

(January 5, 1935).

THE CORROSIVITY OF SOILS

The following abstracts and summaries have been prepared from publications relating to soil corrosion of ferrous and non-ferrous metals and are intended to give a fairly complete outline of recent investigations in this field. They do not fully cover the various theories of corrosion, but apply more particularly to practical investigations under field conditions. Where more detailed information is desired, the unabridged articles should be consulted.

Bureau of Standards publications referred to may be obtained from the Superintendent of Documents, Government Printing Office, Washington, D.C., at the prices indicated below, or may be found in libraries in many cities. A complete journal reference for each paper is given in the text. The prices quoted are for delivery to addresses in the United States and its possessions, Canada, Cuba, Mexico, Newfoundland, and the Republic of Panama; for delivery to other countries add one-third of price of paper in your remittance. Remittances should be made payable to the "Superintendent of Documents, Government Printing Office, Washington, D.C." and sent to him with the order.

Logan, K.H., S.P.Ewing, and C.C.Yeomans, Bureau of Standards soil corrosion studies. I. Soils, materials and results of early observations. Tech. Pap. BS 22, 447 (1927-1928); T368, 50¢.

Logan, K.H., and V.A.Grodsky, Soil corrosion studies, 1930 - Rates of corrosion and pitting of bare ferrous specimens, BSJ. Research 7, 1 (1931); RP329, 10¢.

Logan, K.H., Soil corrosion studies - Nonferrous metals and alloys, metallic coatings and specially prepared pipes removed in 1930, BS J. Research 7, 585 (1931); RP359, 10¢.

Logan, K.H., and R.H.Taylor, Soil corrosion studies 1932. Rates of loss of weight and pitting of ferrous and non ferrous specimens and metallic protective coatings, BS J. Research 12, 119 (1934); RP638, 5¢.

Denison, I.A., and R.B.Hobbs, Corrosion of ferrous metals in acid soils, J.Research NBS 13, 125 (1934); RP696, 5¢.

1. Shipley, J.W., (University of Manitoba), The corrosion of cast iron and lead pipes in alkaline soils, J.Soc.Chem.Ind., 41, 311 (September 30, 1922).

Summary on corrosion of cast iron. (1) The corrosion of cast iron by soil salts is of the graphitic softening type. (2) Magnesium salts are the most corrosive of the soil salts, and magnesium sulphate is the most effective of the salts experimented with. (3) Local action induced by naturally occurring concentration cells may easily be a factor in the soil corrosion of cast iron pipes. (4) The presence of calcium sulphate in a limy silt soil gives a slight acidity to the ground waters. (5) Auto-corrosion of the cast iron is promoted by this acidity of the ground waters due to the stimulation provided to the graphite-iron galvanic couple by the presence of the hydrogen ion. Iron more readily displaces hydrogen when the latter is present in the ionic condition.

The soil corrosion of iron structures is thus seen to be an electrochemical process, complicated by its dependence upon several variables, of which the composition of the metal in the structure, the nature of the soil in contact with the metal, and the movements of the ground waters are the most important.

Summary on corrosion of lead. (1) Salt solutions attack lead, a carbonate of lead being the final product when exposed to the air. (2) Sodium carbonate was the most corrosive of the salts experimented with. (3) Lead cathodes exposing an area of 37.5 square centimeters are not attacked by currents of from 4 to 10 milliamperes. (4) "Coefficients of corrosion" are not applicable to electrochemical decomposition. (5) The presence of ammonium nitrate appears to inhibit corrosion by the formation of a protective coating of lead oxide over the surface. Such a protective coating may only be temporary. (6) The soils of the Winnipeg district have a decidedly corrosive action on lead, the nature of the corrosion being usually that of a crater-like pitting of the surface, with or without an adhering deposit of lead sulphate or carbonate. (7) Contact with a foreign substance localizes the corrosion. (8) The cause of the corrosion may be attributed to local galvanic action due to differences in the physical structure of the lead, to the presence of impurities lodged between the crystals of the lead, or to concentration cell effects.

2. Shipley, J.W., I.R.McHaffie, and N.D.Clare (University of Manitoba), Corrosion of iron in absence of oxygen, Ind. Eng. Chem., 17, 381 (April, 1925).

The corrosion of iron in the absence of oxygen is proportional to the hydrogen-ion concentration down to a pH of 9.4, when hydrogen evolution and solution of iron cease.

The rate of corrosion in the absence of oxygen is determined by the hydrogen-ion concentration, and the continuance of the corrosion by the total available acidity. If the solution in contact with the iron is not buffered, corrosion will continue, but at a diminishing rate and diminishing hydrogen-ion concentration until a pH of 9.4 is reached.

Oxidation of iron requires a potential a little less than the potential required for the evolution of hydrogen. Consequently, in the presence of oxygen, hydrogen will not be evolved at a H-ion concentration corresponding to the solubility of ferric hydroxide or lower.

The submerged corrosion of iron imbedded in impervious clay is due (1) to the buffer action of the clay at a H-ion concentration sufficiently acidic in the absence of oxygen to produce the evolution of hydrogen, and (2) to the lowering of hydrogen over-voltage by the thin film of solution on the extremely fine subdivision of the clay in contact with the metal.

The location of pits is determined by the constituents of the iron. When oxygen is present the migration of electrically charged colloidal particles of ferric hydroxide to cathodic areas on the metal perpetuates and enlarges these cathodic areas. The metal underneath becomes anodic. If the noncorrodible constituents are sufficiently cohesive, as is the case in gray cast iron, graphitic softening rather than pitting is produced, and no holing of the metal results.

3. Holler, H.D., Bureau of Standards, Corrosiveness of soils with respect to iron and steel, Ind. Eng. Chem. 21, 750 (August 1929).

A method of studying soil corrosion based on the relation of salt content, acidity, and corrosiveness of soil to rainfall is suggested. The corrosiveness of soils as indicated by the initial losses of buried specimens in humid areas of the United States has been correlated with their acidity.

The total acidity of soils may be estimated by titration using the hydrogen electrode; and also by comparing the pH value of the soil in water and in a potassium chloride solution. A relation exists between the ability of a soil to react on iron with liberation of hydrogen and its total acidity as indicated by titration.

The corrosiveness of a soil in humid regions may possibly be indicated by its total acidity or by its action on iron with evolution of hydrogen.

4. Logan, K.H., S. P. Ewing, and C. D. Yeomans, Bureau of Standards soil-corrosion studies. I. Soils, materials, and results of early observations, Tech. Pap. BS 22, 447 (1927-1928); T368.

This is the first report of an extensive investigation of soil corrosion which the Bureau of Standards started in 1922. At that time a large number of specimens of different commercial pipe materials were buried in 47 locations throughout the country representing a wide variety of soil types. A list and description of the materials under test is given, as well as a technical description of the 47 soils.

At approximately two-year intervals representative samples have been removed and the extent of corrosion carefully determined. Examinations after 1, 2, and 4 years permit no definite conclusions to be drawn regarding the corrodibility of different metals of similar groups. The work thus far shows that the type of corrosion of a group is influenced by the nature of the soil. Most soils are but slightly corrosive. In many cases the corrosion rate and pitting rate fall off with time. Galvanized pipes are in general more resistant to corrosion than untreated pipe. The corrosiveness decreases with increasing weight of zinc coating. Some soils corrosive to steel cause the formation of a protective film on zinc which affords good protection. Thin bituminous coatings yield insufficient protection against severely corrosive soils, probably because of the poor methods available for application. Lead and zinc fail by pitting in some soils, and aluminum is readily attacked. Copper and high-copper alloys are generally resistant in all soils. The investigation has not proceeded sufficiently far to warrant definite conclusions to be drawn regarding the relative merits of metals of the same type.

5. Logan, K.H., and V. A. Grodsky, Soil-corrosion studies, 1930.- Rates of corrosion and pitting of bare ferrous specimens, BS J. Research 7, 1 (1931); RP329.

This is a report of the Bureau of Standards soil corrosion studies based on the inspection of specimens which had been in the ground eight years. The results in general confirm the conclusions reached after previous inspections, as reported in Technologic Paper No. 368. Throughout the eight years during which the specimens have been exposed, characteristics of the soil rather than of the ferrous materials have controlled the kind and extent of the corrosion. Because there is a possibility that at later periods differences in the materials will result in appreciable differences in rates of corrosion, the Bureau believes that it should not make comparisons of materials at this time; moreover the data now available do not indicate that any one of these is best for all soil conditions. So far, materials which appear best under one soil condition have appeared inferior to some other material in a different soil.

A statistical study of the data shows that the standard error for the average performance of any one material in all soils is between 6 and 10 percent. Considering the character of the investigation and the number of uncontrolled variables that influence the rates of corrosion, the precision of the data appears somewhat better than was expected. It should be remembered, however, that the data record only what has happened and not what will be the result at the conclusion of the work.

Rates of corrosion vary somewhat from year to year because of settling of the trench in which the specimens were buried and changes in the supply of moisture. There is no constant relation between the rate at which specimens lose weight and the rate at which the depth of pits increases. Some soils cause the materials to pit badly, although the pitting results in comparatively little loss of weight. In other soils the corrosion is more uniformly distributed over the surface of the material, and a considerable loss of weight occurs with a low rate of penetration. As, in most installations of pipe, much thicker material is used than is necessary to withstand the pressure of the fluid carried, the loss of weight is not of great importance if uniformly distributed, but the formation of even a few deep pits may be a serious matter.

Rate of pitting, therefore, rather than rate of loss of weight is frequently the best indication of the corrosiveness of a soil. While data to be secured later may indicate relative merits of materials, the data so far obtained are chiefly valuable in connection with the study of field methods for determining soil corrosivity. When these methods are further developed, it will be practicable to make a soil-corrosion survey, from the results of which the owner can tell whether he should use a corrosion-resistant pipe material or apply a protective coating to his line.

6. Logan, K.H., Soil-corrosion studies - Nonferrous metals and alloys, metallic coatings and specially prepared pipes removed in 1930, BS J. Research 7, 585 (1931); RP359.

The information concerning soils which has been obtained as the result of the Bureau's soil-corrosion investigations makes it clear that the rate of corrosion of any metal exposed to soil can not be accurately expressed by a single figure or group of figures. On account of the variations found in all soils, the influence of the character of the soil differences in contact between the soil and the metal, changes in the supply of oxygen and moisture, and the effects of the corrosion products, the best that can be hoped for is an expression representing the average rate of loss of weight or pitting accompanied by a figure for the standard deviation, probable error, or some other expression indicating how much the behavior of any single specimen may be expected to differ from the behavior of the average of a representative group of specimens.

Average values sufficiently accurate to show small differences in the performance of competing materials can only be secured through the testing of a very large number of specimens. Since in any one case any material may prove considerably better or worse than the average, it is doubtful whether the drawing of fine distinctions between materials would be of practical value except for the consumers of very large quantities of materials. Attention should, therefore, be directed chiefly to the unmistakable differences between different kinds of materials rather than to possible small differences between nearly similar materials.

The most general conclusion to be drawn from the data is that for best results the material must be chosen to fit the soil in which it is to serve, since no one material is best for all soil conditions. Another general conclusion is that small differences in the data should not be considered significant, since it is improbable that a repetition of the test would yield identical results.

In nearly all soils copper and alloys high in copper resist corrosion well. Muntz metal shows at least slight dezincification after six years burial in half of the soils investigated and serious dezincification in a few of them.

In nearly all of the soils considered, lead corroded much less rapidly than iron or steel. The rates of pitting of commercial lead specimens were 3 mils per year or greater in 25 percent of the soils. The lead containing antimony showed rates of pitting greater than 3 mils per year in nearly 50 percent of the test locations.

The outer metallic ribbon of the parkway cable showed corrosion in most test locations. The inner ribbon was somewhat less corroded. Serious pitting of the lead sheath occurred only in the soil containing alkali carbonates.

All of the metallic coatings tested appeared to increase the life of the material to which they were applied. Comparison of the effectiveness of the metallic coatings is difficult because they differed in thickness. All coatings showed evidences of deterioration in several soils. In most of the soils, there was no evidence that the rate of penetration by pitting increased after the lead coating had been punctured. The possibility is suggested that the relative positions of lead and iron in the electrochemical series depends upon the soil in which specimens composed of lead and iron are placed. The precision of the data is insufficient to show at this time whether one base material is better than another for galvanized sheets to be used underground, but it appears that any difference which may exist is not great.

7. Bridge, A.F., and F.A.Hough, Copper pipe for gas distribution, Gas Age Record, 69, 503 (April 23, 1932).

General Conclusions. (1) In many corrosive soils the rate of corrosion of copper is less than that of steel by an amount sufficient to justify its use for gas services and for two-inch and three-inch mains, provided internal corrosion is not a limiting factor. (2) If, in a given soil, copper does corrode rapidly, usually an alloy high in copper content can be found to which conclusion (1) applies. (3) Copper pipe is probably unsuited for underground pipe in areas where stray current electrolysis is severe. (4) Copper pipe should not be used to distribute gas containing as much as one grain of hydrogen sulphide per 100 cubic feet, unless the gas is dry. (5) Undehydrated oil gas as ordinarily purified, will corrode copper pipe. (6) The corrosion of copper pipe by purified but undehydrated oil gas, is more rapid than that due to many corrosive soils. (7) Dehydration greatly reduces the rate at which the corrosive gases, normally present in purified manufactured gas, attack copper. (8) From the standpoint of both mechanical strength and soil corrosion resistance, a wall thickness of 0.065 inch (No.16 gage) is sufficient for copper gas mains and services three inches in diameter and smaller. (9) Brazed joints are satisfactory for copper pipe in soils that do not tend to dezincify bronze. (10) Soldered copper-sleeve joints appear to be satisfactory for both mains and services in all soils. (11) When a reduction in pipe size is permissible, it is practical and economical to replace old mains and services by using them for conduits for copper pipe, thus avoiding much cutting of pavement and lawns. (12) Because of the low cost of installation, the use of copper pipe inside existing steel mains and services is fully justified, regardless of the rate at which the soil attacks steel. (13) When chemical and physical conditions are such that copper pipe can be used, it is economically sound at now existing prices, to use it for two-inch and three-inch mains in soils where the life of wrapped steel mains is less than 19 years, and for services in locations where wrapped steel services have an expectancy less than 22 years. (14) If the mains and services are to be installed under expensive pavement, the required life for wrapped steel mains given in item no. 12 above, is increased to 22 years and that for services, to 25 years.

8. Scott, G.N., Adjustment of soil corrosion-pit depth measurements for size of sample, Proc. Am.Pet.Inst. 14, 204 (1933).

About 8,800 pit-depth measurements on small isolated specimens and 7 actual operating pipe lines have been studied with reference to their significance as a measure of soil corrosion.

1. The important facts upon which this paper is based are:
 - (a) Pit-depth measurements involve the selection of the deepest pit from an array of individuals.
 - (b) The value obtained for the deepest pits is dependent upon the size of the sample (number of specimens or surface extent) from which it is selected.

2. These generalizations lead, for any rational distribution of pit depths, to the following qualitative axioms stated in terms of the problem at hand; all other things being equal, and in the long run:

- (a) The larger the number of specimens, the deeper the maximum pit that will be obtained.
- (b) The larger the size of the specimen, the deeper the maximum pit and the larger the average maximum pit.
- (c) The larger the area (diameter and length) of a pipe line, the deeper the maximum pit, and the average of a number of deepest pits from a number of equivalent areas, and the shorter the time for the first puncture of the pipe wall.

3. The quantitative relation between the average deepest pit and the number or area of the specimens will depend upon the law of distribution of pit depths (shape of the distribution curve). For the distributions of pit depths considered in this investigation an empirical linear relation between the logarithms of average pit depths and area reproduces the experimental data satisfactorily for all practical purposes within moderate ranges of area. The formula $\log \bar{P} = a \log A + \log b$ where \bar{P} is the average maximum pitting on each of a number of specimens of area A and a and b are parameters. This equation can be transformed into

$$\frac{P_2}{P_1} = \left(\frac{A_2}{A_1}\right)^a$$

where P_1 and P_2 are average maximum pit depths on areas A_1 and A_2 . The parameters a and b are functions of soil and pipe conditions.

4. The distributions of pit depths on pipe lines apparently vary with the character of the pipe material and the character of the soil, but have two noteworthy characteristics in common.

- (a) The distribution curve is asymmetrical, the range of the pit depths less than the average being invariably smaller than the range of the pit depth greater than the average.
- (b) The spread of the pit depths (standard deviation of the distribution) is large in comparison to the average magnitude of the effect (mean) itself.

5. Two illustrations of the practical use of the pit depth-area relation have been given in detail.

(a) An economical method employing a limited number of measurements for obtaining a figure for the average maximum pitting, associated with a given area, of a section of pipe line has been suggested and illustrated.

(b) Factors by which data on pit depths obtained from small soil-corrosion specimens must be multiplied to convert these data to a basis comparable to what would be obtained for the average pitting on 20-ft. lengths of 8-in. pipe have been calculated for a set of assumed conditions.

6. Since average maximum pit-depth measurements have little or no significance unless the area over which the measurements are made is specified, it has been suggested:

(a) That pit depth be taken consecutively on each running foot of pipe, within the extent of the inspection hole, and that preferably 8 or more, but certainly not less than 4, such measurements be taken per hole.

(b) That all pit-depth measurements on pipe lines be corrected to a standard area of 45.16 sq. ft. corresponding to a 20-ft. length of 8-in. pipe when comparison with data from different sources is intended.

9. Scott, G.N., A preliminary study of rate of pitting of iron pipe in soils, Proc. Am. Pet. Inst., 14, 212 (1933).

Pit depth measurements are usually reported as rates, i.e. pit depths divided by time. Since it is now well established that the corrosion time curve for iron in soil is far from linear, this method of reporting results is misleading. As the theoretical derivation of a quantitative relation would involve several factors, it is much simpler to find an empirical equation which approximately fits the available data. The equation

$P = \frac{UT}{B+T}$ expresses roughly the relation between depth of pitting and time for a considerable number of soil conditions. In this equation P = pit depths, T = time, U and B are parameters depending on soil or other conditions. The value of B is usually approximately 5. U is the ultimate value of P .

Substituting the wall thickness of the pipe W for P and the time for puncture L for T the above equation can be written

$$L = \frac{WB}{U-W}$$

which gives the time to puncture of a pipe of known wall thickness when the soil parameters are known.

The paper also gives explanations for the change in rates of pitting with time.

10. Logan, K.H., The use of Bureau of Standards soil corrosion data in the design and protection of pipe lines, Am. Soc. Test. Mtls. Trans., 34, Part 2, 138 (1934).

The average maximum pit on a group of specimens increases with the area of the individual specimens. The pitting rates in the Bureau of Standards data are based on what is approximately equivalent to the observation of the maximum pit on 0.23 sq. ft. of pipe surface. This is equivalent to the observation of the deepest pit on 0.1 linear foot of 8-inch pipe or the averaging of the ten deepest pits per foot of such pipe. The magnitude of this value is obviously less than The single deepest pit on a length of pipe. In applying Bureau data to the estimation of the life of a pipe line the data given must therefore be adjusted to take account of the area of pipe involved.

The dispersion of the data is such as to make impossible detection of small differences in the performance of different materials. Since the uniformity of conditions under which the Bureau tests were conducted is greater than that of conditions to which working lines are exposed, the dispersion of the Bureau data also indicates that no conclusions should be drawn from the relative performance of a very limited number of field observations.

The Bureau data indicate that in most of the test locations the rates of corrosion during the first four years were greater than the rates for longer periods. Curves showing the relation of pit depth to time for the first ten years are hyperbolic in form but if only the data for specimens four years old or older are considered straight lines indicate the progress of pitting as well as any other form of curve. It is possible therefore that if the pitting over a long period is to be considered a straight line can be used to express the corrosion-time relation without appreciable error although the line would not pass through the origin of the coordinates.

Corrosion on pipe lines may be more rapid than that on the Bureau specimens in similar soils because of additional factors tending to destroy the lines.

If the relatively rapid corrosion during the first few years after a pipe is buried is due to differential aeration of the pipe resulting from non-homogeneous backfill a coating which will protect the pipe until the soil has settled around it will extend the life of the pipe longer than the time required for the coating to deteriorate.

11. Shepard, E.R., Some factors involved in soil corrosion, Ind. Eng. Chem. 26, 723 (July, 1934).

The rate of penetration from soil corrosion is affected by the character of the corrosion. Uniform corrosion progresses at a much slower rate of penetration than localized pitting. The reason for this is to be found in the character of the electric circuits involved in the two types of corrosion. Electric currents which take the form of radial stream lines from the surface of a pipe, and thereby produce uniform corrosion, encounter a very much higher circuit resistance than currents which assume divergent stream lines such as occur in pitting action. Mathematical relations between current densities and other factors are developed.

Other things being equal, the density of discharge of current from the surface of a pipe to a remote ground is inversely proportional to the diameter of the pipe. This principle accounts in some cases for excessive corrosion of pipe threads, fittings, flange bolts, and other points of prominence or sharp curvature on underground metal structures. Where corrosion is the result of a general discharge of current from one portion of a metal system to some other portion of the system, the density of the discharge at any point is affected as much by the curvature of the surface as by the electrical resistivity of the surrounding soil.

Bright iron is found to be anodic with respect to iron covered with mill scale when the two are buried in soil. The initial potential difference between a pair of such specimens ranges from 0.15 to 0.6 volt, depending upon the kind of soil. When the specimens are shortcircuited for a period of weeks the open-circuit potential difference between the two usually falls below 0.06 volt and in some soils has been found to reverse.

In most soils the local action on bright iron specimens is much greater than the circuit action between such specimens and those covered with mill scale.

A continuous and unbroken film of mill scale retards soil corrosion but a discontinuous film permits excessive corrosion at points where the bright iron is exposed.

The unequal distribution of oxygen on buried metal surfaces appears to be the chief source of galvanic potentials. Under such conditions areas deficient in oxygen are anodic with respect to those areas having a greater supply of oxygen.

Unequal distribution of oxygen occurs in dry or porous soils and in non-homogeneous soils. The supply of oxygen varies with the depth, with moisture content, with the topography, and with the nature of the soil. All such irregularities give rise to galvanic currents, the character of the circuits depending upon the degree of irregularity.

Potential differences of from 0.6 to 0.9 volt have been observed between iron surfaces in contact with soils of different moisture content.

Over a period of 60 days, iron specimens were found to corrode faster and pit deeper in soils of low moisture content than in those of high moisture content. In the drier soils the corrosion took the form of rusting, while in the wet soils there was more of a tendency toward the formation of black iron oxide. The tests do not indicate what the rates of corrosion in the different soils would be over a period of years.

Soil resistivity is an important factor in soil corrosion but other factors of a less definite nature often are the controlling or major influences.

Many secondary effects such as polarization and the solubility and resistivity of corrosion products, of which little is known, may have a marked influence on the rate of corrosion.

The experiments here described are not of sufficient scope to base definite and final conclusions on but they may serve as a guide and stimulus for further study of the corrosion problem.

12. Denison, I.A., and R.B.Hobbs, Corrosion of ferrous metals in acid soils, BS J. Research 13, 125 (1934); RP696.

The rates of pitting of ferrous specimens at test sites located in acid soils are determined chiefly by the total acidity of the soils. The effect of acidity in inducing corrosion is attributed to its action in preventing the formation of protective layers of ferrous and ferric hydroxides. Low rates of corrosion in mildly alkaline soils result from the partial exclusion of oxygen from the cathodic surfaces by adherent hydroxide films. High rates of corrosion in very acid soils are explained by assuming that the metal ions diffuse readily outward into the soil and that the acidity of the soil neutralizes hydroxyl ions as they are formed at the cathode, thereby preventing the formation of a protective rust layer.

A correlation between the corrosion of specimens in a laboratory test and the total acidity of soils has been obtained. The laboratory test consists in measuring the loss in weight of small steel disks which have been maintained in contact with moist soils for a period of two weeks.

The pitting factor, defined as the ratio of the maximum depth of pits to the average depth of penetration is shown to be roughly proportional to the rates of uncorroded to corroded area on a metal surface.

Measurements of several physical properties of soils which determine their permeability are correlated with the pitting factor, indicating that the more permeable the soil, exclusive of sands, the greater is the tendency for corrosion to take the form of pitting, other conditions being the same. Certain very acid soils may be so impermeable that the rate of pitting in them is very low.

13. Scott, G.N., Application of a few statistical principles to corrosion problems, Oil & Gas J., 33, 74 (1934).

This is a mathematical paper setting forth a method for estimating the condition of a pipe line from a relatively few observations of pit depths along that line.