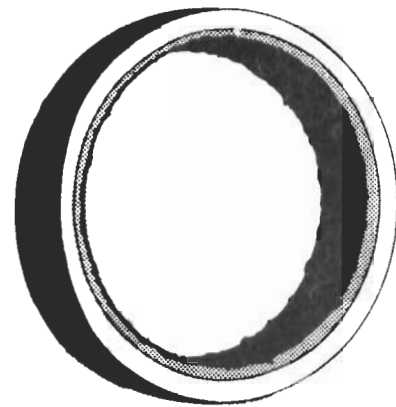


Figure 5. Uniform Dezincification

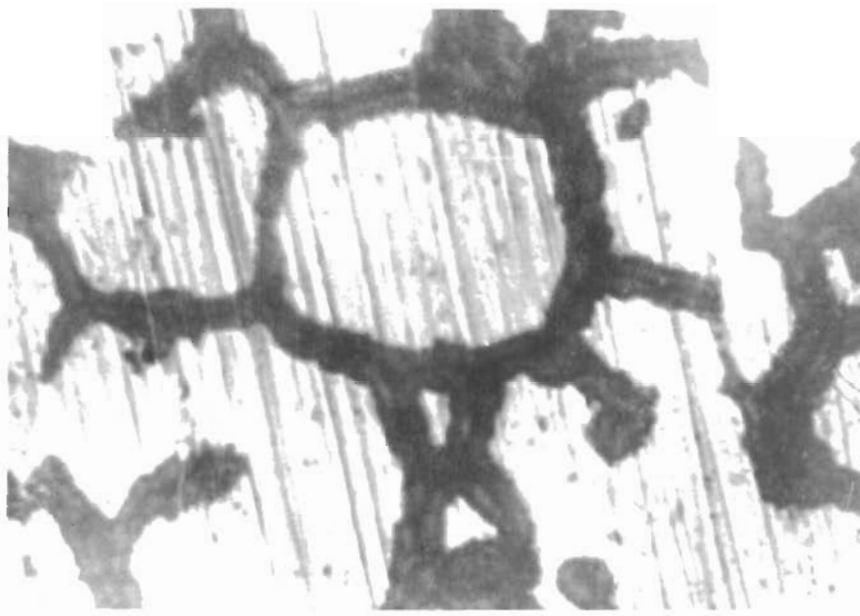


Figure 6. Intergranular Corrosion



ASD TDR 62-396

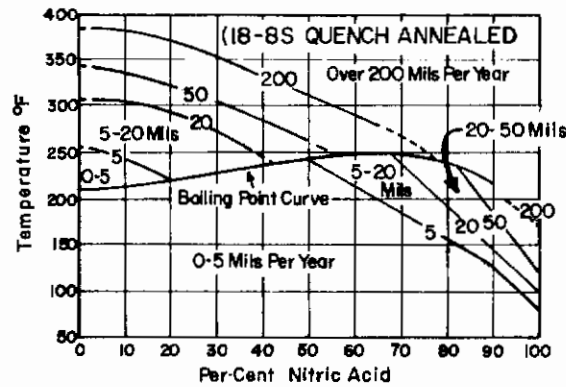


Figure 7. Corrosion of Quench-Annealed 18-8S by Nitric Acid as a Function of Temperature

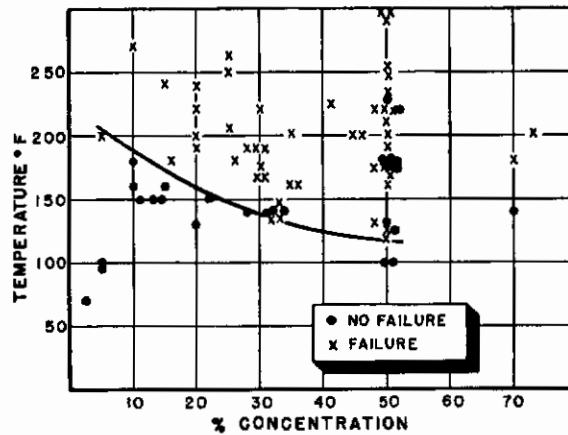


Figure 8. Effects of Temperature and Concentration on Cracking in Sodium Hydroxide Based on Service Experience

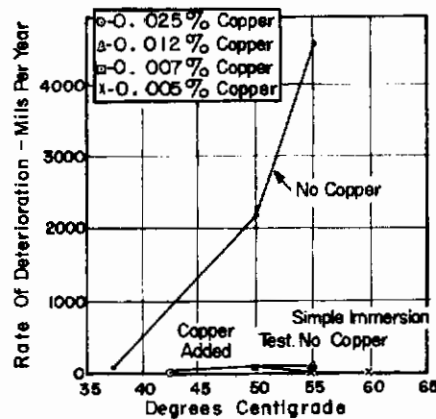


Figure 9. Inhibiting Effect of Copper in a Sulfuric Acid Slurry on Erosion - Corrosion of 18-8S Mo Stainless Steel

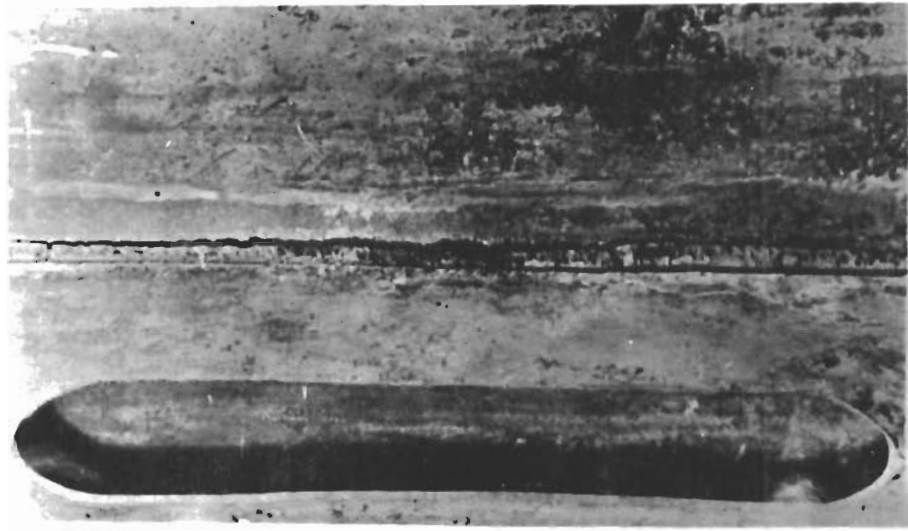


Figure 10. Stress Corrosion--Welded Steel

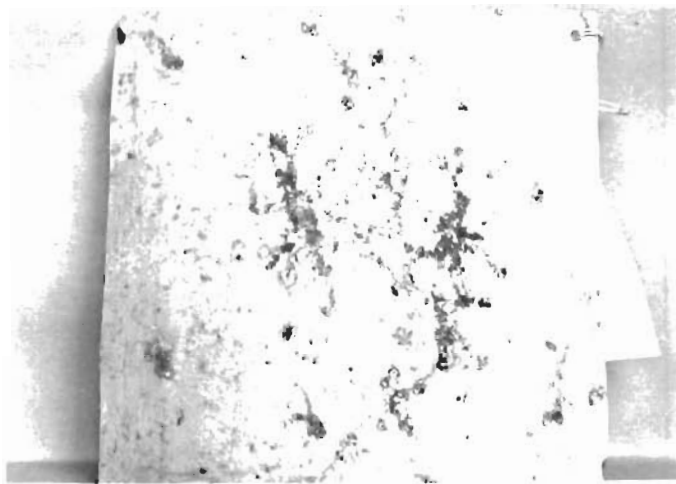


Figure 11. Stress Corrosion of Type 304 Stainless Steel from Outside (insulated side)

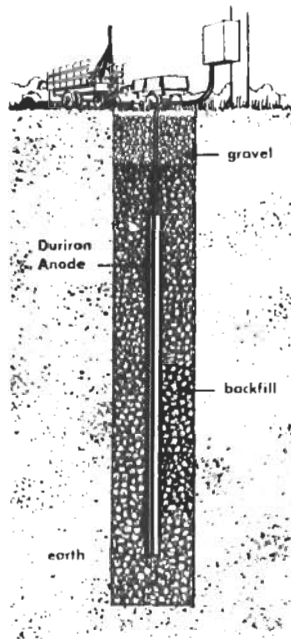


Figure 12. Installation of Duriron Impressed Current Anodes for Protecting Underground Structures

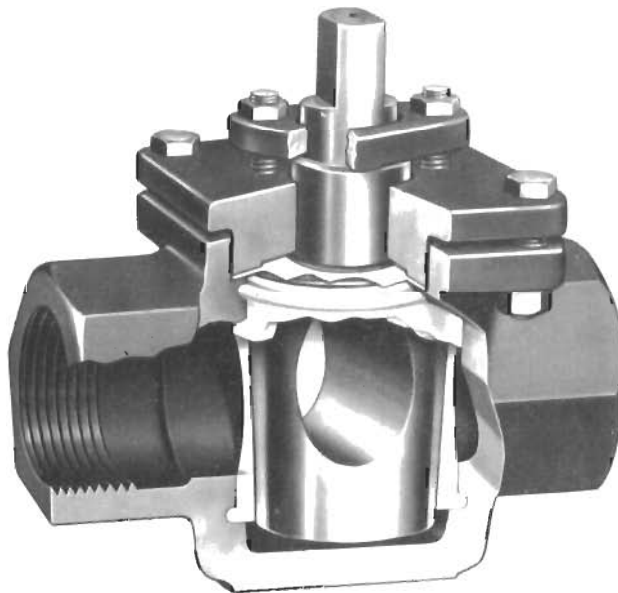


Figure 13. Non-Lubricated Plug Valve Illustrating Use of Teflon Sleeve to Separate Plug and Body



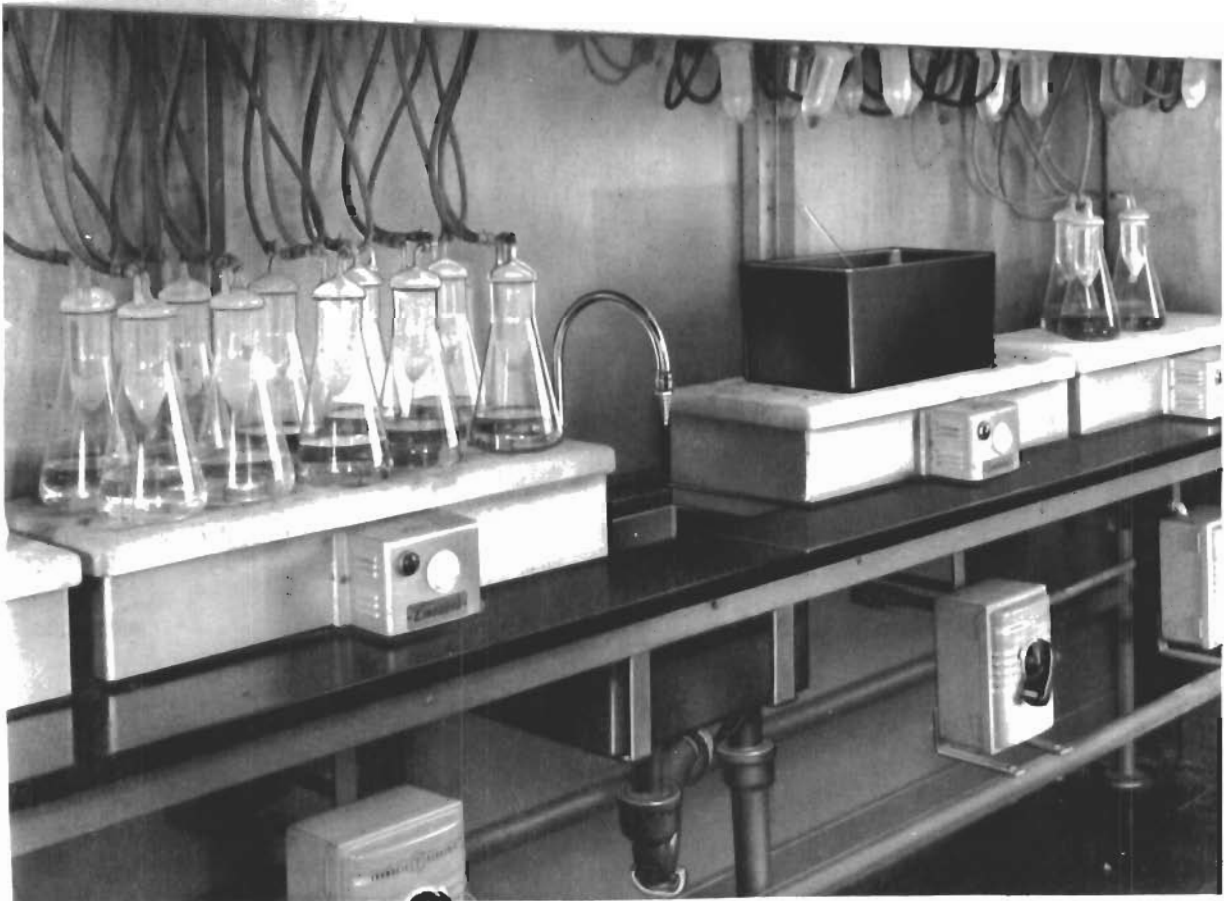


Figure 14. Durcon (Epoxy) Sinks in Chemical Laboratory. One Sink Recessed in Table Top with Durcon Outlet; the Second, is on a Hot Plate for Etching Parts