

DEPARTMENT OF DESIGN

Corrosion Fundamentals and Materials Properties

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The theory of corrosion and a number of the more important forms of corrosion, particularly those most likely to be found associated with highway structures and equipment, are discussed. Also, information on the properties of various ferrous and non-ferrous alloys and their behavior under different environments is presented.

Corrosion data for industrial and marine atmosphere exposures are presented to show the effect on corrosion resistance of minor alloy additions in steel. Information also is presented to show the degree to which this better resistance of low alloy steel will improve the performance of protective coatings.

• ACCORDING to a study (1) made by H. H. Uhlig, the corrosion bill for 1957 was estimated at 6 billion dollars. The percentage of this amount borne by the highways of the nation was not given in the estimate; however, highways did not escape the ravages of this deterioration. Although it may not be necessary to replace highway structures at frequent intervals, constant vigilance is necessary to assure proper protective measures before serious damage occurs.

When design engineers have some knowledge of (a) corrosion processes, (b) the resistance of alloys when exposed to various environments, and (c) the effects of design on promoting various forms of corrosion, they can incorporate in new structures materials and features which will reduce future maintenance.

The principal forms of corrosion (2) are uniform attack, oxygen concentration cell, metal-ion concentration cell and galvanic (two-metal) corrosion. Erosion and dezincification may also be experienced in equipment such as pumps and valves.

Corrosion is a complex phenomenon — the fundamental reaction involves a

transfer of electrons in which some positively charged ions in the corroding solution (usually hydrogen ions) lose electrical charges which are acquired by the metal or alloy going into solution or being corroded. The complete corrosion reaction is divided into an anodic portion and a cathodic portion occurring simultaneously at discrete points on the metal surfaces. The anodic reaction (oxidation) represents the acquisition of charges by the corroding metal, while the cathodic reaction (reduction) represents the loss of charges by the hydrogen ions which are discharged. The flow of electricity between the anodic and cathodic areas may be generated by local cells set up either on a single metallic surface, or between dissimilar metals. Sometimes an electric current may be applied from some external source either accidentally or deliberately.

This is the essence of the generally accepted electrochemical theory of corrosion which provides the basis for modern methods of corrosion control. The basic cause of corrosion is the instability of metals in their refined forms. Because of this free energy relationship, the metals

tend to revert to their natural states through the process of corrosion. In the case of iron, the action of rain forms rust. Analysis of rust shows that it is iron oxide; analysis of iron ore shows it is also iron oxide. In rusting, iron has reverted to its original state.

The uniform appearance of a corroded metal surface may erroneously lead to the conclusion that all areas were corroded simultaneously when, actually, attack probably occurred only at anodes. During the time a surface is corroding, the anode and cathode areas may shift from time to time. This permits substantially uniform corrosion to occur.

Oxygen concentration cells (3) may be developed when a metal or alloy is in contact with a solution in which the concentration of dissolved oxygen at one point is considerably greater than at another point on the same metallic surface. The flow of current is from the metal to the solution at the point of low oxygen concentration, and from the solution to the metal at the point of high oxygen concentration. This flow of current will cause corrosion of the metal where the current enters the solution at areas having the least oxygen concentration.

Oxygen concentration cells may initiate pitting in almost any metal or alloy under loosely attached, porous materials which shield the underlying metal from free contact with a solution, especially if the main body of the solution is in motion. Similarly, crevices between overlapping metallic surfaces may become the sites of anodic areas with resulting severe corrosion. For this reason, whenever it is practical, crevices should be avoided in the fabrication of equipment required to resist corrosion.

Figure 1 shows the manner in which

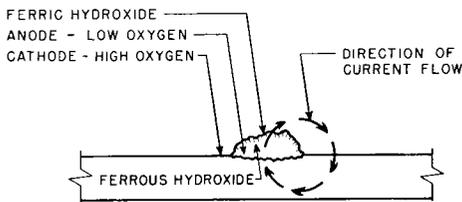


Figure 1. Pitting corrosion.

corrosion will progress when a pit is initiated on a steel surface. When steel corrodes in the presence of an oxygen-bearing solution, it reacts with the oxygen and water to form ferric hydroxide. As the corrosion product accumulates on the surface, the oxygen in the pores of the mass near the iron immediately disappears in reacting with the iron. The oxygen in the solution around the mass is renewed by convection and diffusion; a cell is set up with a low concentration of oxygen in the mass of precipitate and a higher concentration in its neighborhood. The metal in contact with the higher concentration becomes the cathode; that in contact with the low concentration in the precipitate, the anode. The longer this action goes on, the thicker the precipitated mass becomes. A barnacle will eventually result that is relatively adherent to the steel. In addition to forming on steel surfaces that are unprotected, barnacles of this type can also form beneath ruptures in painted coatings. Before they can be completely removed, it is frequently necessary to resort to the action of a scraper or wire brush.

Figure 2 shows a riveted joint and the location of the anodic area in the crevice where corrosion occurs. The mechanism of attack is identical to that which takes place in pitting corrosion. The oxygen in the crevice is consumed by corrosion of the metal, and it thus becomes lower at this location than in the body of the solution.

Figure 3 is another view of a riveted joint and shows the manner in which corrosion will progress when a metal-ion

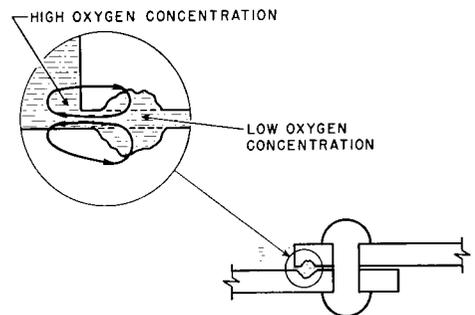


Figure 2. Oxygen concentration cell riveted lap joint.

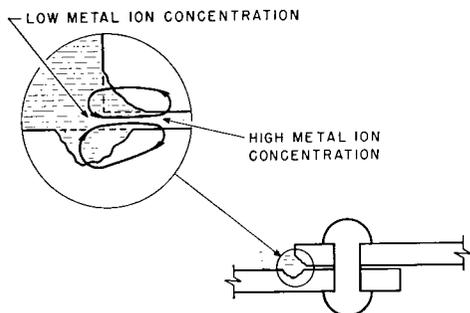


Figure 3. Metal ion concentration cell riveted lap joint.

concentration cell is established. When the concentration of metal ions within the joint becomes greater than the concentration of metal ions in the solution circulating about the outer edge of the joint, a difference in potential will result and cause an electric current to flow between the two areas. The direction of current flow will be from the metal (anode) to the solution at the point where the metal-ion concentration is low, and from the solution to the metal (cathode) at the point where the metal-ion concentration is high.

After considering the foregoing information, it becomes obvious, from the standpoint of concentration cell corrosion, that a butt-welded joint is more desirable than a riveted joint, when welding will meet the mechanical strength requirements.

Galvanic (two-metal) corrosion, the fourth principal form, occurs when two dissimilar metals are electrically connected in a corrosive liquid which serves as an electrolyte. Table 1 shows a galvanic series for a number of metals and alloys when exposed to sea water moving at high velocity.

In any couple, the metal near the top of this series will be the anode and suffer accelerated corrosion in a galvanic couple, while the one nearer the bottom will be the cathode and receive some galvanic protection. Magnesium, for example, at the top of the scale, will suffer galvanic corrosion when in contact with carbon steel. Except for the extremes, any given metal may be an anode or a

TABLE 1
GALVANIC SERIES OF METALS AND ALLOYS
IN SEA WATER

Magnesium
Zinc
Aluminum
Carbon steel
Alloy steel
Cast iron
Stainless type 400 (active)
Stainless type 300 (active)
Ni-resist
Yellow brass
Red brass
Copper
Aluminum bronze
90-10 Copper-nickel
70-30 Copper-nickel
Nickel
Inconel
Silver
Stainless 400 (passive)
Stainless 300 (passive)
Monel

cathode depending on the other metal with which it is coupled and their galvanic relationship in the environment encountered.

One factor which determines the speed at which galvanic corrosion will proceed is the degree of difference in electric potential between the two metals. A metal coupled with another close to it in this list will usually corrode more slowly than when coupled with one which is further below. For example, zinc coupled with aluminum in sodium chloride solution will generate a potential of about 300 millivolts, whereas with zinc coupled to copper in the same solution, the potential is over 700 millivolts. The greater the potential, the greater will be the driving force behind the galvanic corrosion.

Another important effect of galvanic corrosion involves the ratio of the anode area to that of the cathode. The smaller the anode area, the greater will be the current density and thus the galvanic effect. The reverse will be true when the cathode area is smaller than that of the anode. This effect is demonstrated by the riveted plates shown in Figure 4. One specimen consists of two copper plates joined with steel rivets. After immersion in sea water, the steel rivets have been attacked quite severely. The second specimen, consisting of two pieces of steel joined by copper rivets, presents a sharp contrast to the first plate. The copper rivets are still in good condition and

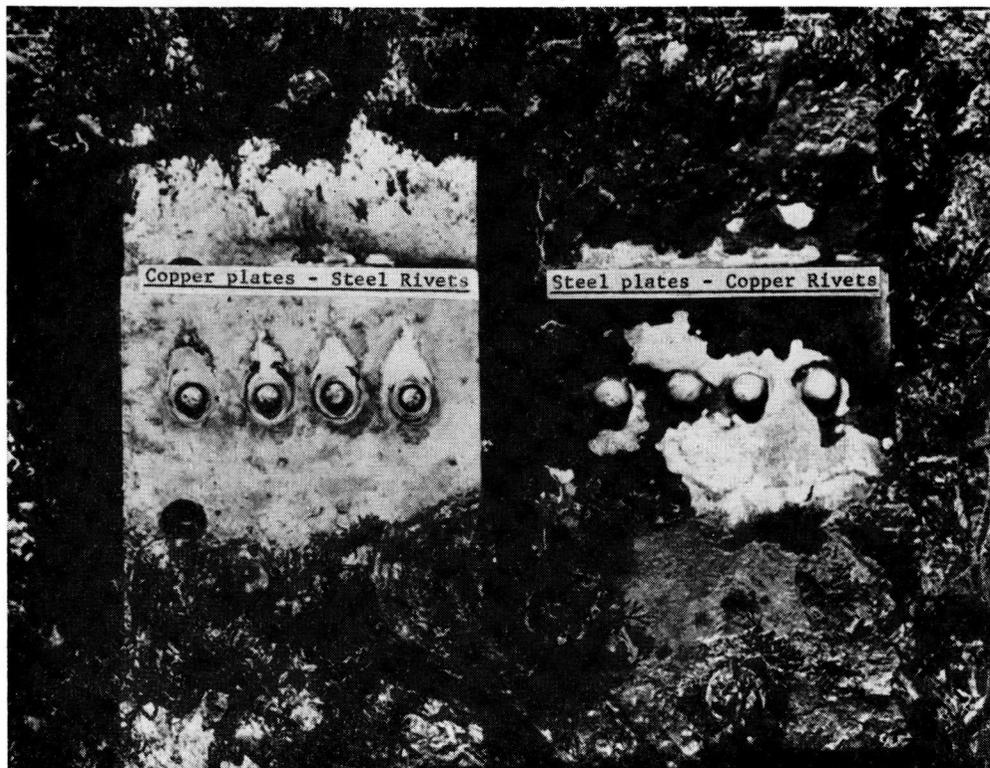


Figure 4. Galvanic corrosion — area effects.

there is no significant acceleration of the corrosion of the steel in their immediate vicinity. The metals are the same in each case, but the unfavorable area relationship of the large copper cathode and small steel anode was responsible for the severe galvanic corrosion of the steel rivets.

Erosion and cavitation-erosion are two forms of deterioration which occur to metals when exposed to liquid streams moving at relatively high velocities. Metal loss resulting from these forms will be found on the surfaces within such equipment as piping, valves and pumps.

Erosion can be defined as "the destruction of a metal by the combined action of corrosion and abrasion or attrition by a liquid with or without suspended matter." When the liquid contains particles which are harder than the metal surface affected, erosion will be by the combined action of corrosion and abrasion. When

the liquid does not contain suspended matter, or contains matter which is softer than the metal, then erosion will be by corrosion and attrition. Many metals rely upon the formation of a protective film for their good resistance to a particular environment. When, because of erosion, this film is continually removed, corrosion of the metal can proceed without inhibition.

When, because of flow irregularities, low pressure areas are produced and vapor pockets are formed which later collapse with a shock pressure upon the metal surface because of an abrupt change in pressure or flow conditions, the resultant effect is referred to as cavitation erosion. When this collapse occurs, there is a severe impact or explosive effect which can cause considerable mechanical damage and greatly accelerated corrosion due to the destruction of protective films. This effect is characterized

by pitting on the surface of metals which are of relatively low strength, such as cast iron. When a material has a dense structure and high fiber strength, the surface will show a roughened appearance.

Dezincification is corrosion of an alloy containing zinc, in which the principal product of corrosion is metallic copper which may occur as plugs filling pits (plug type) or as continuous layers surrounding an unattacked core (general type). The mechanism may involve overall corrosion of the alloy followed by redeposition of the copper from the corrosion products or selective corrosion of zinc, or a high zinc phase, to leave a copper residue. This form of corrosion is commonly encountered in brasses that contain more than 15 percent zinc and can be either eliminated or reduced by the addition of small amounts of arsenic, antimony, or phosphorus to the alloy. In a paper by Tabor (4), the conclusion was drawn that a copper-base alloy containing approximately 5 percent nickel, 5 percent tin, and 2 percent zinc was the logical choice to resist this form of corrosion. Brass alloys are frequently used in valves and pumps for trim, such as stems, shafts, seats, and packing sleeves; and it is these parts that have been found to fail by dezincification when exposed to the action of some purified and contaminated waters.

There are other forms of corrosion which may be found to cause deterioration of equipment employed by highway departments; however, it is thought that the foregoing will be found the most prominent types.

Most metal oxides are sparingly soluble and they are usually poor electrical conductors. Addition of small amounts of

certain alloying elements has been found to appreciably improve the resistance of iron or steel to the ravages of atmospheric corrosion. However, under submerged exposure in various waters, these additions have been found ineffective over a long period. When it is not practical or economical to provide protective measures for steel or iron surfaces under these latter conditions, the selection of a more highly resistant alloy is required.

When called upon to select materials that will be resistant to a particular environment, it is important to take first into consideration the characteristics of the environment, giving special consideration to extraneous factors that may influence corrosion. Next, a knowledge concerning the characteristics and also general behavior of materials when exposed to certain environments is essential.

In the absence of actual corrosion information for a particular environment, a reasonably good selection is possible from data for the resistance of materials to a nearly identical environment. A good practice would be to use these data for the selection of materials that would be worthy of further study in the environment under consideration.

One of the most corrosive solutions with which highway engineers must contend is road moisture. During rainy periods, the corrosivity of this solution will vary depending upon the amount of sulfur, chlorine and nitrogen absorbed from automobile exhaust gases. During winter months, in areas where salt is used for de-icing, further contamination with chloride compounds will result. Table 2 shows the compositions for samplings of road slush accumulated from two different highways in Detroit, Michigan, at 14-day intervals. This information was

TABLE 2
ANALYSIS OF ROAD SLUSH

Sample	Date Sampled	pH	Concentration, g/l		
			NaCl	Sulfur	Nitrate Nitrogen
West Chicago	1/14/54	7.80	39.714	0.272	0.0105
Joy Road	1/14/54	7.55	22.050	0.268	0.0011
Joy Road	1/28/54	7.90	3.409	0.043	0.0010
West Chicago	1/28/54	7.70	10.458	0.098	0.0009

obtained by the American Electroplaters Society when they conducted a study to determine the corrosion resistant qualities of various electroplated surfaces to road moisture.

This information should be of interest to highway engineers concerned with the problem of dowel corrosion in concrete highway load-transfer devices. Because of slab movement resulting from volume change and loading, the corrosive compounds in road moisture will work their way into the joint by either saturation of the subsoil or through breaks which occur in the joint sealing compound.

With the exception of one or two states that are now specifying steel dowels clad with a corrosion resistant alloy, steel dowels without a protective coating are still the standard installation in most concrete highway load-transfer devices. These dowels, when wetted with moisture having compositions similar to those in Table 2, will be susceptible to attack by one or more of the forms of corrosion previously described. Some states permit the use of a graphite-containing grease as a bond breaker on the dowel end which they wish to have move freely

after the concrete sets. Graphite being considerably more noble than steel, in fact than most alloys that would be practical for this use, will galvanically accelerate corrosion of the dowels when immersed in a solution that will serve as an electrolyte. Bond breaker lubricants should be used that do not contain compounds that will be cathodic to the dowel material.

Van Breemen (5) reported the results of a complete study, conducted in New Jersey, of various forms of dowel protection. This study revealed that, of the protective measures tested, steel dowels clad with either Monel or stainless 18-8 provided the best performance.

Van Breemen also demonstrated that restraint to movement of steel dowels was caused by the pressure created between the dowel and concrete when corrosion products formed. Moreover, studies conducted in his laboratory revealed that this pressure could be of such magnitude as to cause cracking of a mortar block. Specimen 12 in Figure 5 shows this condition.

Specimen 13 (Fig. 5) consists of two pieces of 4-6 chromium steel in a mortar

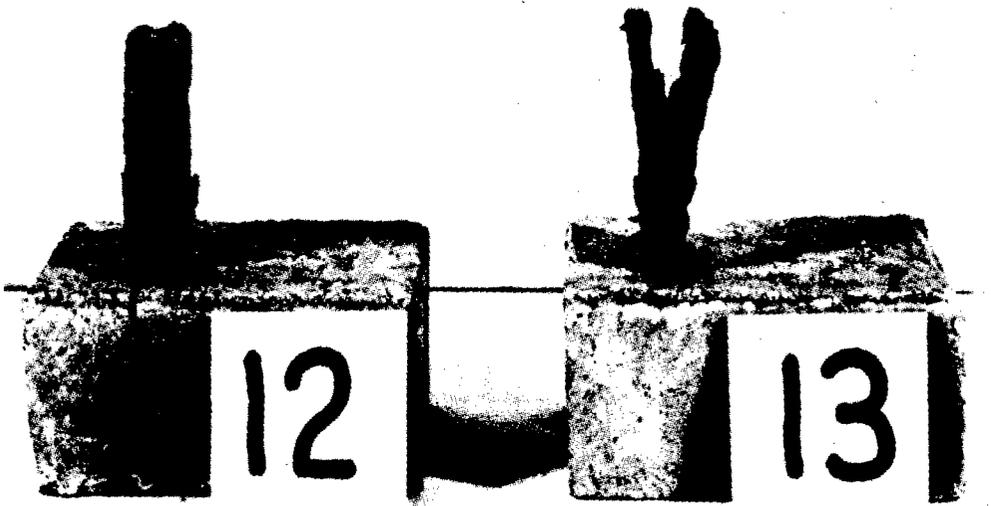


Figure 5. Effect of rust expansion.

block. Owing to the expansion caused by rust formation, there is a pronounced spreading apart of these two specimens.

Restraint to movement and also a relatively high rate of metal loss at the joint, as well as for several inches in from the joint on the free end, are the two principal causes for improper performance of steel dowels. Directly at the joint, corrosion products formed on a steel dowel are broken loose by joint movement and are finally washed away by road moisture. This action results in a relatively high rate of attack by continually exposing fresh metal. In some instances, it was found to reduce the diameter to a point where the dowel no longer had sufficient strength to withstand the stresses imposed, and failure resulted by cracking.

When corrosion products formed on the surface of a steel dowel, some two or three inches in from the joint on the free end, are removed by cyclic loading, the clearance between the dowel and concrete is gradually increased. This can eventually cause bending of the dowels, misalignment of slab faces, and excessive joint movement.

It is thought that salt is used more extensively for de-icing in Michigan than in New Jersey. Assuming this to be true, then the analyses shown in Table 2 would not be typical for slush accumulated on New Jersey highways.

In the absence of specific corrosion data for various alloys exposed to the Michigan conditions, a review of data for exposure to a solution containing sodium chloride in approximately the same concentration as the slush will indicate the

manner in which alloys will perform in this environment.

Table 3 gives data for the exposure of various alloys to a well brine, the composition of which closely approximates that of the Detroit slush. These data show Monel, nickel, Inconel, and stainless type 316 to have the most satisfactory resistance. These are the materials that would be worthy of further test as dowel cladding to determine their performance under actual field conditions.

These data show that stainless type 302 was quite heavily pitted during this exposure. This confirms virtually all data for the exposure of this alloy to solutions which contain chlorides. The straight chromium grades (stainless 400 series) are also susceptible to pitting corrosion when exposed to these conditions. When molybdenum is added to the 18 percent chromium, 8 percent nickel stainless steels (stainless type 316) a much improved resistance to pitting corrosion by chlorides has been observed. However, even this grade under some conditions will show evidence of pitting.

The stainless alloys are dependent upon an oxidizing environment for their passivity and good corrosion resistance. When chloride ions are present in the solution, they can cause a breakdown of the passive film at discrete locations where pitting will be initiated. Monel, nickel and many of the copper base alloys are most suitable in environments which are non-oxidizing; they do not depend on the formation of a passive film for their good resistance and, therefore, are not susceptible to this damaging effect by chloride ions.

TABLE 3
WELL BRINE CORROSION DATA ^a

Material	Avg. Corr. Rate (in./yr)	Max. Pitting (in.)
Monel (67 Ni, 30 Cu)	0.004	0
Nickel (99 Ni)	0.003	0
Inconel (77 Ni, 15 Cr)	0.000	Some etching
Stainless type 302 (18 Cr, 8 Ni)	0.001	0.20
Stainless type 316 (18 Cr, 8 Ni, 2.5 Mo)	0.000	0
Mild steel (15 C)	0.180	Completely corroded away
3% Ni steel	0.080	Completely corroded away
5% Ni steel	0.090	Completely corroded away
Everdur (96 Cu, 3 Si)	0.150	Completely corroded away

^a Description of exposure: Field spool test of 61 days duration with spool located in discharge line from pump, subject to well brine, 4% NaCl, 0.005% H₂S, pH 7.4. Some aeration. Agitation-flow 38 ft/min.

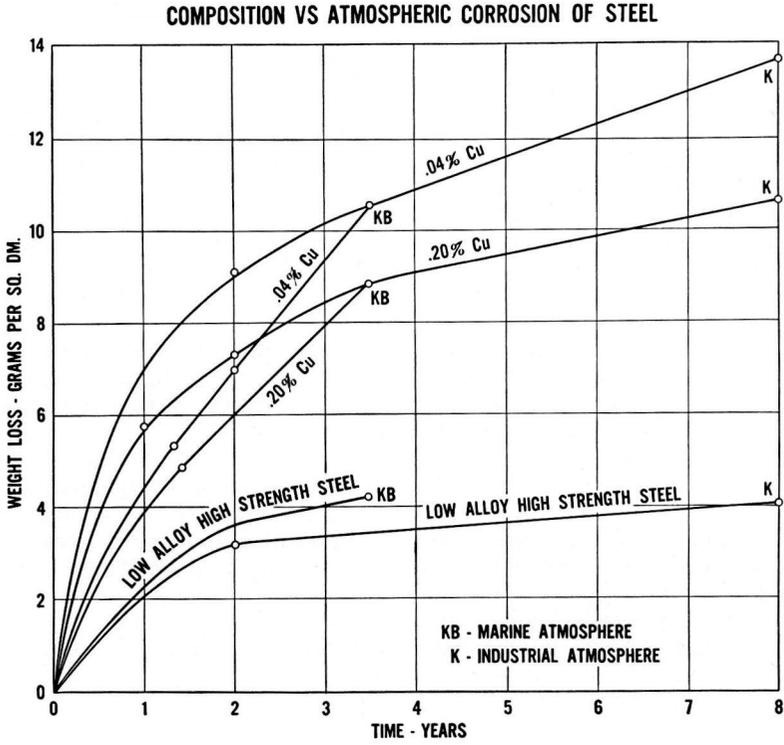


Figure 6. Effect of composition on atmospheric corrosion of steel.

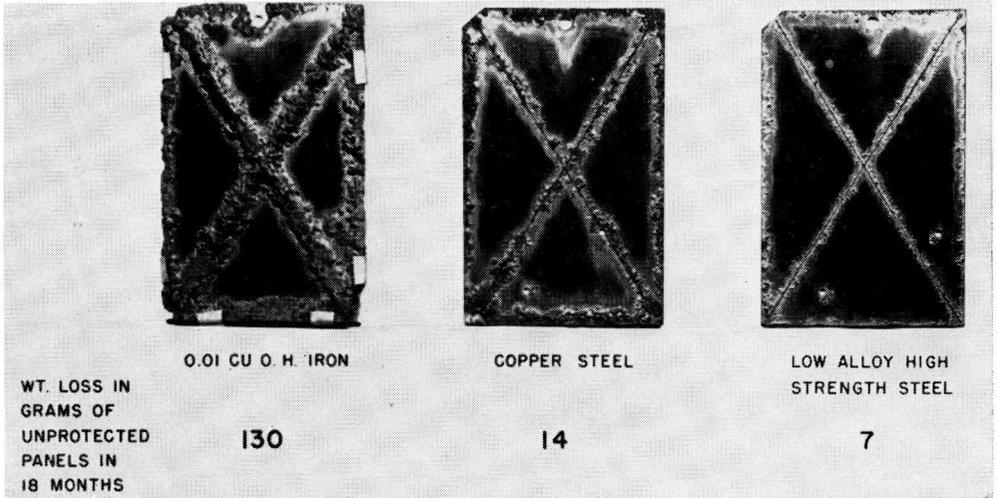


Figure 7. Effect of composition on corrosion resistance of steels and performance of protective coatings.

Considerable work has been done by a number of investigators (6, 7, 8) to show the effect of steel composition on the rate of corrosion, when exposure is to various atmospheres. Curves were plotted (Fig. 6) which were developed from corrosion data obtained for the exposure of several years of (a) a carbon steel containing residual copper, (b) a representative copper-bearing steel, and (c) a low-alloy high-strength steel to both an industrial and marine atmosphere. The low-alloy high-strength steel used in this study contained small additions of chromium, nickel and copper, and the more protective value of the rust on this grade is attributed to the formation of compounds from these elements.

This superior corrosion resistance of the low-alloy high-strength steel can be taken advantage of when it is desired to keep maintenance painting at a minimum (9). The effect of composition on paint performance is shown in Figure 7 for three different alloy panels which were painted with the same system and scribed to expose unprotected metal prior to test. Weight loss data for unprotected panels are also shown under each grade.

The more protective quality of the rust on low-alloy high-strength steels not only protects the steel at breaks in the coating, but minimizes the amount of paint damage that can be caused by the formation of a voluminous, less-protective corrosion product.

The good mechanical properties (yield strength 50,000 psi min, ultimate tensile strength 70,000 psi min) and the exceptional corrosion resistance of low-alloy high-strength steels to atmospheric en-

vironments makes them an economical selection for various highway structures. Although the unit cost of these steels is higher than that of carbon steels, it is offset by weight savings, lower maintenance, and prolonged service life.

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