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CORROSION RESISTANCE OF BARE AND ZINC-COATED IRON AND STEEL

Contents.

	<u>Page</u>
I. Introduction . . . . .	1
II. Influence exerted by chemical composition and certain physical conditions on the corrosion-resistance of iron and steel.	
A. Chemical composition . . . . .	1
(1) Carbon; (2) manganese; (3) phosphorus; (4) sulphur; (5) silicon; (6) copper; (7) nickel; (8) chromium.	
B. Physical conditions . . . . .	4
(1) Mechanically strained metal	
(2) Character and uniformity of surface finish	
(3) Segregation of impurities.	
III. External factors influencing rate of corrosion in atmospheric, submerged and underground (buried) corrosion . . . . .	5
A. Atmospheric . . . . .	5
B. Submerged . . . . .	6
C. Underground (buried) . . . . .	8
IV. Relative corrosion-resistance of different irons and steels, as determined by field or service tests. . . . .	9
A. In various atmospheres . . . . .	9
B. Partially or fully submerged in liquids . . . . .	12
C. Buried in soils . . . . .	16
V. Corrosion fatigue of ferrous metals . . . . .	17
VI. Some remarks concerning principles of corrosion-resistance testing . . . . .	20
VII. Selected bibliography	
A. Bibliographies	
B. Books	
C. Monographs	
D. Symposia on corrosion	
E. Continued reports	
F. (a) General articles of a scientific nature	
(b) " " " " technical "	
G. Effect of additions, such as copper, to iron and steel	
H. Chromium steels	
I. Nickel steels	
J. Silicon irons and steels	
K. Corrosion of cast iron and comparison of cast iron with other ferrous products	
L. Comparison of wrought iron and commercially pure iron with other ferrous products	
M. Corrosion in automotive engines	
N. Corrosion of zinc-coated irons and steels	
O. Corrosion-Fatigue	
P. Cleaning of metal surfaces; pickling.	



## I. Introduction.

There are received at this Bureau many inquiries relating to the corrosion-resistance of various iron and steel products when exposed to one or more of a variety of types of service conditions. Some of these inquiries involve the expression of an opinion on the suitability of specific makes or brands of these materials for specific uses. It is contrary to the policy of the Bureau to recommend or decri specific makes or brands of any article of manufacture. The Bureau undertakes, among its activities, investigations and tests dealing with the comparative merits of types of material, not with the merits or demerits of any certain manufacturer's product. This Letter Circular has been prepared in the endeavor to answer such inquiries on types of material by putting the inquirer in touch with published data and conclusions drawn by various investigators, especially, in so far as possible, the committees sponsored by different technical organizations and investigators acting under governmental authority. Information obtained under such auspices should be expected to be impartial and be more or less comprehensive on the subject in question. A selected bibliography is appended for the benefit of those interested in following up the subject further.

The limited scope of this Letter Circular does not permit any discussion of the various theories as to the causes of corrosion; this subject is fully treated in the text-books on corrosion and in a number of journal articles, which are listed in the bibliography. The discussion here is confined to practical phases of the subject, as have been determined by investigation and experience.

The Letter Circulars of this Bureau, which are designed to answer, as far as practicable, specific inquiries and at the same time to obviate the necessity for the preparation of a large number of letters of reply on the same general subject, are not available at the Government Printing Office; they may be obtained at the Bureau of Standards, although the supply is necessarily limited.

## II. Influence exerted by chemical composition and certain physical conditions on the corrosion-resistance of iron and steel.

### A. Chemical composition.

It is of interest to know, in a general way, what influence, if any, the different chemical elements, ordinarily present or specially present as the alloying element, in commercial irons and steels, have on the corrosion-resisting properties of the material. According to Speller (his book, "Corrosion-causes and prevention"):

1. Carbon has little effect on the resistance of steel to corrosion, although it exerts an important effect on the physical properties of the

steel. This conclusion was based upon the results of numerous long-time exposure tests in both sea-water and fresh water which have been reported upon in the technical literature. Carbon in cast iron exists in the form of graphite flakes or cementite particles (carbon combined with iron to form the compound, iron carbide or cementite). The graphite flakes probably exert a mechanical protective influence; on the other hand, they tend to accelerate corrosion, especially in salt water, since they are cathodic to iron. The net result is that cast iron, exposed with a clean metallic surface, corrodes at about the same rate as rolled iron or steel when continually immersed in salt or fresh water. In certain kinds of water the solution of the metal becomes very rapid along the graphite flakes and results in the "graphitization" of iron. As the proportion of combined carbon is increased, the rate of corrosion and the tendency towards "graphitization" are decreased. The statement is made by Evans that cast iron is more quickly attacked by dilute sulphuric acid than pure iron since the graphite acts as the cathodic member of the corrosion couple; but in nitric acid cast iron is attacked less readily than pure iron, because, owing to the presence of the graphite, a high current density is set up at the anodic areas, and passivity rapidly sets in. Cast iron corrodes at a slower rate in the atmosphere, probably due to the formation of a protective coating, made up of the rust and the non-metallic constituents of the metal, which serves to retard the rate of attack.

2. Manganese does not appear to have any appreciable influence on the corrodibility of commercial steels in which the manganese-content ranges from about 0.2 to 0.6 per cent. This is especially true when the metal is practically free from manganese oxide and sulphide. When manganese is associated with an unusually high sulphur-content, the rate of corrosion is accelerated, particularly in acid media and in the air.

3. Phosphorus, when present in the usual amounts, seems to have very little influence on corrosion. In the large tonnage of steels which have been made into welded pipe for use underwater and underground, no consistent difference, with respect to the effect exerted by phosphorus, has been found in practice between low-carbon acid bessemer steels, containing 0.1 per cent phosphorus and basic open-hearth steels with under 0.02 per cent phosphorus.

4. Sulphur in moderate amounts has very little influence on the corrodibility of steel in neutral water, although it may produce a noticeable effect in acid waters. The rate of corrosion in the atmosphere, especially in industrial districts where the air contains a certain amount of acid, is materially increased by high sulphur-content unless this is neutralized by the presence of copper. It has been claimed (Buck), as a result of field tests of copper-bearing and noncopper-bearing steel sheets carried out in a severe industrial atmosphere, that 0.25 per cent copper will overcome the accelerating effect of 0.14 per cent sulphur. This effect is in addition to the usual effect of copper in increasing the corrosion-resistance of steel by the formation of an adherent oxide scale.

The practical application of this effect, if true, in the protection of high-sulphur steel made for screw stock and other purposes where good machining properties are necessary, would seem to be of considerable practical importance. To cite an example, pipe and couplings for some purposes are threaded before being pickled in acid preparatory to the application of enamel or electroplated coatings. The steel should contain about 0.08 per cent sulphur to produce good, clean-cut threads, even though the rate of solution of the steel in acid is materially increased. However, with over 0.15 per cent copper the steel is sufficiently resistant that the surface may be pickled free from scale without the threads being seriously attacked.

5. Silicon, when present within the range of from 1.2 to 2.3 per cent, seems to have no influence on the corrodibility of cast iron either immersed continuously in dilute acid and neutral solutions or exposed to these solutions by the alternate wet and dry method of testing. However, a silicon-content of over 2 per cent begins to show an inhibiting effect on the corrosion of ferrous metals. A practical application of this fact is the manufacture of various commercial products such as "duriron", "corrosiron", "tantiron", etc., which contain about 14 per cent silicon and possess high resistance to corrosion, although a low degree of ductility. The variations within the amounts of silicon usually found in commercial steels are hardly expected to exert any influence on the corrodibility of the steel.

6. Copper, present in the amount of 0.10 to 0.25 per cent, confers a decidedly beneficial effect on the corrosion resistance of open-hearth and bessemer steel when the bare steel is exposed to wet and dry weather conditions. The maximum effect is obtained at about 0.15 per cent with 0.05 per cent sulphur contents. The results of varied but still not very comprehensive series of investigations indicate that the addition of copper to steel and iron has no decided influence one way or the other when the metal is exposed underwater, in the soil, or in places where the air does not have free access. Under atmospheric conditions the effect of copper is much more marked than the purity of steel or iron; the coating of rust on copper-bearing steel has been observed to be more adherent, denser and harder than that found on non-copper-bearing steel. Since the advantage of copper-bearing steel when exposed to atmospheric conditions has been satisfactorily demonstrated, a considerable amount of this material is now being used for construction which is exposed to such conditions. Copper-bearing steels and irons are dealt with further on in this Letter Circular, in connection with several investigations made on the comparative service behavior of various steels and irons subject to different conditions of exposure.

7. Nickel exerts a marked retarding influence on the rate of corrosion in dilute acids, when the nickel content ranges from 2 to 26 per cent. Increasing nickel content also tends to decrease the corrosion rate in fresh- and sea-water and air, a minimum of 2 per cent nickel being required to produce a marked effect on the corrosion resistance.

3. Chromium confers decided corrosion-resisting qualities on iron and steel under a great many conditions, if present in sufficient amount. There are two classes of this material now on a commercial production basis. One of them is the "stainless"<sup>(a)</sup> steels, containing about 13 per cent chromium and 0.25 to 0.4 per cent carbon; these steels require heat treatment and polishing to bring out their best resisting qualities. "Stainless"<sup>(a)</sup> irons constitute the second class, and contain less than 0.10 per cent carbon, 11 to 15 per cent chromium and a little silicon or copper; these irons usually can be readily rolled or forged, and can be produced in relatively large tonnages at moderate cost. Hydrochloric, sulphuric, or sulphurous acid attack stainless steel or iron rapidly, but nitric acid in all strengths has practically no action, probably due to the passifying action produced in the presence of oxidizing compounds. Stainless steel in the hardened condition is not attacked in mine water, which contains sulphuric acid and ferric sulphate, unless the ratio of the acid to the sulphate exceeds 5 to 1 (this sulphate in acids has the opposite effect on ordinary steel since it acts as a depolarizer and thus increases the rate of corrosion). While it is important to impart a very smooth finish to stainless iron or steel to get the best results, this steel or iron shows with a rolled or forged finish nearly ten times the durability of ordinary carbon steel with the same finish when exposed underwater or to the atmosphere. For any definite chromium content and heat treatment, the corrosion resistance of stainless steel increases with a decrease in its carbon content; conversely, with a definite carbon content and heat treatment, an increase in the chromium content within limits gives additional resistance to corrosion. Chromium-nickel steels containing about 25 percent nickel and chromium up to about 15 per cent offer exceptional resistance to corrosion by natural agencies, as well as to oxidation by high heat. They possess the advantage over "stainless" steel in that neither heat treatment nor a polished finish is necessary to obtain good results. However, their first cost is much higher and they are used at present only for special purposes where the highest resistance to corrosion and oxidation is required.

#### B. Physical conditions.

1. Mechanically strained metal. Cold working and overstrain accelerate the localized corrosion of steel. The strained areas form the anode of a galvanic couple with the adjacent unstrained parts and consequently corrode; in other words a difference of electrolytic potential exists between the strained and unstrained areas of the steel article. The localizing effect of strain may be due to (a) variations in surface film protection, caused by the breaking of the film on certain areas; or (b) to differences in surface finish of the strained areas; or (c) to differences in grain distortion. In practice, the effects of variation in

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(a) The term "stainless" applies, throughout this letter circular, to this type of material and not to any particular manufacturer's product.

internal strain are usually manifested only at the portions of the fabricated steel which have been punched, cold-riveted, or otherwise distorted after hot finishing. If cold-worked metal is to be subjected to corrosive conditions, it should preferably be annealed to a sufficient extent to remove all internal strains. In hot-working, the work should be finished before the metal has cooled below the lower critical range. The corrosion-fatigue of iron and steel will be discussed in a later section.

2. Character and uniformity of surface finish. Experience has indicated that variations in surface finish have, in most cases, a much greater influence on the life of the metal than variations in chemical composition or other internal factors. The presence of mill scale, patches of rust, etc. results in localized corrosion or irregularly distributed corrosion. A surface which is highly polished is attacked very much less than a rough surface. Frequently a polished surface will withstand exposure for a considerable length of time before showing any signs of corrosion, while a rough surface exposed to the same conditions may be badly corroded in a relatively short time. Polished surfaces usually corrode more evenly; this is particularly true of high-chromium steels. The rougher, more strained and less uniform a surface, the sooner corrosion will start and the more localized the action will be.

3. Segregation of impurities. In the process of fabrication the segregated impurities in steel are rolled out in laminae, and if present in excess, they may give rise to serious defects in the steel. As corrosion of the metal article proceeds and the inner portions become exposed, the segregated areas may become an accelerating factor in the rate of corrosion. Precautions should, therefore, be taken to avoid excessively segregated material.

### III. External factors influencing rate of corrosion in atmospheric, submerged, and underground (buried) corrosion.

A. Atmospheric. Oxygen, in conjunction with moisture, is necessarily the most important factor in atmospheric corrosion. It is a well-established fact that iron and steel do not corrode in dry air at normal temperatures. The presence of a film of moisture on the surface of the initially uncorroded metal is required for corrosion to set in. The formation of the film is often facilitated by the presence of iron rust on the surface. The amount of condensed moisture may be so small that the film is invisible yet sufficient in extent to permit corrosion reactions to start and proceed slowly. The rusting of iron and steel progresses very quickly, however, in climates where considerable differences between the day and night temperatures exist, causing a large amount of moisture to be precipitated. Thus humidity and temperature must be classed among the important factors. Condensed moisture absorbs with facility not only

oxygen but any gaseous or chemical compound present in the atmosphere, such as sulphuric and carbonic acids (from the burning of coal), sodium chloride in the form of salt mist from the ocean, dust particles brought down by rain-water (these particles may contain salts as dried sea-mist carried inland by winds, alkalis from desert regions, etc.). All of these compounds tend to accelerate corrosion. Vernon (Trans. Faraday Soc., 22, pp. 113-204; 1927) has shown that by screening a piece of iron with a layer of muslin cloth the rusting of the iron indoors may be prevented, even in the presence of relatively high humidity, for a period of at least several months. Without such screening the suspended solid particles in the air coupled with a sufficiently high humidity (as may obtain in a room not artificially heated) may accelerate the rate of corrosion attack from the outset, due to the deposition of the particles and the concomitant precipitation of moisture on the surface of the iron. Vernon determined experimentally that specimens of commercial grade ingot iron, highly purified iron, and 0.5 % C steel behaved alike in manifesting this phenomenon. Fumes from chemical works constitute another means of contaminating the atmosphere, though local in extent. The corrosion of iron and steel is, as a rule, considerably more rapid in urban and industrial districts than in rural districts. The effect of alternate wetting and drying periods and the action of sunlight, coupled with seasonal variations in temperature, are also to be considered. The protective character of the rust formed by atmospheric exposure is determined largely by the composition of the metal, hence the greater importance of the chemical composition of the metal in atmospheric corrosion than where the metal is immersed continuously in water or buried in the soil.

B. Submerged. A large number of factors are involved in the submerged corrosion of iron and steel, the relative importance of the different factors depending on the conditions to which the metal is exposed. Some of them may have an important rôle in one set of conditions and be absent or be of little significance in another set of conditions. The action on the metal may, in some cases, be the resultant of two or more factors acting in the same or in opposite directions. Among the factors the following may be mentioned: (a) rate at which oxygen from the air dissolves in the solution - this is influenced by the oxygen solubility in the liquid in question, by the degree of saturation of the liquid containing one or more dissolved substances, air-pressure, humidity of the air (in the case of quiet liquids), the exposed area of the liquid surface, and by the amount of agitation at the liquid surface; (b) transfer of the dissolved oxygen from the air - water interface to the vicinity of the metal - this depends on convection currents or motion in the liquid, viscosity and temperature of the liquid, and depth of immersion of the metal (in the case of unagitated liquid); (c) diffusion of oxygen to the metal surface through the quiescent film of liquid and the layer of corrosion products against the metal - this is directly proportional to the concentration of oxygen in the liquid and inversely proportional to the thickness of the film. Convection currents or agitation of the liquid tend to thin the film or remove the layer of corrosion products; (d) the



formation of a protective coating, through the accumulation of corrosion products, which would tend to insulate the corroding solution from the metal surface and, at the same time, to exclude the dissolved oxygen, and also to prevent the action of factors promoting the formation of pitting. Neither the amount nor the structure of the rust formed, under similar conditions of exposure, by the incompletely oxidizing conditions of submerged corrosion is influenced to any appreciable degree by the usual variations in chemical composition of commercial iron and steel; (e) the rate of oxygen depolarization and hydrogen-gas evolution in non-oxidizing acid solutions; (f) degree of alkalinity in alkaline waters or solutions - an increase in the alkali-content decreases the corrosion rate of iron, and this retardation seems to become less effective with an increase in concentration of dissolved salts, especially the chlorides; (g) duration of exposure - the rate of corrosion may change considerably with time, the slowing down of the rate at which the metal is corroding is nearly always the result of the accumulation of corrosion products, etc., on the surface of the metal. On the other hand, the corrosion rate of a smoothly polished metal is initially very slow in a natural water solution, but speeds up as corrosion proceeds and rust forms until it is eventually as rapid as that of a non-polished surface.

There are several other factors, which influence the distribution of corrosion on the surface of the metal and produce a "localized corrosion" or pitting. These are: (a) dissimilar materials in contact - two such materials when submerged complete an electrical circuit, thus permitting one metal to become anodic and corrode and the other to become cathodic and be plated with atomic hydrogen (a practical case of this, according to many writers on the subject, is the irregular distribution of mill scale, which produces this contact effect on iron or steel with the consequent formation of pitting); (b) concentration cells, produced by variations in the concentration of dissolved substances in the corroding solution - a practical and commonly occurring instance of this is the difference in the concentration of dissolved oxygen at the metal surface ("differential aeration") whereby the portion of the surface shielded from the oxygen supply or in contact with the part of the solution low in oxygen-content becomes anodic to that in contact with the part of the solution richer in oxygen; (c) electrical conductivity of the corroding medium - the cathodic portion of the metal surface which the anodic portion keeps saturated with atomic hydrogen is limited by the conductivity of the corroding solution, hence, other factors remaining the same, the tendency for the metal to pit should increase with the conductivity; (d) the relative size of anodic and cathodic areas is influenced by the above-mentioned localizing factors - the smaller the anodic areas compared with the cathodic areas, the greater the pitting and, conversely, the smaller the cathodic areas the less the pitting; and (e) water-line corrosion, which is frequently met with in service and usually results in an accelerated attack (marked pitting) at or near the water-line.

Mention should be made here, with reference to the two above mentioned types of corrosion, of the results of a laboratory study of the corrosion occurring at different kinds of discontinuities in certain non-ferrous metal coatings applied to a low carbon steel, that have very recently been reported by U. R. Evans to the British Institute of Metals (Jour. Inst. Metals, Vol. 40, 1923). There were included in this study sprayed coatings of copper, nickel and aluminum, as well as zinc coatings produced by hot-galvanizing, electrodeposition, spraying and sherardizing (zinc-iron alloy coating). With copper, nickel and zinc, four types of sprayed coating were employed: (a) intentionally discontinuous, (b) thin, continuous and porous - about 0.001 cm thick, (c) thicker and less porous - about 0.01 cm thick, and (d) a coat similar to (c) applied to steel which had been intentionally rendered slightly greasy by being burnished with a greasy wire brush before being sprayed with metal. The specimens, including the aluminum-coated ones which had two thicknesses of coating - 0.015 and 0.007 cm, were in the form of strips 2.5 cm wide and either 5 or 10 cm long, and were tested in the unbent and bent states. The six types of corrosion the specimens were subjected to are partial immersion in N/2 sodium chloride solution and in hard water (town tap water), intermittent spraying in N/2 sodium chloride and N/100 sulphuric acid solutions, and exposure to air containing sulphur dioxide and moisture and to air containing hydrogen chloride. Some of the conclusions Evans drew from his tests are as follows. The cracks produced by bending are more dangerous than uniformly distributed pores. Of the coating metals which are cathodic to steel, copper causes under some conditions, a marked acceleration in the corrosion of steel at exposed places, while nickel produces much less acceleration. Zinc, which is anodic to steel, protects the steel at the exposed places by electrochemical protection as long as the zinc coating in proximity to the areas of exposed steel lasts. A fairly thick zinc coating is usually advisable, notwithstanding the increased tendency to cracking, the best thickness of coating depending on the purposes for which the material is intended; this conclusion should be supported by the fact that galvanized sheet made years ago carried more zinc than the modern material does and has generally shown a longer life in service. Coatings of aluminum or zinc-iron alloy are themselves less attacked than those of zinc, and for this reason they offer less protection to the exposed steel in bent specimens than the zinc coating in certain waters. Zinc itself is rather rapidly attacked when partially immersed in a chloride solution, but alternate spraying with salt spray or dilute acid spray and drying was found to build up a protective film - a fact which explains the relatively good behavior observed for galvanized iron in service. In immersed corrosion rust is actually precipitated outside the copper or nickel coat (at the point of discontinuity in the coating), which continues to adhere until a quite advanced stage of attack. In atmospheric corrosion, rust is formed below the coating, and owing to its greater volume soon pushes the coating away from the steel; this effect is more marked if the coating has been applied to greasy steel.

C. Underground (buried). This type of corrosion combines some of the characteristics of each of the two foregoing types, and in addition, shows certain individual characteristics. (The subject of electrolysis from stray currents is not considered here). Corrosion underground is, in general, similar to underwater corrosion, but is complicated by the presence of other factors which may altogether change the nature and progress of the reactions. This entire subject of underground corrosion is not yet fully understood, although an active program of research in this problem is in progress at the Bureau of Standards. The distinguishing characteristic of soil corrosion is the marked pitting produced by the effect of dissimilar soils, varying composition of soil waters, texture of adhering soil particles, and other localizing factors. An important factor would seem to be the amount of dissolved oxygen in the soil. This depends on the amount of soil water, structure and composition of the soil, the distance of the buried metal below the surface, the rate of diffusion of air, and the rate of flow of the soil water.

IV. Relative corrosion-resistance of different irons and steels, as determined by field or service tests.

A. In the atmosphere. The great practical importance of the findings of several investigators that copper added in small amounts to iron and steel increases the corrosion-resistance of the material when exposed in several different types of atmosphere led to the institution some 10 years ago of field test programs made on various ferrous materials in the United States, Germany and England. The atmospheric tests were carried out at three or four localities, representing different types of atmospheric conditions. To make these test programs still more comprehensive, completely submerged tests were also made on specimens of the same ferrous materials in several types of liquids. (fresh (city) water, brackish water and acid mine water in the United States, and sea-water in Germany, England and three British overseas provinces).

The German tests were carried out by Dr. O. Bauer of the German Materialsprüfungsamt, whose report of these tests was published in *Mitteilungen Materialsprüfungsamt*, 23, p. 35 (1920) and in *Stahl und Eisen*, 41, pp. 27, 76 (1921). Atmospheric exposure tests, lasting 4 to 4 1/2 years, were carried out in three localities: (a) in a relatively pure (city) atmosphere; (b) in one contaminated by industrial smoke and gases at a steel works, and (c) in the salt air on the North Sea coast. The materials tested, in the form of large sheets not freed from scale, were several series of steels averaging in chemical composition about 0.09% C, 0.45% Mn, 0.10% Ni, and varying in copper-content from 0.10 to 0.40%. Unfortunately, no material practically free from copper was included in the tests, which fact increases the difficulty of drawing definite conclusions. Bauer concluded, apart from the fact that the copper-rich material was decidedly less attacked than those lower in copper-content when exposed to the presumably sulphurous atmosphere of the steel works, that under all the other conditions of exposure there was no consistent difference in behavior which would warrant accepting

the idea that a variation in copper content of 0.10 to 0.40% had any clearly manifested effect upon the life of the sheets. Later, Daeves (Stahl und Eisen, 4c, p. 1957; 1922) reviewed Bauer's data and interpreted them as showing the beneficial effect of copper in some cases where Bauer did not so interpret his own data. In addition to the atmospheric tests, Bauer carried out tests where large sheets were kept immersed in the sea-water of the North Sea for 14 months and other sheets were buried for five years in the ground at the three localities where the atmospheric exposures were made. Furthermore, he carried out many laboratory tests on smaller specimens, freed from scale, in various corroding media.

In the United States the program of tests carried out by the American Society for Testing Materials, through its Committee A-5, was planned on more comprehensive and longer-continued lines. Several types of iron and steel much used in this country and not included in the German tests were incorporated in these tests. The materials under test included, in the form of 1c- and 22-gauge sheets, puddled iron, wrought iron, commercially pure open hearth iron, open hearth steel and Bessemer steel low in copper and a similar series ("copper-bearing") with 0.15 to 0.2% copper. The exposure tests were started at three locations having different types of atmosphere, stated parenthetically as follows: Pittsburgh (heavy industrial); Fort Sheridan, Ill. (rural); and Annapolis, Md. (sea-coastal). The tests at Pittsburgh were concluded in 1922 after 2 1/4 years' exposure, and those at Fort Sheridan in 1923 after 11 years' exposure, and those at Annapolis are still in progress (nearly 12 years). The results of the periodical inspections of the test sheets are given in detail, by means of tables and photographs, in the progress reports published in the Proceedings of the American Society for Testing Materials from 1919 to the present time. At the conclusion of the Pittsburgh tests, none of the 122 1c-gauge copper-bearing steel and iron sheets had failed while 102 out of 122 non-copper-bearing steel and iron sheets had reached the failure point. Of the 24 that did not fail 7 (out of a total of 58 included in test) were commercially pure iron and 17 (out of 45) were open-hearth steel. With the 22-gauge sheets, 122 out of 14c copper-bearing and all of the non-copper-bearing steel and iron sheets (practically all of them after 3 years) had failed. 13 of the 23 unfailed sheets were of Bessemer steel (out of 23) and the other 5 (out of 74) were of open hearth steel. The various 22-gauge materials used were rated by Committee A-5, according to the results of the Pittsburgh exposure tests, in the following order, the most resistant types coming first:

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Rating	Type of Material.
First	Copper-bearing Bessemer steel.
Second	Copper-bearing Acid Open-hearth steel.
Third	Copper-bearing Basic Open-hearth steel.
Fourth	Copper-bearing Pure Iron.
Fifth	Copper-bearing Wrought Iron.
Sixth	Non-copper Wrought Iron.
Seventh	Non-copper Pure Iron.
Eighth	Non-copper Basic Open-hearth steel.
Ninth	Non-copper Bessemer steel.

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The terms "copper-bearing" and "non-copper" indicate a copper content of 0.15 per cent or over and less than 0.15 per cent, respectively.

While the Fort Sheridan tests were, by reasons of necessity, not carried to as conclusive an end as the Pittsburgh tests, the results obtained were such that these tests had served sufficiently in furnishing the desired information. At the conclusion of the tests none of the 132 16-gauge copper-bearing steel and iron sheets had failed while only 4 out of 124 16-gauge non-copper-bearing steel and iron sheets reached the failure point (4 out of 12 Bessemer steel specimens). With the 22-gauge sheets, 50 of the 132 copper-bearing and 77 of the 93 non-copper-bearing steel and iron sheets had failed. Among the 50 failed copper-bearing sheets 28 (out of 28) were commercially pure iron, 2 (out of 14) wrought iron and 10 (out of 63) open hearth steel. Among the 77 failed noncopper-bearing sheets 28 (out of 28) were commercially pure iron, 3 (out of 9) wrought iron, 21 (out of 25) open hearth steel and 17 (out of 19) Bessemer steel. The order of corrosion resistance drawn up by Committee A-5 for the 22-gauge sheets based on the results of exposure at Fort Sheridan, is as follows:

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Rating	Type of Material
First	Copper-bearing Basic Open-hearth steel. Copper-bearing Bessemer steel (Series A). Copper-bearing Acid Open-hearth steel. Non-Copper Bessemer steel (Series B, 2 specimens with 0.13% Cu). Copper-bearing Bessemer steel. Copper-bearing Open-hearth steel (Series B, one maker).
Second	Copper-bearing Wrought Iron. Copper-bearing Open-hearth steel (Series A; Series B, two other makers).
Third	Copper-bearing Pure Iron.
Fourth	Non-copper Pure Iron.
Fifth	Non-copper Wrought Iron.
Sixth	Non-copper Bessemer steel (Series A; Series B, 2 specimens with 0.01% Cu).
Seventh	Non-copper Open-hearth steel.

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These ratings are substantially the same as those for the Pittsburgh 22-gauge sheets.

At the time of the last inspection made (11-1/2 years after the start) in the Annapolis tests, none of the 16-gauge copper-bearing and non-copper-bearing steel and iron sheets (252 in all) had failed, while, with the 22-gauge sheets, only one (open-hearth steel) out of the 143 copper-bearing

steels and iron sheets and 23 out of the 72 noncopper-bearing steel and iron sheets had failed. Among the 23 failed sheets 10, (of a total of 13) were open-hearth steel, 10 (of a total of 23) commercially pure iron and 3 (of a total of 20) Bessemer steel. No table of corrosion resistance rating for these materials has, as yet, been published.

At first glance it might appear logical to assume that the best combination to resist atmospheric corrosion would be that of copper-bearing steel or iron sheet plus a heavy zinc coating, on the assumption that, since bare copper-bearing sheet is resistant to atmospheric corrosion, it would also show superior resistance after the zinc had been corroded away. This does not necessarily follow, however, because the resistance of the bare copper-bearing sheet is undoubtedly due to the adherent type of rust which forms on first exposure. There is no assurance that, under the electrochemical conditions set up as patches of the steel become bared and some zinc still remains, the adherent type of rust will be formed. Before drawing final conclusions as to the proper base for zinc-coated sheets, results from exposure tests undertaken to examine this very point should be awaited.

An extensive series of atmospheric exposure tests on zinc-coated (galvanized) corrugated iron and steel sheets were inaugurated in the spring and early summer of 1928 at five different locations. The types of atmosphere represented by these locations are: (a) humid sea-coast - Key West, Fla.; (b) foggy, temperate sea-coast - Sandy Hook, N. J.; (c) severe industrial - Pittsburgh, Pa.; (d) moderate industrial - Altoona, Pa.; and (e) pure rural - State College, Pa. (The results of the May, 1929 inspections of the exposed sheets at Altoona have shown that this location should be classed rather as "severe industrial" than "moderate industrial." In fact, Committee A-5 reported that "the galvanized sheets and bend tests on the Altoona test rack show more pronounced corrosion than any of the others.") Five base metals were used for the zinc-coated sheet material, namely (1) basic open hearth steel and (2) iron each with a maximum of 0.05% Cu, (3 & 4) the same each with a minimum of 0.20% Cu, and (5) wrought iron. Five weights of zinc coating were included, viz: 2 1/2, 2, 1 1/2, 1 1/4 and 0.75 to 1 oz. per square foot of sheet. The sheets were of 22-gauge, also 18-gauge with 2 1/2 oz. coating for the first four bases, and 22-gauge with 0.75-1.0 oz. coating for the first four bases. Bent specimens of these various sheets were also included in test to observe the effect of bending on the corrosion-resistance of the coated materials. Later, there were added to the above series of specimens other zinc-coated specimens in the form of wire, fencing, structural shapes (as flats, angles, T-bars and window frame sections), conduits, hot-welded pipe, bolts, hardware and fittings, roofing nails, and wood screws. While it is too early yet to look for a marked occurrence of failure among the sheet specimens, even in the Pittsburgh and Altoona tests, definite progress in the breaking down of the zinc coating was noted, in the spring of 1929 inspections, among the sheet specimens with the lighter zinc coatings. Of the lightest coated sheets (0.75 oz. per sq. ft. of sheet) at Altoona, 7 of the 22-gauge sheets

(of a total of 14) and 4 of the 28-gauge sheets (of a total of 10) were rated as "R", i.e., as showing a rusting of the base metal (the coating having been corroded away at these points). Likewise at Pittsburgh, for specimens with the same weight of coating, 5 of the 14 twenty-two gauge sheets and 2 of the 10 twenty-eight gauge sheets were rated "R". None of the sheets in the sea-coast exposure tests had reached this stage of corrosion. Both the sheet and bend test specimens at State College showed less deterioration than those at the other localities; the zinc coating on the sheets appeared still intact and quite clean. It may be ten years or more before the tests at the more favored locations will be concluded, especially in the case of the heavier zinc coatings. It is a rather well-established fact that, within the limits set by the cracking or flaking of the coating on material formed after the zinc-coating operation, the life of the coating is, broadly speaking, the greater the heavier the coating is. The effect of differences in technique or method of zinc-coating and of the composition or purity of the coating will, in general, be secondary to the main factor of the thickness of coating. Further, it is obvious that for any given composition of base metal, the thicker the sheet, wire, etc. (i.e., the heavier the gauge) the longer the life of the coated material will be. Coating a fabricated article such as garbage cans or wire fencing, after fabrication allows the employment of a heavier coating than would resist cracking during fabrication. Coating after fabrication is generally believed to produce a superior article, provided a sufficiently heavy coating is applied.

The British tests are being carried out at four widely separated sea-ports: Plymouth, England; Halifax, Nova Scotia; Colombo, Ceylon; and Auckland, New Zealand. These tests include three types of exposure (aerial, alternate wet and dry - as placed between high and low tides, and completely immersed), five types of specimens (isolated bars, pairs of dissimilar bars in contact, single bars with four rivets in each, single bars with four bolts in each, and four bars bolted together to form a square frame), and three periods of exposure (5, 10, and 15 years). The materials included in test consist of four main sections: (a) wrought iron, Swedish charcoal iron and commercially pure open hearth iron; (b) mild steel with low Mn and high S and P, mild steel with 0.70% Mn, medium carbon steel with low S and P, and 0.40 C steel; (c) mild steel with 0.50% Cu, mild steel with 2.00% Cu, 3.5% Ni steel, 3% Ni steel, and 12.5% Cr steel with 0.4% C; and (d) cold-blast cast iron and hot-blast cast iron. All the specimens, in the form of bars 24" x 3" x 1/2", were in the "as rolled" condition (excepting the cast iron ones) so as to retain the oxide skin (excepting the wrought iron, Swedish charcoal iron and commercially pure open hearth iron specimens which had their oxide skin removed by grinding). They were mounted in concrete frames, the exposed length of the bars being a little over 1 1/2 feet. There were added to these specimens bars of medium carbon steel with low S and P and mild steel with 0.7% Mn that had their oxide skin ground off. The "aerial" specimens were placed at the harbor dock and well above high tide, so they were exposed to the sea-air and to salt water spray. The results for the five-year exposures at Halifax and Auckland have been reported recently. For the isolated bars in the atmospheric exposure tests at both places the 3% Ni and 12 1/2% Cr steel specimens stood

up very well, as did the hot-blast and cold-blast cast iron specimens, which were remarkably resistant as regards both loss in weight and freedom from pitting. The 2 1/2% Ni, 2% Cu and 0.5% Cu steel specimens showed good resistance while all the others were badly corroded. The addition of copper to the mild steel produced a marked increase in corrosion-resistance. The wrought iron specimens showed a lower degree of corrosion-resistance than the mild steel ones. The mild steel specimens with high sulphur and phosphorus were the poorest of the whole lot. The results for the edge-to-edge, bolted, riveted and bars bolted together specimens likewise exposed indicate a superior and even very satisfactory behavior for the 28% Ni and 13-1/2% Cr steels and the hot-blast and cold-blast cast irons when in contact with other materials. It was stated that the isolated 28% Ni, and 13-1/2% Cr steel specimens at Colombo were in good condition, while all the others were in a badly corroded condition after five years' exposure. At Plymouth the isolated 28% Ni steel and hot-blast and cold-blast cast iron specimens were stated to be in good condition after five years' exposure while all the others were badly corroded. The climatic conditions at these widely separated places would, of course, be expected to be different, yet the results do indicate that 28% Ni and 13 1/2% Cr steels and hot-blast and cold-blast cast irons quite consistently show good corrosion-resistance in the different conditions of sea-coastal atmospheric exposure.

B. Partially or fully submerged in liquids. In the American Society for Testing Materials program of total immersion tests, the same series of materials employed in the atmospheric tests were included. The specimens were 2" long and 2" wide, and were the same in number as in the atmospheric tests. They were mounted in racks, which were placed within boxes, and exposed to the corroding liquid flowing through the boxes. The tests were carried out in acid mine water (Pittsburgh district), in normal city water (Washington, D. C.) and in the brackish water of Severn River (Annapolis, Md.). The Pittsburgh and Washington tests have been completed and the Annapolis tests nearly so. The results clearly show that corrosion-resistance of iron and steel when submerged is practically uninfluenced, within the range of the tests, by copper contents. The 16-gauge sheet specimens, either copper-bearing or noncopper-bearing, showed a life a little over twice as long as the 22-gauge sheet specimens. The average life, in days, shown by all the materials, irrespective of their copper-content, was approximately 50 for 22-gauge and 120 for 16-gauge at Pittsburgh, 350 for 22-gauge and 1200 for 16-gauge at Washington, and 1250 for 22-gauge and over 2000 for 16-gauge at Annapolis. The longer life of the specimens exposed in brackish water, as compared with that for the same material in Washington city water, constantly renewed, may be due to the combined influence of a number of factors. The greater amount of silica found in both the scale and rust from the Annapolis specimens suggests that the deposits on these specimens were more protective. The average oxygen-content and the temperatures were lower in the Annapolis water; each of these factors would tend to slow down the rate of corrosion.



This program of tests was extended when in the spring of 1927 samples, cut from the same sheets as in the above series of tests, were immersed in the running sea-water at the U. S. Navy Yard at Portsmouth, N. H. and at the U. S. Naval Station at Key West, Fla. There were also placed in the test boxes, containing these specimens, one 12" long piece each of 2" low copper and 1% Cu steel tubing. In the previous summer a set of riveted ship plate specimens and a set of three 2" tubes 30 inches long of 0.1-0.2% carbon steel ranging in copper content from 0 to 1.0% and of three 3" tubes 30 inches long of 0.2-0.4% carbon steel having a copper content of from 0.25 to 1.1 per cent, were put into the test at each of the above-mentioned places, and also in a bayou 2 miles from the Gulf of Mexico at Port Arthur, Texas. The set of riveted ship plate specimens, the dimensions of which were 22" x 12" x 1/2", consisted of three kinds of steel ship plate (0.04% Cu, 0.22% Cu, and 0.13% Si) riveted with four different kinds of rivets (0.07% Cu steel, 0.24% Cu steel, low Cu puddled iron, and "ship quality" steel). These riveted ship plate and tube specimens, the latter being mounted in racks, were suspended below the docks and at a sufficient distance below low tide at Portsmouth and Key West so that there would be little or no wave action at the point of suspension, and those at Port Arthur 2 inches below mean low Gulf level and subjected to the usual Gulf tide variations. The proportions of sea-and fresh-water at this last location varied according to the wet and dry seasons. It is too early yet to look for any extensive results from these tests, even though an inspection made in March 1928 of the sheet steel specimens at Key West showed 6 failures among the 22-gauge sheet specimens.

It was mentioned in the section on atmospheric tests (Sec. IV a) that there were included in the British test program alternate wet and dry and complete immersion tests made in sea-water at the docks of four widely separated ports; the details as to materials and specimens are also mentioned there. Some of the conclusions drawn by Dr. J. N. Friend from the results of a final examination of the first, or five-year, series of specimens exposed at Halifax and Auckland are as follows. The 2% Ni and 12 1/2% Cr steel specimens were very resistant to wet and dry conditions of exposure, although in the continuously immersed tests they showed a less marked advantage over the wrought iron and carbon steels. The hot-blast and cold-blast cast irons appeared to be remarkably resistant to corrosion in both types of exposure, as regards both loss in weight and freedom from pitting, although these specimens were still under further investigation for any internal corrosion present. The addition of copper up to 2% improves to an appreciable extent the corrosion-resistance of mild steel, although the curious fact remains that in the wet and dry tests at both Halifax and Auckland the 2% Cu steel specimens showed a greater loss in weight than the 0.5% Cu steel specimens. There was, in general, but little difference between the rates of corrosion of wrought iron and mild steel when totally immersed in sea-water, although in the alternate wet and dry tests the wrought iron specimens showed up better. The presence of sulphur in steel tends to enhance its rate of corrosion.

Mild and medium carbon steel specimens ground free from adhering scale before being put into test showed a sometimes less and at other times greater loss in weight than similar specimens with the mill scale not removed. But the cleaned specimens were generally free from pitting or were less deeply pitted than the uncleaned bars - this is a point of great practical importance. The results of the tests in which dissimilar metals were placed in contact, riveted, or bolted together showed that the tendency for one metal to be preserved from corrosion at the expense of the other was more regular and decided in the alternate wet and dry and complete immersion tests than in the aerial (atmospheric exposure) tests. The 3% Ni and 13 1/2% Cr steel specimens were very well preserved by contact with the more corrodible wrought iron and mild carbon steel specimens. Wrought iron in contact with mild steel corroded more rapidly than the latter, which was partially preserved. Hot-blast cast iron was partially preserved at the expense of mild steel in the alternate wet and dry tests, while the opposite was the case in the complete immersion tests.

Friend has recently reported the results of a four years' exposure to sea-water in the Bristol Channel, England, of a series of ferrous materials in the form of 1 1/8" round bars, 2 feet long, mounted in a wooden frame, which was fastened to the rocky bottom of the sea. The specimens were subjected to a severe tide movement and remained submerged for about 25% of the time. The conditions of exposure resembled closely those to which metals on the exposed parts of ships, buoys, caissons, and other marine structures are exposed. The materials tested included wrought iron, cast iron, carbon steels with 0.05 to 0.3% carbon, chromium-nickel steels with 2.5 to 5% Ni and 0.05 to 1.0% Cr, stainless steel with polished surface, 12% Mn steel and commercially pure open hearth iron. In addition to the sea-exposure tests, a laboratory test was run on the same materials. The specimens were kept for 5 years on top of a wax-coated false bottom of a large galvanized steel tank filled with about 1/2 ton of artificial sea-water (2% rock salt solution). This laboratory test was, of course, not an exact replica in miniature of the channel tests, for the specimens in the former were free from marine adhesions and were kept immersed in still liquid. The order of merit, as regards the corrosion-resistance of the various materials, was found to be the same for the channel and laboratory tests. The polished stainless steels stood up best, while chromium-nickel steels, wrought iron, cast iron and carbon steels (worst) followed in order. In a test made with galvanized commercially pure open hearth iron, the zinc coating was found to have prolonged greatly the working life of the steel in sea-water, the coated surface being in a good condition and quite free from pitting. The stainless steel bars resisted the sea-action remarkably well, except at the points where they were fastened in the wooden frame. The general surface of the cast iron bars was in excellent condition and free from pitting. The removal of the casting skin by machining did not appear to have appreciably influenced the resistance of the metal to corrosion in sea-water.

To cite a practical case as to the service behavior of copper-bearing steel in sea-water, the surprising freedom from adhering marine growth, pitting and other evidences of severe corrosion reported for the hull of the steamship "Leviathan" (known as the "Vaterland" before its internment in New York at the outbreak of the World War), after about five years' lack of attention accorded it, was ascribed to the copper-content, amounting to about 0.15%, of the German steel used. On the other hand, a skeg of British steel plates analyzing 0.022% Cu, which was riveted to the bottom shell of this ship early in the above mentioned five-year period, was found to be badly corroded. Specimens of these and similar steels differing in copper content have been compared as to their corrosion resistance in laboratory tests made at the Bureau in sea-salt solutions (2 1/2 per cent by weight). So far, these tests have failed to show any important difference in the behavior of the various steels when corroded by total immersion or by repeated immersions in this solution. The Bureau has been advised informally that in the very recent inspection of this ship in dry dock no distinct difference in the surface condition of the original copper-bearing steel plates and of the ordinary steel plates without copper, that had been inserted subsequently, was to be observed. This would appear to add further evidence to the conclusion that additions of copper, within the limits usually employed, confers no decided improvement in the corrosion-resistance of steel when more or less completely immersed, and to indicate that other factors play an important role in cases where the copper-bearing or noncopper-bearing steel shows superior behavior to the other.

C. Buried in soils. There has, during the last few years, been a considerable interest manifested in the corrosive effects of soils on buried metals. The Bureau of Standards has had under way since 1922 an investigation on the corrosion of pipe and other materials in some 50 soils located in different parts of the United States. A progress report covering the various phases of the investigation to the present time has very recently been issued (Bureau of Standards Technologic Paper No. 283: "Bureau of Standards Soil-Corrosion Studies. I. Soils, Materials, and Results of Early Observations" by K. H. Logan, S. P. Ewing, and C. D. Yoemans). The ferrous pipe materials (wrought iron, commercially pure open hearth iron, cast iron, open hearth steel, Bessemer steel, and copper-bearing steel) used in this investigation were selected from stock and included the various kinds and grades of pipe ordinarily purchased by public utility companies and other organizations. A large variety of other ferrous and non-ferrous materials and various coated materials were also included in the tests at different intervals. The data now available indicate that, so far as corrosion during the first four years of the test is concerned, no one of the commonly used pipe materials is superior under all soil conditions. The following are some of the tentative conclusions drawn from the available data. The type of corrosion is in some way associated with the locality in which the specimens are buried. While several soils show considerable corrosiveness, the rate of corrosion produced in the majority of soils is low and even practically negligible in some cases. There seems to be a tendency for the rate of corrosion to decrease with time in many soils, and

the rate of penetration of the pipe wall apparently decreases still more rapidly. While no one material that is suitable for general use in pipe lines now appears superior to all others in all soils, there is an indication that a saving can be effected by a proper selection of a pipe material with respect to the soil condition which it will encounter. There is, in addition to the field study of soil corrosion, some laboratory investigational work being undertaken on various problems connected with soil corrosion, such as texture of soil, moisture conditions, effect of temperature, extent of protection due to galvanizing, galvanic currents, etc.

A number of organizations, such as the Bureau of Public Roads of the U. S. Department of Agriculture, various state highway departments, engineering departments of various railroads and others, have at different times during the past 10 or 15 years been studying the problem of metal culvert corrosion, but no comprehensive reports have been forthcoming. The American Society for Testing Materials has organized a sub-committee (IX) of its Committee A-5, whose functions are to correlate the different sources of information that may be available as a result of past or present investigations on the flexible metal culvert as an engineering material. A questionnaire was sent out by the sub-committee and it was evident from the data thus obtained from a large number of carefully prepared answers, that the question of comparative merits of the different types of base metal is as yet unsettled. This sub-committee is now making efforts towards the early formulation of concrete plans for a comprehensive research program that would furnish reliable information on this important engineering material.

By reference to pp. 9-11, 13, 14 and 17 it will be noted that the conditions of exposure, i.e., the corrosiveness of the air, the liquid, or the soil in contact with the specimens, make enormous differences in the life of the specimens. Only major differences in the composition of the iron or steel specimens, such as the addition of around 12% of either chromium or silicon, cause differences in life comparable to those caused by differences in the corrosive environment. Small differences in copper, carbon or slag content, while they may show a detectable effect, show an effect whose order of magnitude is often far less than that of a change in the corrosive environment.

#### V. Corrosion fatigue of ferrous metals.

The foregoing discussion has dealt chiefly with the corrosion-resistance of unstressed or statically stressed material. Where the material is subjected to corrosion and at the same time to repeated or vibrating stress, the extent to which the fatigue limit or endurance limit is lowered by the corrosion becomes important. It would be difficult to avoid

in certain types of machinery the slight degree of corrosion that is sufficient to make "corrosion fatigue limit" (i.e., the endurance limit of specimens simultaneously exposed to corrosion by a liquid corroding medium), rather than "endurance limit" the most important physical property. The term "endurance limit" is restricted here to mean the fatigue limit obtained by tests in air with specimens as free as possible from stress concentration and from corrosion. McAdam has done considerable experimental work during the last few years in determining the corrosion fatigue limit of a large variety of ferrous materials, and also of non-ferrous materials, in both the unheat-treated and heat-treated conditions. The materials included carbon steels with the carbon content ranging from 0.03 to 1.1 per cent, ingot iron, stainless iron and steel, 3 1-2% Ni and 5% Ni steels, Cr-Ni, Cr-V and Cr-Mo steels. The specimens were subjected to repeated cycles of stress in a rotating cantilever machine and a stream of the corroding medium was applied diagonally so as to sweep the specimen from the outer to the inner fillet and completely surround the stressed surface. The corroding media used in the various tests were a calcium carbonate water, soft water and brackish water with about 1/3 and 1/2 the salinity of sea-water.

The experiments showed that even slight corrosion simultaneous with fatigue may cause failure at nominal stresses far below the ordinary endurance limit. Severe stressless corrosion prior to fatigue ("prior-corrosion-fatigue") was found to be usually much less damaging than slight corrosion simultaneous with fatigue. The relative effect of prior stressless corrosion on the fatigue limit, however, is thought by McAdam to vary with the electrolytic potential of the material. The corrosion fatigue limit, which is represented in a stress-cycle graph as a curve approaching a horizontal asymptote, apparently depends more on electrochemical than on physical properties. Chemical composition, heat treatment, and cold working have little effect unless there is a corresponding change in corrosion resistance, on which the corrosion fatigue limit seems to depend chiefly. The corrosion fatigue limits for carbon steels and those alloy steels having about the same corrosion resistance were found to vary by only a small amount. The addition of chromium and nickel in sufficient quantity to increase the corrosion resistance of the steel produces a corresponding increase in the corrosion fatigue limit. The effect of variations in physical properties, as determined by the usual tensile and impact tests, on the corrosion fatigue limit is insignificant in comparison with the effect of corrosion resistance. Lower values for the corrosion fatigue limit were generally obtained in the salt water tests than in the carbonate water and soft water tests.

With carbon steels ranging in carbon-content from 0.03 to 1.1 per cent the corrosion fatigue limit for all sorbitic steels and for pearlitic steel with 0.3 to 1.1% C was found to be practically the same (20,000-25,000 lbs./in<sup>2</sup>, as tested in carbonate water), while it was somewhat lower for low carbon pearlitic steels. Hence sorbitizing heat treatment does not appear to improve the corrosion fatigue limit of any of the carbon steels within the above mentioned range of carbon-content, excepting the low carbon steels. The corrosion fatigue limit of a copper-bearing 0.15% C steel

in the sorbitic condition was found to be lower than for a similar steel in the pearlitic condition. The pearlitic copper-bearing steel had a slightly higher, and the sorbitic copper-bearing steel a slightly lower, corrosion fatigue limit than the corresponding 0.15% C steels without copper. Hence the presence of copper appears, within the limits of the tests, to have produced little, if any, effect on the corrosion fatigue limit of these steels in the fully annealed and in the quenched and tempered conditions. High chromium steels showed a much higher corrosion fatigue limit in carbonate water than carbon or 3 1/2% and 5% nickel steels, either in the annealed or quenched and tempered condition. This corrosion fatigue limit evidently depends chiefly on corrosion resistance, and the latter in turn on the amount of chromium in solid solution. Chromium-nickel steels with high chromium- and medium nickel-content and those with high chromium- and high nickel-content showed a corrosion fatigue limit of about 50,000 lbs./in<sup>2</sup> (in carbonate water), which is about 50% higher than that for stainless iron and steel. This high Cr-Ni steel showed the best resistance to corrosion fatigue in salt water. The corrosion fatigue limits for stainless iron and steel tested in fresh- and salt-water were from 50 to 100% higher than those for carbon and ordinary alloy steels.

The impairment in endurance properties, due to the combined action of corrosion and fatigue, appears to be localized at those regions where corrosion and stress are the greatest. The corrosion of the metal may be in the form of pitting. This combined action starts transverse cracks, which are the regions of such stress concentration that failure occurs at nominal stresses below the endurance limit. The results of some tests indicate that the corrosion fatigue limit for low cycle frequency is no lower, and may even be slightly higher (probably due to the presence of a protective coating on the surface of the specimen) than that for high cycle frequency.

McAdam's later work dealt with the investigation of the effect of cyclic stress on corrosion, undertaken for the purpose of obtaining a better understanding, not only of corrosion-fatigue, but also of the behavior of metals under ordinary service conditions, in which cyclic stresses do not exceed the corrosion fatigue limit. Chief consideration was given to the effect of corrosion on the fatigue limit. Using the fatigue limit of the corroded specimen as a criterion, an investigation was made of the effect of time and cyclic stress on corrosion. A knowledge of the effect of cyclic stress on corrosion pitting was necessary for an understanding of corrosion fatigue. The results of this investigation, made with a number of ferrous and non-ferrous metals, not only threw light on the corrosion-fatigue process, but were applicable to all conditions of service in which metals or alloys are subjected to simultaneous corrosion and cyclic stress, whether the stress be below or above the corrosion fatigue limit. A thorough investigation of the effect of cyclic stress-range, time, and number of cycles on the corrosion of a variety of carbon and alloy steels was made. The effect of diameter or thickness of specimen on the corrosion fatigue limit and the torsional corrosion-fatigue of steel were also studied.

Speller, McCorkle and Mumma recently published a paper giving the results of fatigue tests made with a sufficient quantity of inhibitor present in the water to passify the steel and to prevent general corrosion. Corrosion is, in the long run, mainly a question of surface protective films. It is generally agreed that in ordinary corrosion the most stressed part is anodic. The lower concentration of dissolved oxygen at the base of a fissure acts in the same way to render the metal more anodic. Cyclic stress above a certain value tends to prevent the formation of natural protective coatings of self-healing films. In corrosion fatigue these three tendencies probably work together in the same direction to accelerate the rate of penetration. The results of their tests confirmed McAdam's experimental work as to the effect of corrosion on the fatigue of steel, and also showed that sufficient inhibitor (sodium dichromate) added to the water to stop corrosion in the presence of fatigue prevents the reduction of the air fatigue endurance limit when the metal is subjected simultaneously to cyclic stress and ordinary corrosion. They also concluded that external factors which tend to localize corrosion have a dominating influence in determining the point of failure under corrosion fatigue, and that this effect can be neutralized to a certain extent by the use of inhibitors of sufficient strength. The need of developing protective coatings that will not break down in service under cyclic stresses was pointed out.

#### VI. Some remarks concerning principles of corrosion-resistance testing.

Information regarding the suitability of any particular metal, or the comparative merits of two or more metals, for a definite purpose, as the construction of structures, apparatus, etc. is oftentimes desired, especially in connection with the development of new products with improved corrosion-resisting properties. The conditions of service vary so greatly that it is, so far, impossible to predict the life of any ferrous material in any given service. The most reliable method is, of course, to build the material into a structure and test the latter to destruction under service conditions to which the material is intended to be exposed. This procedure is generally expensive, or prohibitive in cost, and a considerable period of time may elapse before any conclusive results are obtained. Each of the metals and alloys now available is known to be well able to resist corrosion under some conditions and poorly able to resist it under others. To defeat corrosion, one must adapt the materials to the conditions of service or alter the conditions to meet the requirements of the material.

The question would arise as to how small-scale tests of reasonably short duration may be developed that will give results truly indicative of the behavior of the material under actual service conditions. Such an "accelerated test" should be so designed that it will reproduce as fully as possible all the important factors involved in service exposure. Unless direct correlation is shown between a given accelerated test and a given service, the accelerated test serves the purpose only for what it indicates rather than what it might at first sight appear to prove.

Some accelerated tests certainly give useful information, whether or not they correlate exactly with service results. Much of the corrosion data in the literature, either based on laboratory tests or service records, has to be read with the realization that different results might be obtained under conditions other than those to which the data refer. More reliable results can generally be obtained in corrosion testing by allowing the corrosion to proceed continuously or by frequently repeating the cycles of operation than by intensifying a single factor for the sake of rapid acceleration.

A common error in the consideration of corrosion tests is to assume that satisfactory or unsatisfactory performance under one set of conditions means that performance will be similar under another set of conditions. The relative standing of different materials is very often altered as the conditions are altered. An example of this is the rather commonly used method of testing the comparative corrosion resistance of ferrous materials by immersing specimens in an acid solution and noting the loss in weight due to solution. It would be fruitless to test two different materials in any one specific acid, if one or both of the materials are to be exposed in service to a different acid, for the two materials may show entirely different corrosion-resisting qualities in the latter acid. Another and an important consideration is that in the laboratory acid corrosion tests, which may consist of simple immersion in a quiet solution, the effect of oxygen often is not a prominent factor while under service conditions the oxygen would play a far more important role, as in the movement or agitation of the liquid, resulting in a greater degree of corrosion due to the aeration of the liquid. Thus, these two materials may show a comparative behavior, when exposed to aerated conditions, markedly different from that in simple immersion under quiet conditions in the same acid solution.

The American Society for Testing Materials, through its Committee A-5, has very recently reiterated its stand concerning the trustworthiness of the rapid tests of materials by acid immersion, as follows (Proc. Am. Soc. Testing Materials, Vol. 23, Part I - not due to come off the press before the end of 1929): "Notwithstanding the fact that this committee, in its annual report of 1909, pointed out as clearly as it could that the tentative suggestions made by it in 1907 as to the conditions for carrying out the so-called acid corrosion test were not to be considered a recommendation of the test, and that the results of such test are unreliable as truly measuring the tendency to natural corrosion, the name of the American Society for Testing Materials continues to be used as having recommended the acid corrosion test, and by inference as having endorsed the same. For this reason the Committee desires at this time to again disclaim any recommendation or endorsement of the acid test as a measure of natural corrosion, and to point out that any use of the name or authority of the American Society for Testing Materials in this connection is unwarranted."



At the Bureau of Standards a couple of years ago a study was made of the comparative effect several selected corrosion testing methods would have on the determination of corrosion resistance. Several copper-nickel alloys, together with copper and nickel, all of commercial grade and in sheet form, and six corrosive solutions were used for this investigation. Four types of corrosion testing methods, three of which have found, to some extent at least, practical application in corrosion-resistance testing, were employed for applying the corrosive solutions to the specimens so as to obtain a wide range in the possible effect of aeration and film formation. The corrosion rate and order of relative corrodibility of the five materials were found to vary very considerably for the different testing methods, thus showing that a corrosion test designed to give information concerning the suitability of a metal for some particular type of service should embody the essential features of the service which is to be met. A report of this investigation has been published as a Bureau of Standards Technologic Paper No. 337, "Effect of the Testing Method on the Determination of Corrosion Resistance" by H. S. Rawdon and E. C. Groesbeck. Later another investigation was undertaken to determine the relative merits of certain laboratory accelerated corrosion testing methods for evaluating the "life" of the zinc coating on iron and steel coated by the hot-dip galvanizing process. The "simulated atmospheric corrosion" test method, in which the specimens were subjected to repeated cycles of exposure first to a muggy acidic atmosphere, simulative in a concentrated degree of that prevailing in certain heavy industrial districts, then to a rain-like washing action and finally to a drying period, was found to reproduce corrosion phenomena much more like those occurring in service conditions than the spray test method. The spray method, when used with a solution of either sodium chloride or ammonium chloride of normal strength, failed to reproduce a progressive corroding away of the zinc coating in a manner similar to that occurring in the atmosphere under service conditions. A report of this work has been published in the Bureau of Standards Journal of Research, 1, No. 2, August, 1928 ("Accelerated Laboratory Corrosion Test Methods for Zinc-Coated Steel" by E. C. Groesbeck and W. A. Tucker).





