

## THE EIGHT FORMS OF CORROSION AND THE CORRECTIVE MEASURES

By

Mars G. Fontana Ph.D. and M.S. Mitra Ph.D.

Corrosion has been justifiably attributed to cause more loss in money than any other single factor. Corrosion has also been an important factor in causing some outstanding cases of failure.

Valuable information for the solution of a corrosion failure can often be obtained through careful observation of the corroded test specimens or, failed equipment. 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. Some of these eight forms are unique and distinct but all of them are to varying degrees interrelated. These are:—

1. Uniform attack or, general corrosion.
2. Intergranular corrosion.
3. Pitting
4. Galvanic or two-metal corrosion
5. Concentration cell corrosion
6. Dezincification
7. Erosion-Corrosion
8. Stress-corrosion

1. *Uniform Attack* is the most common. It is normally characterised by chemical or electro chemical reaction which proceeds uniformly over the entire exposed surface. The metal becomes thinner and eventually fails. Uniform attack or general over-all corrosion represents the greatest destruction of metal on a tonnage basis. This form of corrosion, however, is not of too great concern from the technical standpoint because the life of equipment can be accurately estimated on the basis of comparatively simple tests or, experience.

Most of the other forms of corrosion are insidious in nature and they are considerably more difficult to predict. They are the forms that cause unexpected or premature failures and consequent headaches for the management.

2. *Intergranular Corrosion* consists of selective or localized attack at the boundaries of the metallic crystals. Sometimes whole grains are thereby loosened and fall away. Complete disintegration of the metal result even though a relatively small portion of it corrodes on a weight-loss basis. The 18-8 chromium-nickel stainless steels are particularly susceptible to intergranular corrosion when they are not properly heat treated or otherwise stabilized. If plain 18-8 stainless steel is subjected to a temperature in the range 900 to 1400°F. for an appreciable time, this alloy becomes susceptible to intergranular attack in many corrosive media. The commonly accepted explanation is, briefly, that chromium carbides precipitate in the grain boundaries of the metal, and this precipitation "ties up" some of the chromium and depletes the chromium content of the alloy in the areas adjacent to these carbides, and thus decreases the effective corrosion resistance of the grain boundary material. This is one reason why the carbon content of 18-8 is kept low (below 0.08% in Type 304 stainless steel) for optimum corrosion resistance—that is, there is less

carbon to form carbides. These effects can be minimized or practically eliminated by stabilizing the alloy by the addition of either columbium (as is contained in Type 347 stainless) or titanium Type (321). These elements in preference to chromium combine with the carbon and depletion of chromium is thereby avoided. If 18-8 steel has been heated in the precipitation range, its corrosion resistance can be restored by heating to a high temperature (1850 to 2050°F), which takes the carbides back into solution, and cooling rapidly, which will retain the carbides in solid solution.

The so-called weld decay zone in 18-8 steels is the result of carbide precipitation followed by intergranular corrosion.

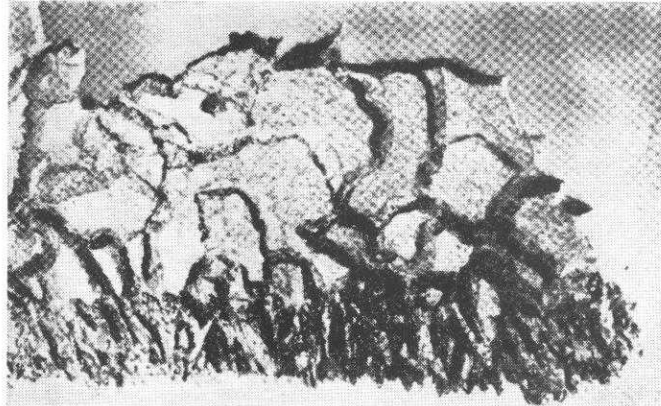


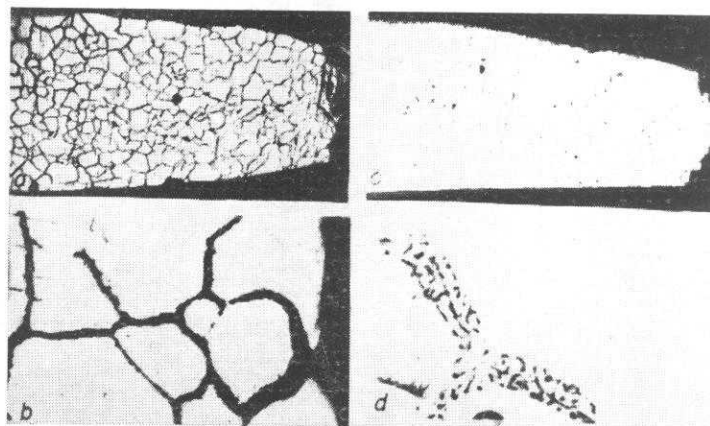
FIG. 1.—Coarse Grains in High-Alloy Stainless Casting Revealed After 9 Months in Pickling Acid. Smaller crystals at lower surface were due to more rapid solidification alongside mold sand

Figure 1 is an example of intergranular corrosion, which shows a high-alloy stainless casting at approximately actual size after nine months of service in a tank for pickling steel. This casting was not heat treated. High alloy castings contain very large grains when cast in thick sections, as Fig. 1 shows. The smaller grain size shown along the bottom of the photograph is due to chilling and rapid solidification because of contact with the sand mould.

Intergranular corrosion is by no means confined to stainless steels and alloys. Figure 2 shows nickel shrouding after several years of service in a high-temperature steam turbine in chemical plant.

(a)—As removed; 50 ×

(c)—After heating in hydrogen; 50 ×



(b) and (d)—Grain boundaries at 500 and 2000 ×

FIG. 2.—Nickel Shrouding Embrittled in High-Temperature Steam Service. All views unetched

Nickel is normally a ductile material, but this material becomes brittle as a result of intergranular attack. Figure 2a shows the complete cross section of the shrouding as removed from the turbine. The holes or pits on the surface and edges are due to the complete loss of actual grains of metal, either during service or during polishing in the preparation of the specimen for photographing. Figure 2b at 500 diameters indicates the complete envelopment of grains by the intergranular corrosion products. Figure 2c is similar to 2a, except that the material was heated in hydrogen at 1475°F. for 2 hr. The absence of the network indicates that the grain boundary material was nickel oxide which was reduced by the hydrogen treatment. Figure 2d shows grain boundaries at 2000 diameters after hydrogen treatment; the intergranular constituent was not completely reduced.

3. *Pitting* is perhaps the most destructive and insidious form of corrosion; containers fail because of perforation, yet only a small amount of metal is lost in the entire structure. In addition, pitting is difficult to evaluate on an experimental basis, and the service life of equipment is correspondingly uncertain. Pitting is probably responsible for more unexpected plant equipment failures than any one of the other seven forms of corrosion.

Pitting is readily recognized. Frequently, most of the surface of the metal shows practically no attack, but the corrosion is localized in more or less isolated areas. For these reasons pitting can be considered as an intermediate situation—something between general overall corrosion and immunity from attack. For example, a plate of 18 % chromium, 8% nickel stainless steel exposed to stagnant sea water may appear to be in perfect condition, but close examination will show the presence of tiny holes that look as though they had been drilled.

In general, chlorides and other halogens are the chief pitting agents, particularly for stainless steels and chromium-nickel alloys. Ferric chloride is particularly bad. In fact, few, if any, of the commercial alloys of any type available today are suitable for handling mixtures of appreciable concentrations of ferric chloride and hydrochloric acid. However, such active reagents are not always necessary for pitting. For example, Fig.3 shows pitting on a copper pipe which handled domestic fresh water.

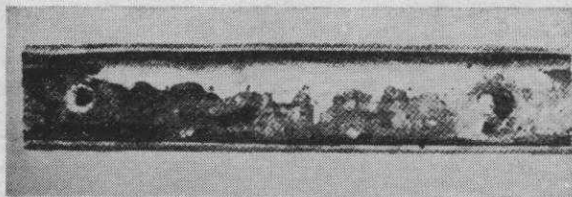


FIG. 3.—Example of Pitting in a Copper Pipe Handling Nothing More Corrosive Than Potable Water

The reasons why pitting occurs at a certain point and leaves adjacent areas relatively unattacked are somewhat obscure, but several factors may contribute towards it. Apparently, localized corrosion occurs because of a lack of complete homogeneity in the metal surface. The presence of impurities, such as inclusions, or rough spots, scratches, or nicks in the metal surface, could promote the formation of pits. Pits often form under deposits on the metal, foreign materials resulting from corrosion products or precipitation from the environment. If the "passive film" on corrosion resistant metals and alloys is broken, this crack would be a potential pit former. Unfortunately, after pitting is started, it tends to progress at an accelerated rate.

Determination of weight loss are of practically no value when studying pitting. Penetration should be determined by direct measurement with a focusing microscope, or by removing metal mechanically until the pit disappears. In general, vagaries of pitting make it almost imperative to avoid the use of materials in permanent construction, if that material will pit during corrosion tests.

4. *Galvanic Corrosion*—when two dissimilar metals are in contact with each other (or otherwise electrically connected) and exposed to a corrosive liquid or conductive solution, a potential is set up between these two metals and a current flows. Corrosion of one metal is often accelerated and of the other reduced, as compared to the behaviour of these metals when they are not in contact. The historic voltaic cell and the ordinary dry cell battery are examples of such action, planned to produce current. Because of the electric currents and dissimilar metals involved, this form of corrosion is called “galvanic” or “two-metal” corrosion.

So far as galvanic corrosion is concerned, E.M.F. series gives an indication of the potential that should exist when any two of the metals are connected. In addition, it tells us that the metal higher up in the series will suffer and the lower one will be protected. The further apart the metals in the series, the greater is the potential and the greater the likelihood of galvanic attack. For example, magnesium and copper represent a bad combination, with corrosion of magnesium greatly accelerated.

In general, the electromotive series also indicates the corrosion resistance of the elements. The metals high in the series are less resistant and more chemically active than one, lower down. The elements above hydrogen tend to oxidize readily as shown by the fact that these elements are found in nature as oxides, sulphides, or other compounds. Those below hydrogen, such as copper, silver, and gold, often exist as metals in the natural state.

The corrosion engineer only usually has academic interest in the E.M.F. series because it is the condition of the metal or alloy surface under actual exposure that determines whether or not material will corrode. For example chromium occupies an unfavorable position in the E.M.F. series, yet this element is a good metal for bright plating and is the major constituent of stainless steels. Aluminium is nearer the top, yet is widely used for exterior architectural trim and for the construction of domestic utensils and chemical process equipment. The phenomenon of “passivation” is one of the reasons why metals and alloys behave differently in relation to their position in the E.M.F. series. Passive surfaces on metals and alloys show more “noble” characteristics than the metals themselves—“noble” meaning superior corrosion resistance. The behaviour of a metal can be markedly changed because of numerous surface reactions, such as oxide formation, presence of physically or chemically adsorbed gases, or adherent corrosion products. To predict the performance of a combination of metals or alloys in contact, tests on the actual materials in the specific corrosion environment under consideration, have to be performed. Recognition of Galvanic Corrosion—Galvanic corrosion can often be recognized by visual observation. The accelerated corrosion of the less noble metal is usually localized near the points of contact and often appears as grooves or deep channels. A good example of premature failure of plant equipment because of galvanic corrosion was that of a shell and tube exchanger for heating process water (inside the tubes) by steam on the outside. The tubes and tube sheets were made of aluminium. Because of the length, a perforated support was placed in the centre of the shell. Unfortunately, this sheet was made of steel. Examination of failed tubes showed grooves approximately  $\frac{3}{8}$  in. wide in the aluminum at points of contact with the steel. The grooves eventually penetrated the walls and the attack was so localized that the tubes looked as if they had been machined. Condensing steam provided the electrolyte. In another instance involving air conditioning equipment, the aluminum tubes in the heater were equipped with brass fittings; the aluminum corroded rapidly in the areas adjacent to the brass.

These examples indicate that the design engineer should particularly take note of the possibilities of galvanic corrosion, since he often specifies the materials to be used in equipment. It is often economical to use dissimilar materials in contact—for example, water heaters with copper tubes and steel tube sheets. If galvanic corrosion occurs, it accelerates the attack on the heavy tube sheet (instead of the thin copper tubes) and long life is obtained because of the thickness of the tube sheets. Accordingly, expensive bronze tube sheets are not required. For more severe corrosion conditions, such as acidic solutions, the bronze tube sheets would be necessary.

When the use of dissimilar metals is unavoidable, it is possible to minimize the effects of galvanic corrosion by several methods, as follows: (a) Use combinations of materials as close

together as possible in the E.M.F. series ; (b) insulate the joints (if complete insulation is not feasible, the use of paints or other coatings is helpful) ; (c) avoid large areas of the more noble metal, since this combination further accelerates the galvanic attack—use the reverse ratio if possible ; (d) increase the thickness of the less noble material for example, in fittings and tube sheets ; (e) if paint is used for protection, paint all parts because if only the less noble material is painted, attack at pin-holes or scratches in the coatings would be further accelerated because of the area ratio effect (it may be desirable to paint only the noble metal—for example steel fasteners for aluminum roofing sheet) ; (f) avoid threaded joints because the thickness is reduced threading at points is close contact with the noble metal, and failure is likely to occur at the reduced section.

The principles of galvanic corrosion are put to practical use by methods generally designated as cathodic protection, which often prolong the life of equipment by reducing or almost completely eliminating the corrosion that would normally occur. Cathodic protection consists, briefly of applying an electric current, either external or by galvanic coupling, to the specific metal surface so that the usual electrochemical corrosion reactions are suppressed or counteracted.

### 5. Concentration Cell Corrosion

In the section of this article just finished on galvanic or two-metal corrosion were described the cell and current flow resulting from contact of dissimilar metals. A somewhat similar situation as galvanic corrosion obtains when only one metal is in contact with different concentrations in the environment. In other words, cells, current flow and potential different exist on different areas of the same metal as this metal is in contact with different concentrations of a solution or liquid. For example, current will flow between two copper electrodes if one is placed in a solution of 5% hydrochloric acid and the other in 10% acid, the solutions being separated by porous cups. Localized attack resulting from these effects is designated concentration cell or solution cell corrosion.

Concentration cell corrosion is often associated with crevices, scale, surface deposits and other conditions where the solution in contact with the metal is stagnant. Therefore it is sometimes called service corrosion.

Figure 4 shows two of the most common types of concentration cells :

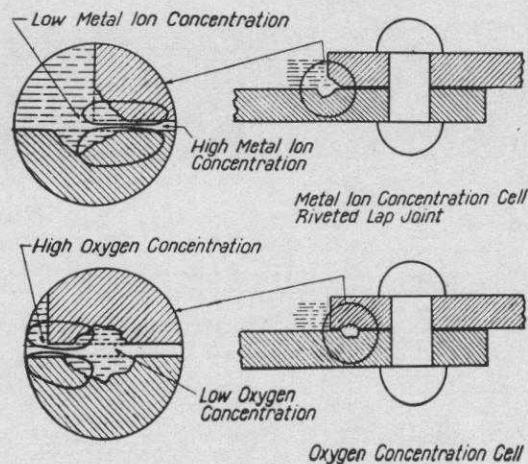


Fig. 4—Diagrams Showing Typical Conditions for Concentration Cells (International Nickel Co.)

The top portion illustrates a metal ion concentration cell and the lower an oxygen cell. In the first, iron ions build up in the stagnant area in the crevice and corner so their concentration is greater than in the liquid somewhat from this area. A similar condition exists in the situation

indicated by the lower sketch, in that oxygen in the crevice is consumed by corrosion so that its concentration is lower here than in the body of the solution.

These cells cause current flow or potential differences in adjacent portions of the steel plate and destructive action occurs. The area undergoing corrosion is anodic and the surrounding area cathodic. Since the attack is localized, the corrosion is further accelerated by the large ratio of cathode to anode areas. Metal ion and oxygen cells often exist simultaneously.

The stainless steels are perhaps particularly susceptible to this form of corrosion. This is shown by failures in static solutions, often at threaded or gasketed joints. Loose gaskets often cause trouble. Incidentally, it is obvious from Fig. 4 that a butt welded joint is more desirable than a riveted lap joint, from the standpoint of concentration cell corrosion.

One reason why the rate of pitting tends to accelerate, once it is started, is the formation of concentration cells between the pit and the adjacent areas of the metal. The bottom of a pit is an almost ideal site for the formation of a concentration cell. The design engineer and the maintenance engineer familiar with concentration cell corrosion could exercise precautions, as follows to minimize failures and excessive corrosion of this form; (a) Use butt welded joints with complete well penetration. (b) If lap joints cannot be avoided, seal the joints by welding or caulking. (c) Clean and seal existing joints. (d) Avoid sharp corners and stagnant areas that would favour accumulation of deposits. (e) Clean equipment periodically.

6. *Dezincification*; as the term implies, was first observed in brasses. The zinc is selectively leached out of the brass to leave a weak porous mass of copper. Dezincification can be readily observed since the attacked areas show the red color of copper as compared to the distinct yellow of brass.

The mechanism of dezincification is still somewhat controversial, but one commonly accepted, envisages the complete solution of the alloy, the zinc stays in solution, but the copper plates back into the metal. There are two general types of dezincification, and both are readily recognizable. The more common type is uniform; dezincification proceeds at substantially the same rate over the entire exposed area. The second is the so-called plug-type dezincification which occurs in localized areas.

Fig 5 shows a section of brass pipe after service in handling water. The dark inner portion of the pipe is dezincified alloy.

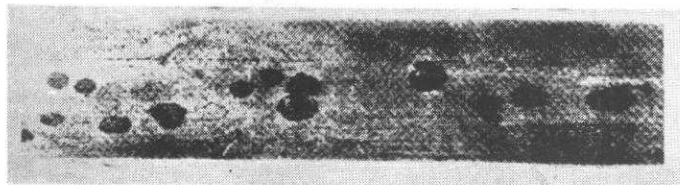


FIG. 5.—Plug-Type Dezincification of Muntz Metal Pipe in an Aftercooler (Boiler Water Inside, Hot Flue Gas Outside)

The outer portion is the unaffected yellow brass. Dezincification has progressed uniformly through half the wall thickness.

The dark areas are the dezincified metal with the remaining portions of the pipe unaffected. Attack was from the inside surface of the tubing in an aftercooler in a plant powerhouse. This heat exchanger carried water inside the tubes, with flue gases at 350°F. outside the tubes. These tubes were made from muntz metal, which is a high-zinc brass, so susceptible to this type of attack that it has been largely supplanted by other copper-zinc alloys.

In general, the dimensions of the brass parts do not change appreciably during dezincification; this may account for the unexpected failures. In one instance a perforated brass plate in a tower handling a warm mixture of water and acetone appeared unattacked after several years of service, except for the coppery colour on the surface. Examination showed that the plate was almost completely dezincified, and it cracked completely after slight bending. Brass is a very ductile material. In another heat exchanger, handling boiler feed water, many tubes failed because of plug-type dezincification in only a few areas on each of them.

The uniform or layer type of dezincification occurs most frequently in the high brasses (high zinc content), and the plug-type seems to favour the low brasses (lower zinc content). More aggressive corrosion conditions—for example higher temperatures—also favour the plug type of attack, which is related to pitting in that localised attack is involved. Dezincification sometimes occurs under supposedly mild conditions of corrosion, but favourable conditions for this type of attack involve a good electrolyte such as sea water, slightly acid conditions, or the presence of appreciable amounts of oxygen in the liquid handled.

The addition of tin, antimony, arsenic and phosphorus to brass aids in resistance to dezincification. Admiralty brass, for example, contains approximately 1% tin, 29% zinc, and 70% copper. Such alloys, plus definite inhibitors, are often used to replace straight brass where service is accompanied by mild dezincification. For more severe conditions, red brass (15% zinc) is often used because this alloy is practically immune. For very severe conditions it is often economical to use the binary copper-nickel alloys.

The phenomenon of selective leaching of one of the elements of an alloy is by no means confined to the brasses. For example, a hard facing alloy of cobalt, chromium and tungsten known as Stellite No. 1 became soft after several weeks of handling a waste sulphuric acid slurry containing solid ferrous sulphate. Chemical analysis of the soft material and the hard, unaffected alloy showed that cobalt had been selectively removed, leaving a weak porous structure.

7. *Erosion-Corrosion* often causes unexpected and rapid deterioration of plant process equipment. The rate of corrosion can be greatly accelerated when mechanical or abrasive conditions are present, such as liquids moving at substantial velocities, presence of solids in suspension (that is, slurries), marked turbulence, and impingement of fluid streams. Examples of equipment that may be subject to erosion-corrosion are pumps, valves, centrifugals, measuring devices (such as an orifice), agitators, pipe lines, particularly at elbows and tees, and heat exchanger tubes. The corrosion effect known as "cavitation" is one type of erosion-corrosion.

Most metals and alloys depend upon the automatic development of a thin protective surface for their resistance to corrosion. This may consist of an oxide film, a corrosion product (such as lead sulphate which forms on lead in sulphuric acid), or an adsorbed film of gas. If protective surfaces are removed locally by abrasion and fresh metal exposed the material deteriorates more rapidly than under the sole effects of corrosion.

An excellent example of erosion-corrosion involves hard lead valves in hot, dilute sulphuric acid. Coupon tests made of hard lead immersed in this acid showed practically no corrosion, but throttled valves failed in less than one week! In this same service, lead lines with slight bends in them were cut through in a few months.

There is a large difference between the erosion-corrosion data and the data obtained on specimens (solution tests) hung in the glass-lined tank, subject only to a mild swirling motion. Figure 6 shows what is left of an elbow removed from a steam condensate return line.



FIG. 6 Impingement Attack on Elbow in Steam Condensate Return Line

The vertical straight run of pipe just ahead of this elbow showed very little attack, but the elbow failed where the liquid was forced to change direction and impingement effects were present.

Finally, Figure 7 graphically shows the destructive effect of erosion-corrosion on a high-alloy stainless pump impeller after a relatively few weeks in service.

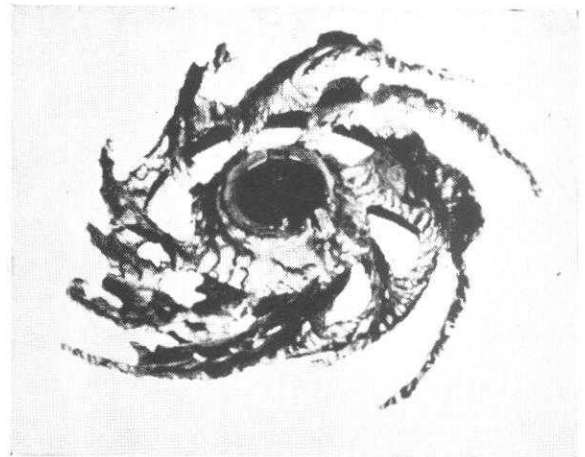


FIG. 7 Remains of Stainless Steel Pump Impeller, Ruined by Erosion-Corrosion

It is obvious that sound engineering must pay attention to velocity of corroding medium as well as its nature.

8. *Stress-Corrosion* is the general term describing corrosion accelerated by internal stresses or externally applied stresses. The stresses are sometimes complex, but tension stresses are generally if not always required. High internal or residual stresses are often produced during the forming of the part, by heat treatment, or other means such as locked, in stresses resulting from welding.

In practically all instances, stress-corrosion manifests itself in the form of cracks without appearance of ductility. Accordingly, this phenomenon is also designated "stress-corrosion



cracking", although the word cracking is superfluous. If the stresses are fluctuating or cyclic in nature, the failure is often described as corrosion-fatigue—it being well known that the endurance of a metal part is reduced by corrosive surroundings.

Two of the earliest recognized instances of stress-corrosion, and perhaps the most widely known, are the season cracking of brass cartridge cases, and caustic embrittlement of steam boilers. When brass cartridges were first made, great numbers failed during storage in arsenals. Stationary and locomotive boilers have failed or have required extensive repairs because of stress-corrosion. The cause has been the subject of many investigations but no fully acceptable mechanism for this form of corrosion has been propounded so far.

In general, stress-corrosion for a given material depends upon three factors, namely, the stress, the concentration and nature of the corrosive environment, and the temperature. If one of these factors is present to a high degree, such as high stress or high temperature, the other two factors could be very mild in nature for damage to result. For example, cold drawn or spun brass parts or dishes, containing high residual stresses, sometimes crack when exposed to ordinary atmospheric conditions, especially in the presence of a slight amount of ammonia or amines. (In fact, ammonia and amine-containing atmospheres are used as tests for susceptibility of brasses to stress-corrosion). As another example, the tendency for steel to crack in caustic solutions increases with temperature or concentration of the caustic.

In many stress-corrosion failures, the attack occurs along localized paths. For example, the metal may show no visible corrosion adjacent to the crack. These paths of localized attack may be areas of lower corrosion resistance than the surrounding portions of the metal; in these instances, the corrosion is electrochemical in nature with the attacked area anodic and the surrounding metal cathodic, thus setting up a corrosion cell similar to the cells described in galvanic or two-metal, corrosion. Once localized attack begins—the form of a pit, crack or crevice—the effect is accelerated because these areas serve as stress raisers.

One interesting case of stress-corrosion of steel, involved stresses induced in the metal because of severe thermal gradients across the 2-in. wall of a large autoclave. These vessels contain molten sodium-lead alloy, and they were heated or cooled by a fluid of large heat capacity known as "Dowtherm" circulating in the outer jacket. Decreasing the temperature of the Dowtherm during the cooling cycle from 200 to 100°C., in order to decrease the total time per batch and thus increasing production resulted in rapid failure of the autoclaves, and shut down the plant. This change in the coolant temperature increased the temperature drop across the wall from 110 to 154°C. Calculations showed that a temperature differential of the latter size induced a stress of 39,000 psi, in the metal. This high stress at the temperature of the operation readily accounted for the rapid cracking of the autoclave. The deepest cracks occurred adjacent to the welds, but deep cracks were also observed in the parent far removed from joints.

It is well known that the so-called aging steels are somewhat susceptible to stress corrosion. Gradual precipitation of secondary phases within solid steel and other alloys often contributes to stress-corrosion failures. Mixed acids (sulphuric and nitric), nitrates and caustics are often times the chief offenders as far as corrosive environments to steel are concerned. For example, large steel tanks erected in the field by welding developed very bad leaks and large cracks only a few months of service when storing mixed acid.

A refrigeration condenser cooled by good quality inland river water failed by cracking, with the cracks inside the admiralty brass tubes. The cause of this failure was difficult to find, but it was finally attributed to a small amount of organic matter which deposited on the surface of the tubes. Since this condenser only operated during warm months, it was idle several months each year. Apparently the organic matter decomposed during shutdown, with a resultant formation of ammonia or amines which was destructive to the alloy from the stress-corrosion standpoint.

Perhaps the most common method used for combating stress corrosion consists of prior stress-relieving heat treatments. Internal or residual stresses in the metal or equipment can be greatly

minimized by heating at a moderate temperature. For example, it is common practice to stress-relieve welded steel equipments by annealing in the range of 1100 to 1200°F.

Of course, another effective preventive involves the proper selection of alloys, 18-8 S Mo, for example, is superior to 18-8S for resistance to stress-corrosion. A red brass (15% Zn or less) should be more resistant than a cartridge brass (30% Zn). The selection of materials should balance the probability of stress-corrosion failure and cost of the material. In other words, the economics of the installation must be considered.

A protective metallic or non-metallic coating is often beneficial. For example, the high aluminium alloys are often clad with relatively pure aluminium for better resistance to stress-corrosion. Organic paints, separating corrosion medium from metal or alloy, are often used.

Design of the equipment is also important. Sharp corners or fillets, which would act as stress-raisers, and high applied stresses should be avoided. Corrosion inhibitors are sometimes beneficial. In general, the use of more corrosion resistant materials, and changes which decrease corrosiveness of the environment are helpful.

Combating Corrosion: It may be desirable to list briefly here the eight general methods used for combating corrosion. The following remedial measures should be considered in the solution of any corrosion problem:

1. Alloying or selection of a more corrosion resistant material.
2. Metallic, inorganic or organic coatings.
3. Removal of the corrosive agent (such as deaeration of water).
4. Inhibitors.
5. Cathodic protection.
6. Use of non-metallics (e.g., glass or rubber).
7. Purification of the metal.
8. Improvement of equipment's design.

Methods 1 to 6 are used in many applications, and they are all commercially feasible. Method 7 is the least frequently used, and only in special cases. The method used depends on the nature of the problem involved. Cost is, of course, very important, and in practically all cases the economics of the problem more or less dictates the method used when two or more alternatives are applicable. Sometimes the mechanical properties of the metal of construction are an important factor. Method 8 is usually possible.

Improving the Design: It is generally well known that mechanical failures are primarily due to improper design, and seldom to defective material. However, a failure from corrosion (in a chemical plant, for example) is almost universally ascribed, by the plant man, to "defective material improperly heat treated". In most instances this is not the correct answer.

Variations in corrosion rates are usually allowed for by providing metal thickness twice that which theoretically would give the desired life. Often an increase in thickness, without changing the material, will save a lot of money in the long run. (Automobile drivers in northern latitudes where salt is used on icy streets know that this would be true offenders!) For example, when the tubes in heat exchanges in a contact sulphuric acid plant were changed from 13-gage to 10-gage walls, it saved several thousand dollars annually. Often it is cheaper to provide plenty of cast iron than theoretical amounts of a more noble alloy.

Design of tanks and pressure vessels should avoid chance of stagnant areas. Welded joints with generous radii and smooth surfaces are preferred over riveted construction, to avoid crevices and concentration cells. The lining should be carried out over the rounded top rim and form a gutter leading overflow and splash to a down spout. Bottom outlets should provide for complete

drainage. Heating coils should not touch bottom or sides, else hot spots will speed-up the corrosion. Foundations and supports prevent accumulation of moisture and spills.

Turbulence is often the cause of excessive corrosion at inlets or at changes in cross section-life of the metal at such places can easily be doubled by "stream lining" the passages.

Standardization of design, to permit interchange of equipment or facilitate repair from stock parts, is quite desirable. One extreme instance is where pump casings and impellers are standardized in shape but made and carried in stock of various corrosion resistant alloys. If one combination fails in a certain location, another combination can replace it in a very short time.

### Discussion :

Dr. B.S. Nagraj :

In case of difference in concentration in the top and bottom of a scrubber, would there be any effect on the corrosion of scrubber material ? If so to what extent ?

Dr. M.S. Mitra :

Corrosion due to different concentrations, is significant in cases where there is a sharp difference in concentration. It is very effective when solution in a part of the container is stagnant, thereby accelerating the differences in concentration. It has been explained how this can be avoided by incorporating proper design of the container. In the scrubber there is a very gradual change in concentration which should not have any effect as regards concentration corrosion.

Mr. S. Ramanujam :

Dr. Mitra has referred to the effect of inclusion on corrosion. Could this be considered serious enough to account for some of the heavy corrosion troubles at present experienced by steel boilers recently built in India ? These boilers are said to have been built from imported high quality boiler steel. It has been stated that these suffer from much heavier corrosion troubles, than those built earlier. Though corrosion is a result of so many factors including design, internal stresses, quality of steel, deposits and sludge, etc. ; has anything been conclusively proved as regards the corrosive influence of inclusions incidental to short cuts in the methods of manufacture or any variations in them ? Available information seems to suggest that its influence is not really pronounced so far as corrosion is concerned. The findings of the British Corrosion Committee are not conclusive in this matter. A specification clause regarding 'inclusion count' for steel to prevent corrosion troubles, may have to be introduced in case it is proved that pitting and heavy corrosion can be traced to inclusions above a certain permissible extent.

Dr. M.S. Mitra :

Corrosion by pitting is a result of localised corrosion. Contributory factors are presence of impurities such as inclusion, rough spots, deposits of foreign materials etc., on the metal. It is difficult to give any opinion on the case cited by Mr. Ramanujam without knowing the full back-ground of the case. It is necessary to investigate the material, the type of corrosion etc., before any useful suggestion can be made. As regards the 'inclusion count, for specification of boilers steel the author feels strongly in favour of this. However, before this is done, it is important that a proper study of effects of dispersion of inclusion on the metal surface in relation to corrosion, be made.

Mr. D.V. Reddi :

In case of a cold worked component with certain parts still more severely cold worked, will dezincification be selective ?

While heating a chromium-molybdenum steel (.7% C, 1.8% Cr, 4% Mo) in a lead bath at 840 deg. C. a strong corrosion mark left at a position corresponding to the level about 0.1" below the lead level while the steel piece was immersed. With all precautionary measures taken it was

been possible to get rid of this trouble. Can the authors explain this attack and suggest a possible remedy?

Dr. M.S. Mitra :

Slow dezincification of brass in sodium chloride solution takes place especially in the  $\beta$  phases of an  $\alpha\beta$  brass or, at the grain boundaries of cold worked  $\alpha$  brass, where relatively zinc rich areas exist; at such places zinc passes into solution leaving residual copper. When once a small amount of residual copper has been formed, dezincification can proceed at a serious pace. Accordingly, although it is not expected to have selective dezincification due to difference in cold work, the effect of heavier cold-work would be the easier starting of the process of dezincification.

Regarding the other case, it seems very similar to the water line corrosion. The corrosion is due to a separation line of cathodic and anodic zones. As far as the remedy is concerned the simplest way be to keep the piece fully immersed, if possible.

Mr. D.S. Murty :

Mr. Murty wished to get the following points clarified from the authors. He referred to the stress-corrosion cracking in  $\alpha$ -brasses. It is more the uneven distributed stresses than a uniform residual stress that causes failures of this type, e.g., an indentation in an annealed strip of 70/30 brass is more dangerous than a uniform application of cold work to it. He pointed out that the mercurous nitrate test has proved to be less discriminative than was originally supposed. He wanted to know if there was any other way of finding out the susceptibility of brasses to this type of failure and if there was any known case wherein the outside atmosphere free of ammonia, had caused this type of failure. He pointed out that silicon and other types of varnishes have conferred complete immunity from such embrittlement.

Dr. M.S. Mitra :

He agreed that uneven distribution of residual stress was more harmful than uniformly distributed residual stress. But in general, the residual stresses resulting from cold plastic deformation could not be uniform. The author was not aware of any confirmation of some failures claimed in atmospheres other than ammonia and amines.

Dr. A.K. Chatterjee :

It was an accepted theory that most cases of corrosion are due to electro-chemical actions. It was also an established fact than an eutectic-like structure is basically a mechanical mixture of two phases as alternate laminae. Obviously, if an eutectic like structure was immersed in a corrosive atmospheres one expected the formation of electrolytic cells, as a result of which the corrosion should be accelerated. He wanted to know if the authors, therefore, discouraged the use of eutectic-like materials in corrosive fluid media?

Dr. M.S. Mitra :

Selective corrosion of two constituents in an eutectic mixture was used in etching of metallographic specimens. Even at the boundaries of two differently oriented grains the corrosion was selective. It was not practical to avoid eutectic structures in alloys used in material engineering. The corrosion resistance of the alloy as a whole should be determined before selecting the material, for any particular set of service requirements.