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CORROSION OF FERROUS METALS IN ACID SOILS

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ABSTRACT

Corrosion of ferrous metals in acid soils is influenced largely by the acidity of the soil. A definite correlation was obtained between the average rates of pitting of ferrous specimens exposed to acid soils for 8 and 10 years and the total acidity of the soils. A similar correlation was also obtained between the total acidity of soils and losses of weight of steel specimens in a laboratory test. The effect of acidity in inducing corrosion is attributed to its action in preventing the formation of protective layers of ferrous and ferric hydroxides. 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 ratio of the uncorroded to corroded areas on a metal surface. Measurements of several physical properties of soils which determine their permeability were 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 soils may be so impermeable that the rate of pitting in them is very low.

CONTENTS

I. INTRODUCTION

One of the most important conclusions which has been drawn from the National Bureau of Standards investigation of underground corrosion is that corrosion is determined by the nature of the soil rather than by the kind of ferrous material exposed to the soil. Consequently, efforts are being made to correlate the important physical and chemical properties of the soils at the test sites with their corrosiveness, as indicated by their behavior toward buried specimens of the commonly used pipe materials. Although these studies have not been completed, the results have indicated the influence of several properties of the soil in producing corrosion and have led to methods for estimating the corrosive action of soils.

Since the soils of the United States are diverse, it is to be expected that the causes of corrosion would differ in different classes of soils, and that methods used in estimating corrosiveness should be adapted to the general class of soil to be tested. It has been shown that in certain arid and semiarid regions measurements of the electrical resistivity of soils are useful as one means of predicting corrosion (1).[1] In more humid regions, such as the eastern United States, where the soils have developed varying degrees of acidity, a relation between corrosiveness and soil acidity might be expected, as has been suggested by one of the authors (2, 3).

The development of acidity in soils is a result of natural processes of weathering under humid conditions. In the soils of arid and semiarid regions of the West and Southwest accumulations of soluble salts are of frequent occurrence, but in the more humid regions the rainfall has been sufficient to remove such salts to a considerable extent. In regions of high rainfall not only have the soluble salts and the difficultly soluble carbonates been removed but also the absorbed bases normally present in the colloidal material of the soil have been partly removed and replaced by hydrogen ions. This process eventually gives rise to the condition known as soil acidity. The depth to which this replacement of bases has occurred varies with rainfall, drainage, type of vegetation, and nature of the parent material. The fully developed soils of the prairie region have become acid to a considerable depth, while soils whose development has been retarded by imperfect drainage or by other conditions are alkaline and may even contain appreciable quantities of salts. East of the prairies, the well developed soils are generally acid throughout the soil profile.

Although many important soils occupying extensive areas are known to be very acid at the depth at which pipe lines are laid, little is definitely known concerning their action on ferrous metals, especially with regard to the mechanism of corrosion in such soils. In fact, a systematic study of the properties of acid soils which influence corrosion has not hitherto been possible owing to lack of adequate experimental data. However, with data now available from examination of specimens which have recently been removed from a large number of the National Bureau of Standards test sites after exposure to the soil for 10 years, the corrosiveness of the soils under study has been fairly well established.

The properties of acid soils which appear to be of primary importance in corrosion are the following: Hydrogen-ion concentration, total acidity, texture and the permeability to air and water. Although any one of these factors may possibly exert a predominant influence on corrosion in certain soils it would seem that in well-drained soils of similar texture a single factor such as hydrogen-ion concentration or total acidity might be correlated with corrosiveness. However, before considering the influence of acidity on the corrosiveness of the soils at the test sites, it is preferable first to review certain investigations of corrosion of submerged specimens in which the influence of the acidity of natural waters was specifically studied, and, secondly,

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[1] Figures in parenthesis here and throughout the text indicate references and notes given in the "References" at the end of this paper.

to study the relation between acidity and corrosion in a synthetic "soil" in which acidity is the only variable.

II. INFLUENCE OF ACIDITY IN SUBMERGED CORROSION

It is generally recognized that the acidity of the solution in contact with the metal surface is a factor of great importance in the corrosion of submerged ferrous materials. Baylis (4) has pointed out that the tendency for iron to go into solution would be a function of the H-ion concentration if there were rapid displacement of the solution in contact with the metal and no tendency to form a surface coating. From a large number of tests Baylis has determined the quantities of iron which can remain dissolved in natural waters at various pH values. Practically no iron was found in solution at pH 8 in the absence of oxygen, whereas at pH 6.5 several hundred parts of (ferrous) iron per million remained in solution. The effect of oxygen on such a system in equilibrium is, according to Baylis, to precipitate iron as ferric hydroxide, and to establish an equilibrium at a much lower pH. Baylis has further pointed out that the tendency for iron to go into solution is so great at the pH values of natural waters that the life of iron pipe depends almost entirely on the factors which retard corrosion. The most important of these factors is, of course, the formation of films or protective layers of corrosion products.

The influence of the acidity of water containing oxygen on the protectiveness of rust films has been extensively studied by Whitman, Russell, and Altieri (5) and by Whitman and Russell (6). Employing the oxygen absorption method, these investigators studied the rate of corrosion of iron in a natural water at various pH values and at several oxygen concentrations. They found that between approximately pH 9.5 and 4 the rate of corrosion was unaffected by the H-ion concentration of the main solution, but was determined by the rate at which oxygen diffused to the cathodic surface, and by the protectiveness of the hydroxide film formed on the metal surface. The protective action of this film in water having a pH value as low as 4 was attributed to the fact that the quantity of hydrogen ions coming in contact with the metallic surface was insufficient to neutralize and dissolve the film. However, when carbon dioxide was introduced, rapid corrosion occured at pH 5.4, because then the increased total acidity of the water was sufficient to neutralize the hydroxide film. This result led to the conclusion that total acidity is more important in corrosion by natural waters than is the actual concentration of dissociated hydrogen ions in the solution, i.e., the pH value.

In applying to corrosion in soils the relations between acidity and corrosion which were observed by Whitman and Russell, it should be noted that the acids present in soils are extremely weak. Because of the very slight dissociation of the soil acids, the pH value of a soil may offer no indication of the capacity of the acidic material to prevent the formation of an otherwise protective layer of the hydroxides of iron. A soil having a high pH value and a high total acidity would be expected to be more corrosive than a soil having a low pH value and a low total acidity, because of the greater ability of the soil with the high total acidity to prevent the formation of a protective hydroxide layer.

Further information concerning the influence of total acidity in submerged corrosion can be obtained from the study of systems in which the pH value of the solution was sustained by adequate buffering. Shipley and McHaffie (7) introduced iron filings into solutions buffered at several pH values and found that the rate of hydrogen evolution in the absence of oxygen was directly proportional to the hydrogen-ion concentration of the solution.

Holler (8), as a result of his study of hydrogen evolution from iron filings in contact with soil in the absence of oxygen, found a logarithmic relation between the total acidity of the Bureau soils and the volume of hydrogen evolved, and suggested that the corrosiveness of soils in humid regions might be predicted from their total acidity.

It is seen from these studies that the rate of corrosion of ferrous materials under certain conditions is definitely related to the acidity of natural waters and of soils. It has also been noted that with a definite oxygen concentration the rate of corrosion is determined by the total quantity of ionizable hydrogen which comes in contact with the metal surface, rather than by the hydrogen ion concentration of the corrosive medium. Unless the quantity of acid which comes in contact with the metal surface is sufficient to prevent the formation of protective hydroxide films, these films will tend to form regardless of the H-ion concentration (within the range of natural waters). Although the work of Shipley and of Holler, previously cited, leaves no doubt concerning the relation between total acidity and the corrosion of iron in soils in the absence of oxygen, the influence of acidity in soils in the presence of oxygen is not well understood. Since oxygen is usually present in moderately drained soils, it is important to ascertain the influence of acidity on the rate of corrosion of iron in the presence of oxygen.

III. INFLUENCE OF ACIDITY ON CORROSION OF STEEL IN SYNTHETIC SOIL

The influence of acidity on the corrosion of steel in soil in the presence of oxygen was studied by means of a laboratory corrosion test, which has been described in a previous publication (2). The test consisted in determining the loss of weight of a steel disk in contact with moist soil for a period of 2 weeks.

For the present study a synthetic soil consisting of quartz flour with 10 percent of agar was employed. The acidity of the material was regulated by additions of a mixture of *N* sodium acetate and *N* acetic acid in such proportions and concentrations as to produce the desired pH and total acidity. The latter was computed from pH 8.3, the neutral point of sodium acetate. These mixtures were employed because of their marked buffer capacities, which allowed large changes in total acidity with relatively small change in hydrogen-ion concentration. The use of buffer solutions gave the added advantage of allowing the pH range to be confined to that normally shown by soils.

The corrosion cells were prepared in triplicate according to the following procedure. The surface of each specimen, which consisted of a disk of cold rolled steel 1.74 in. (44.5 mm) in diameter and 12 mils[2] (0.3 mm) thick, was prepared by rubbing with 1G French

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[2] 1 mil=0.001 inch or 0.025 mm.

emery paper and cleaning with ether and alcohol. After weighing, one face of the disk was lacquered in order to confine corrosion to one face only, and the disk was placed in a straight-side crystallizing dish of slightly greater diameter with the unprotected face uppermost. The disk was then covered with 20 g of a quartz flour-agar mixture which had been previously prepared by saturating the material with water, drying slowly on a steam bath, and then crushing the lumps to pass a no. 20 sieve. The material was then compacted by rotating on its surface a brass cylinder weighing about 500 g. A sufficient quantity of the buffer solution was added to produce the desired acidity in terms of milliequivalents of hydrogen per 100 g of soil and to bring the moisture content of the soil up to 40 percent of its dry weight. Each corrosion cell was then inserted in a 1-pint (500 ml) preserving jar in which a small amount of water had been added to produce a saturated atmosphere, and the jars were seled and placed in a chamber maintained at 25 C. In order to maintain the partial pressure of oxygen within the jars approximately the same as that in the outside atmosphere the jars were opened for a few minutes every 5 days. At the end of the test period the disks were removed and cleaned by alternate brushing and immersion in warm 10 percent ammonium citrate solution made alkaline with ammonium hydroxide. The loss of weight was calculated as average rate of penetration in mils per year. Most of the values shown in figure 1 are the averages of three (others of two) concordant results. The agreement of duplicates was usually within about 10 percent.

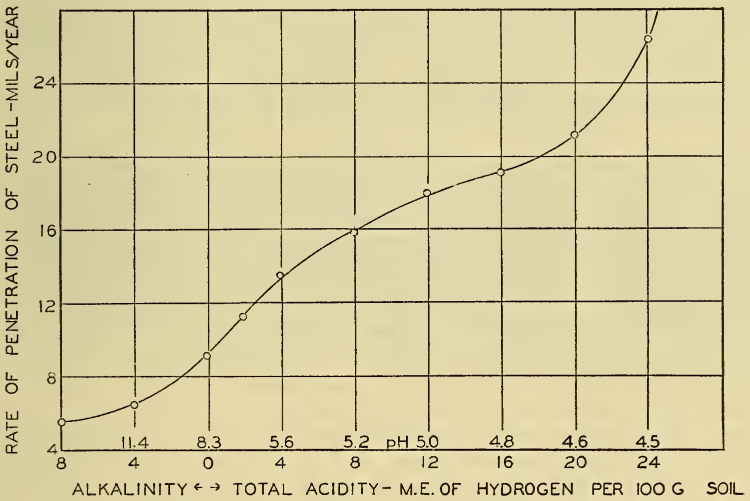

Figure 1.—*Relation between acidity and corrosion of steel in synthetic soil.*

The changes in the rate of corrosion shown in figure 1 can be explained according to the electrolytic theory of corrosion. In the extreme alkaline range, in which the rate of corrosion is very low, it is probable that local anodic areas set up by differential aeration could not develop rapidly because of the protective action of a layer formed by precipitation of ferrous and ferric hydroxide in immediate contact with the metal surface. In the range of slight alkalinity, where there is evidence of partial film protection, it is probable that ferrous and hydroxyl ions migrating along the surface in opposite directions between anodic and cathodic areas were precipitated over some intermediate area when their concentrations became sufficiently great, and thus reduced the accessibility of air to the active cathodic surface. In the acid range, diffusion of ferrous and hydroxyl ions was not restricted to directions parallel to the metal surface, but also occurred outward into the soil, where they came into contact with oxygen, which caused precipitation as ferric hydroxide. Accumulation of the metal hydroxides on the metal surface and in the soil mass, with consequent reduction in the access of air to the cathodic surface, would explain the diminution in the rate of increase of corrosion with respect to acidity. The sharp increase in the rate of corrosion in acid concentrations greater than 16 m.e. of hydrogen, at pH 4.8, accompanies rapid evolution of hydrogen gas in such soils.

IV. INFLUENCE OF ACIDITY ON CORROSION IN NATURAL SOILS

1. RELATION BETWEEN RATES OF PITTING OF BURIED SPECIMENS AND TOTAL ACIDITY OF SOILS

In a paper previously referred to (3) a correlation between the total acidity of soils at the National Bureau of Standards test sites and the rates of pitting of the ferrous specimens was indicated. Although the importance of soil acidity as a factor in corrosion was evident from this study, the nature of the relationship was indefinite because of uncertainty concerning the corrosiveness of the soils. However, with data available from measurements of corrosion made on buried specimens removed after 10 years, the corrosiveness of many of the soils becomes fairly well established and the relation between total acidity and corrosion can be more clearly defined.

From each site at each biennial inspection period, eight specimens of 1.5 in. (38 mm) pipe and eight of 3 in. (75 mm) pipe of each kind were removed. Each specimen was 6 in. (15 cm) long. As the results with pure open-hearth iron, wrought iron, Bessemer steel, open-hearth steel, and steel containing 0.2 percent of copper, were practically the same, the average values for the five kinds of pipe were used in the calculations. Similar results with cast-iron pipes were less concordant and were hence not included in these averages. The tendency for the depth of pits to increase with the area of the specimen was compensated for by averaging the single deepest pits on the 1½-in. specimens and the two deepest pits on the 3-in. specimens as described by Logan and Grodsky (9). The total area represented by the 24 measurements was 4.7 sq ft (44 dm^2).

In calculating the rates of pitting and of average penetration of the specimens the data for the five inspection periods were used. By plotting the depth of pits on the specimens from each site against the time of exposure and drawing a smooth curve through the points, a value is obtained for the average pitting rate during the first 10 years, which is based on 80 measurements instead of only the 16 measurements that would have been available if only the specimens removed after 10 years had been considered. The benefit of the larger number of measurements in the final result is that it minimizes the effects of

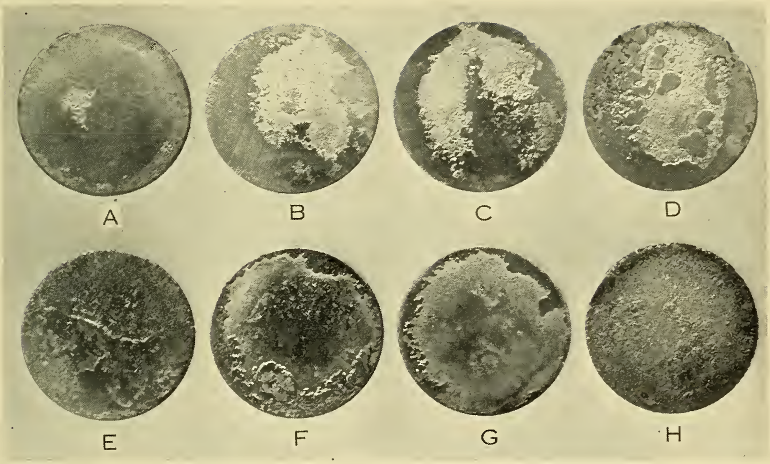

FIGURE 2.—*Appearance of specimens exposed to various soils in laboratory corrosion test.*

Specimen	Soil number	Soil type	Loss of weight	Specimen	Soil number	Soil type	Loss of weight
			gm				*gm*
A	20	Mahoning silt loam	0.074	E	3	Cecil clay loam	0.310
B	9	Genesee silt loam	.101	F	42	Susquehanna clay	.461
C	18	Knox silt loam	.186	G	7	Fairmount silt loam	.496
D	39	Sassafras silt loam	.201	H	43	Tidal marsh	.564

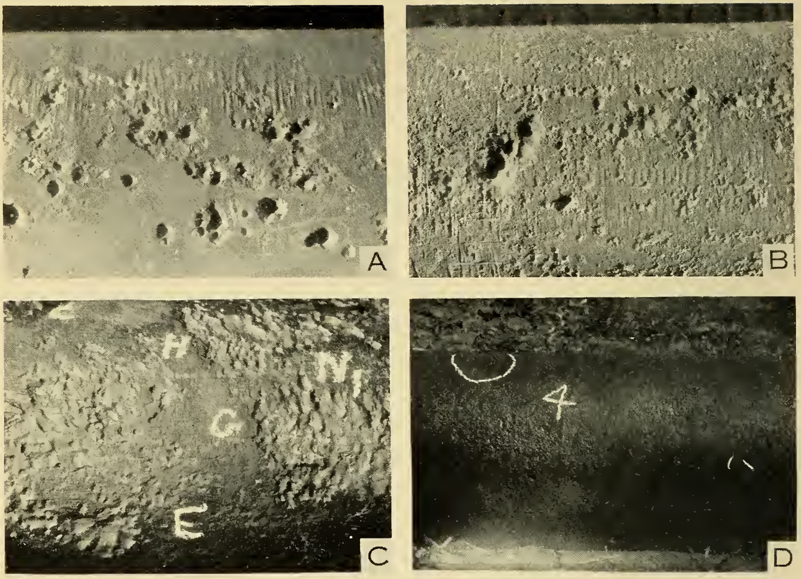

Figure 6.—*Types of corrosion observed on pipe lines.*

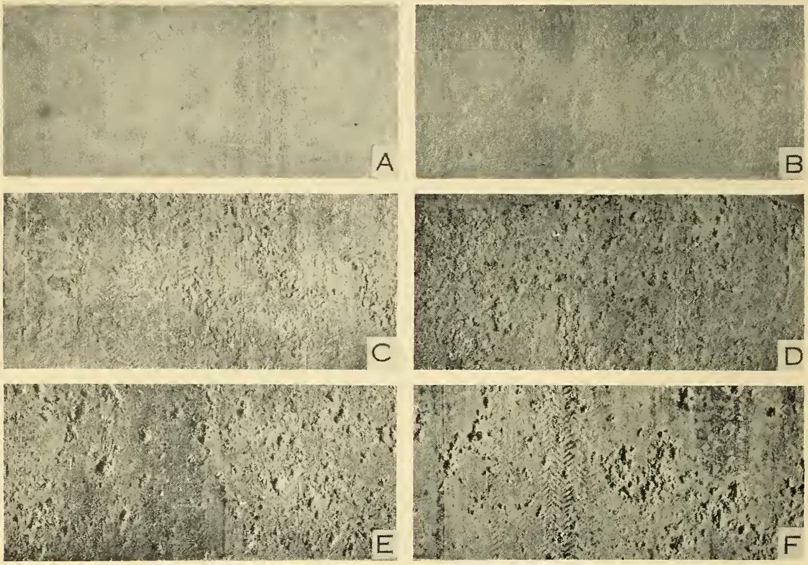

Figure 7.—*Types of corrosion shown by ferrous specimens in various soils.*

abnormal variations in the corrosiveness of the soil at any given site. An added advantage of this procedure is that it becomes possible to include in this comparison data of 8 years' exposure in soils from which the 10-year specimens have not yet been removed.

To supplement the data on the field specimens, laboratory studies were made of the corrosion of steel disks in samples of soil from the same test sites. The laboratory test was conducted as described in a previous section with a few modifications. Instead of protecting one surface of the disk with lacquer both surfaces were exposed to the soil. Five grams of soil were placed in the dish, the soil was compacted, and a definite quantity of water was added. The weighed disk was then placed in position, and two 10-g portions of soil were added with successive compression and addition of water. The quantity of water to be used for each soil was determined in preliminary tests by adding increasing amounts of water to corrosion cells and selecting the concentration which produced maximum corrosion. Since the moisture content for maximum corrosion did not differ by more than 5 percent from the moisture equivalent (the percentage of moisture retained by a definite weight of soil under a centrifugal force of 1,000 times gravity), it was sufficient in testing soils by this method to set up cells with only three moisture contents, namely, moisture equivalent, and 5 percent above and below moisture equivalent. In order to avoid corrosive action from the carbon dioxide produced by bacterial activity, a saturated solution of thymol instead of distilled water was used. This precaution was especially necessary in testing calcareous soils containing large quantities of organic matter.

As preliminary studies showed that the losses in weight of specimens in different soils were in about the same ratio for periods from 2 to 8 weeks, a 2-weeks period was adopted for the tests. The values in table 1 are averages of two or more concordant results. In most soils duplicate results were concordant. Except for very small values and occasional erratic results the agreement between duplicates was within 15 percent. The effects of different soils on steel specimens in the laboratory test are shown in figure 2 (for one month instead of the customary 2-weeks contact).

Determinations of total acidity were made by the methods described in previous publications (3, 10). The general method was based on the principle of electrometric titration. Soil extracts were prepared by adding to 10-gram samples of soil increasing amounts of a saturated solution (0.045 N) of $Ca(OH)_2$ in NaCl, and the pH values of these extracts, determined colorimetrically, were plotted against the quantity of alkali added. The inflection in the titration curve (usually at about pH 7.8) was taken as the end point of neutralization. For organic soils an indirect method was employed to avoid consumption of alkali by processes other than neutralization of acidity.

Determinations of hydrogen-ion concentration were made by the colorimetric method using a 1: 2 soil-water ratio. Each indicator was adjusted isohydrically to its acid, midpoint and alkaline range to avoid altering the pH value of the tested extract.

The electrical resistivity of the soils was determined by means of the wheatstone bridge, using alternating current. The soil samples were saturated with water, mixed thoroughly, and allowed to stand several hours before being tested. The values were corrected to

60 F (15.6 C). Descriptions of the soils have been given in a previous publication (11). It should be noted that soil 7, though so designated in table 1, is not Fairmount silt loam. Soils of the Fairmount series are alkaline below the surface, whereas the soil in question is very acid to a depth of 40 inches. The data obtained from the laboratory and field tests are summarized in table 1.

TABLE 1.—*Relation of soil properties to corrosion*

Soil number	Soil type	Depth	Location	Corrosion rates			Soil properties		
				Average rate of pitting of wrought specimens at 10 years	Rate of average penetration of wrought specimens at 10 years	Rate of average penetration of steel in laboratory	pH	Total acidity (milli-equivalents per 100 grams of soil)	Resistivity of soil at 60 F.
		In.		*Mils/yr*	*Mils/yr*	*Mils/yr*			*Ohms-cm*
1	Allis silt loam	90	Cleveland, Ohio	7.2	1.4	7.0	7.0	11.4	1,215
2	Bell clay	40	Dallas, Tex	4.5	.8	2.3	7.3	3.5	800
3	Cecil clay loam	32	Atlanta, Ga	7.5	.6	9.9	5.2	11.5	30,000
4	Chester loam	36	Jenkintown, Pa	6.0	1.0	6.8	5.6	7.6	6,670
6	Everett gravelly sandy loam.	36	Seattle, Wash	2.0	.2	1.8	5.9	12.8	45,100
7	Fairmount silt loam	40	Cincinnati, Ohio	3.4	.7	13.8	4.4	29.8	2,120
9	Genesee silt loam	22	Sidney, Ohio	(1)	.5	3.6	6.8	7.2	2,820
10	Gloucester sandy loam	30	Middleboro, Mass	4.4	.7	3.4	6.6	3.6	7,460
11	Hagerstown loam	60	Baltimore, Md	7.0	.3	9.2	5.3	10.8	11,000
14	Hempstead silt loam	60	St. Paul, Minn	11.5	.7	4.0	6.2	5.6	3,520
15	Houston black clay	36	San Antonio, Tex	6.0	1.1	5.9	7.5	5.0	570
16	Kalmia fine sandy loam.	30	Mobile, Ala	6.9	1.0	10.6	4.4	11.8	8,290
17	Keyport loam	36	Alexandria, Va	3.9	1.2	15.2	4.5	19.1	5,980
18	Knox silt loam	48	Omaha, Nebr	5.7	.5	5.9	7.3	1.4	1,410
19	Lindley silt loam	36	Des Moines, Iowa	6.0	.5	7.4	4.6	10.9	1,970
20	Mahoning silt loam	50	Cleveland, Ohio	4.1	.7	4.5	7.5	1.5	2,870
21	Marshall silt loam	36	Kansas City, Mo	6.5	.9	9.5	6.2	9.5	2,370
22	Memphis silt loam	33	Memphis, Tenn	6.0	1.1	6.9	4.9	9.7	5,150
24	Merrimac gravelly sandy loam.	33	Norwood, Mass	2.0	.2	3.0	4.5	12.6	11,400
25	Miami clay loam	36	Milwaukee, Wis	4.5	.3	3.1	7.2	4.7	1,780
26	Miami silt loam	48	Springfield, Ohio	(1)	.3	2.8	7.3	2.6	2,980
27	Miller clay	30	Bunkie, La	4.0	.8	4.4	6.6	3.7	500
29	Muck	24	New Orleans, La	10.9	2.3	11.1	4.2	28.1	1,270
30	Muscatine silt loam	36	Davenport, Iowa	4.1	.7	6.3	7.0	2.6	1,300
31	Norfolk sand	24	Jacksonville, Fla	4.0	.4	3.2	4.7	1.8	20,500
32	Ontario loam	48	Rochester, N.Y	4.5	.4	2.7	7.3	.5	5,700
33	Peat	24	Milwaukee, Wis	9.7	1.7	5.9	6.8	36.0	850
34	Penn silt loam	34	Norristown, Pa	6.5	.7	5.6	6.7	7.0	4,900
36	Ruston sandy loam	36	Meridian, Miss	4.7	.4	4.2	4.5	4.6	11,200
37	St. Johns fine sand	30	Jacksonville, Fla	7.3	1.3	7.2	3.8	15.3	11,200
38	Sassafras gravelly sandy loam.	30	Camden, N.J	3.0	.4	3.2	4.5	1.7	38,600
39	Sassafras silt loam	36	Wilmington, Del	5.7	.8	7.6	5.6	6.6	7,440
40	Sharkey clay	30	New Orleans, La	7.3	1.2	8.1	6.0	9.4	970
41	Summit silt loam	36	Kansas City, Mo	6.4	.8	9.7	5.5	11.0	1,320
42	Susquehanna clay	30	Meridian, Miss	9.7	1.6	17.9	4.7	28.2	13,700
43	Tidal marsh	36	Elizabeth, N.J	10.0	1.8	18.1	3.1	36.8	60
44	Wabash silt loam	30	Omaha, Nebr	7.1	.5	7.3	5.8	8.8	1,000

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[1] Not determined.

It will be seen from the table that the soils differ widely with respect to their corrosiveness and their acidity and resistivity. The rate of average penetration of the field specimens is seen to range from 0.2 to 2.3 mils per year (soils 6 and 29) and the rate of pitting from 2 to 11.5 mils (soils 6 and 14). Although the soils that show extreme pitting, i.e., 29, 33, 42, 43, also show large average penetration, there is no consistent relation between pitting and average penetration. The pH varies from 7.5 in soils 15 and 20 to 3.1 in the very acid tidal marsh soil, 43. The total acidity ranges from 0.5 m.e. in soil 32, to 36.8 m.e. in soil 43. There is no consistent relation between the values for hydrogen ion concentration and total acidity; soil 31, having a pH of 4.3, contains 1.8 m.e. of ionizable hydrogen, while soil 42, having the same pH value, contains 28.2 m.e. of hydrogen. Although the influence of the texture of the soil on corrosion will be discussed in a succeeding section, it may be noted at this time that the sandy soils, 6, 10, 24, 31, and 38, are relatively noncorrosive. The data for resistivity cannot be correlated with the corrosion data.

Although there are many exceptions, certain definite trends can be observed between corrosion, as indicated by the field and laboratory tests, and acidity, as indicated by the values for hydrogen-ion concentration and for total acidity. Soils having pH values above 7 (2, 15, 18, 20, 25, 26, 30, and 32) are relatively noncorrosive, while soils having low pH values (29, 37, 42, and 43) are corrosive. The well-drained sandy soils (6 and 24) do not conform to this relation.

If the values for total acidity are now compared with the rates of pitting, a fairly satisfactory correlation is seen. Thus, soils 1 and 33, which are corrosive in spite of their high pH values, have high total acidities. The pitting tendencies are more clearly indicated by the values for total acidity than by their pH values. Thus, according to pH, soils 1, 3, 4, 11, 16, 21, 39, and 41 would be grouped simply as moderately pitting soils. However, when arranged in the order of increasing total acidity, they stand in the order of their corrosiveness with respect to pitting.

In the light of the theoretical considerations advanced earlier in this paper it would be expected that the total acidity of soils would indicate their relative corrosiveness more exactly than would values for H-ion concentration. If it is assumed that corrosion is inhibited by films of hydrated oxides formed on the metal surface, then the formation of such films would be determined by the total quantity of ionizable hydrogen in contact with the corroding metal rather than by the concentration of hydrogen ions. If the quantity of ionizable hydrogen (that is, the total acidity) is sufficient to neutralize hydroxyl ions as they are formed at the cathode, then a protective hydroxide layer will not be produced and corrosion will continue unrestricted. On the other hand, if a high concentration of hydrogen ions is not accompanied by a high total acidity, then the production of hydroxyl ions at the cathode will ultimately result in a decrease in hydrogen ion concentration and in the precipitation of metal ions as hydroxide in the form of a protective film.

The relation between the average rate of pitting of the ferrous specimens and total acidity is best illustrated graphically. In plotting the data shown in figure 3, the values for sandy soils were omitted. The data for certain other soils, nos. 9 and 26, which conformed well to the acidity relation after 8 year's burial, are not shown in the figure since some doubt exists as to their rates of pitting at 10 years.

The relation between pitting and total acidity shown in figure 3 can be explained by assuming that the protective effect of the products of corrosion varies with the acidity of the soil. The relatively slight corrosion observed in the soils having low total acidities, such as 20, 30, and 32, would then be accounted for by assuming that precipitation of ferrous and ferric hydroxides in immediate contact with the metal surface produced a dense rust layer which tended to inhibit further corrosion. The higher corrosion rates in the moderately acid soils, such as 3, 16, 21, and 41, would then be ascribed to the lessened protectiveness of the rust layer with increasing acidity. Because of the greater solubility of the hydroxides of iron in these soils there was probably appreciable diffusion of the metallic and hydroxide ions outward into the soil, precipitation occurring at an appreciable distance from the metal surface when the concentrations of the reacting ions became sufficiently great. Accumulation of the precipitated corrosion products in the pore spaces of the soil would tend to restrict the movement of air through the soil to the cathodic areas, and would result in a reduced rate of corrosion. In the very acid soils, 29, 33, 42, and 43, it is probable that precipitation of the hydroxides in quantities sufficient to affect the rate of corrosion does not take place until a large loss of metal has occurred.

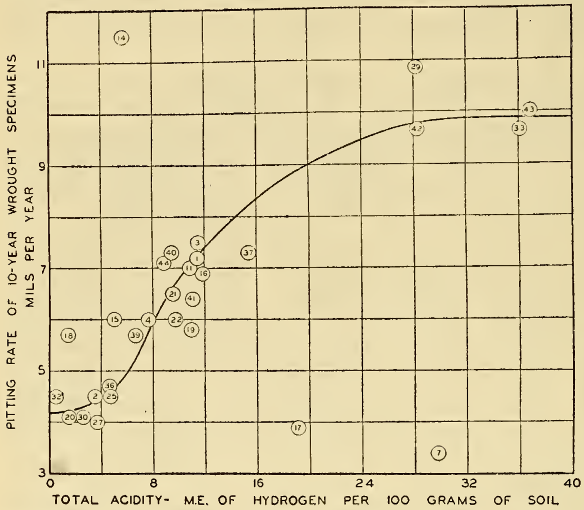

FIGURE 3.—*Relation between pitting rates of 10-year specimens and total acidity of soils.*

It is of interest to note in figure 3 that the rates of pitting in two very acid soils, 7 and 17, are even lower than the rates of pitting in the least acid of the soils. This fact may be taken to indicate the predominating influence of some factor other than acidity in the corrosiveness of these soils. As will be seen in a succeeding section on the physical properties of the soils, the failure of these soils to conform to the acidity relation may be ascribed to their natural impermeability to air. No explanation can be offered at this time for the high-pitting rate in soil 14.

Although the low acidities of soils 2, 15, 20, 30, and 32 are sufficient to account for their relatively low corrosiveness, the presence of calcium carbonate in these soils also probably tends somewhat to inhibit corrosion. Since the solutions in contact with the metal surface in these soils are in equilibrium with calcium carbonate, an increase in the hydroxyl ion concentration at the cathode would result in the precipitation on the metal of a thin layer of calcium carbonate which would have some protective action. Precipitation of this kind is known to occur in the interior of pipes carrying water saturated with calcium carbonate.

Although a correlation exists between rate of pitting and total acidity, no correlation is evident between acidity and the average penetration of the specimens in the field test, and, in fact, none should be expected. Examination of the specimens shows that much of the surface of the specimens from certain soils remains uncorroded even after 10 years' exposure to the soil. Since the unit area on which the calculation of average penetration is based includes uncorroded as well as corroded area, it is evident that the greater the uncorroded area the lower will be the value for average penetration, other things being equal. As will be brought out later, the distribution of corrosion or the relative proportion of corroded to uncorroded area depends largely upon certain physical properties of the soil. According to this view, soil acidity has no effect on the distribution of corrosion and hence affects the average penetration only as it influences the rate at which the corroded areas deepen. If, however, the average penetration were calculated on the basis of the corroded area rather than of the total area, it is reasonable to expect that a correlation between acidity and the average penetration would be obtained.

In considering the application of the total acidity and corrosion tests to estimate the probable corrosive action of soils on a pipe line it should be especially noted that the electrical currents flowing along a pipe line may seriously affect the rates of corrosion which would occur if the pipe were unconnected. Thus the rate of corrosion of a section of pipe line which is discharging current would be expected to be greater than that on a single length of unconnected pipe in the same location. It may therefore be necessary in connection with corrosion surveys to supplement the acidity measurements with data from other tests, such as soil resistivity.

2. RELATION BETWEEN RATES OF PENETRATION OF STEEL IN LABORATORY TEST AND TOTAL ACIDITY OF SOILS

The relation between the rates of penetration of the steel disks in the laboratory test and the total acidity of the soils is shown in figure 4. It will be noted that although this curve has the same general shape as figure 1, in which the relation between acidity and corrosion in synthetic soil was shown, a given value for acidity in a soil corresponds to a much lower rate of corrosion than does the same value of acidity in the acetic acid-sodium acetate mixture. This result is to be expected from the fact that in soils the acid is difficultly soluble and hence, slowly diffusible, whereas in the buffer mixture the reverse is the case.

It is of special interest to note that soils 14 and 17, which departed widely from the relation between pitting and total acidity, conform well when the values from the laboratory corrosion test and total acidity are plotted. Although the plotted value for soil 7 does not lie near the curve, this soil is shown to be corrosive, probably because of its high acidity. Acid soils high in organic matter, namely, soils

29 and 33, did not conform to the relation. It was observed that in these soils the corrosion products of steel formed with the organic matter a dense layer which could be removed from the surface of the disk only with great difficulty. The layer probably excluded oxygen and so checked further corrosion. The rather wide scattering of the points shown in figure 4 indicates the importance of factors other than acidity that influence corrosion.

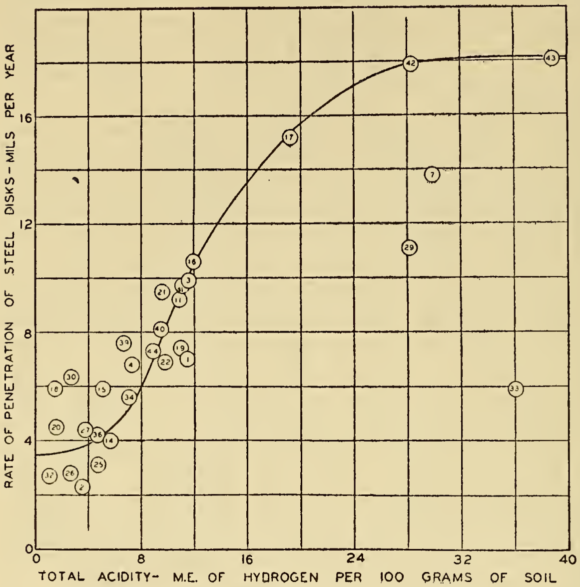

FIGURE 4.—*Relation between rates of penetration of steel in laboratory test and total acidity of soils.*

In order to show the degree of correspondence between the pitting data from the field specimens and the corrosion losses sustained in the same soils in the laboratory, the 10-year rates of pitting were plotted against the average rate of penetration of the disks (see fig. 5). A fairly satisfactory correlation is indicated. The exceptions to the relation are either poorly drained soils in which deficiency of oxygen inhibited pitting at the test site, or organic soils the corrosiveness of which is not well indicated by the laboratory test in its present form. In consideration of the many factors influencing corrosion in the field which cannot be evaluated in a laboratory corrosion test, it would seem that the correlation obtained is as good as could be expected. For most normally developed acid soils, the laboratory test appears to be of

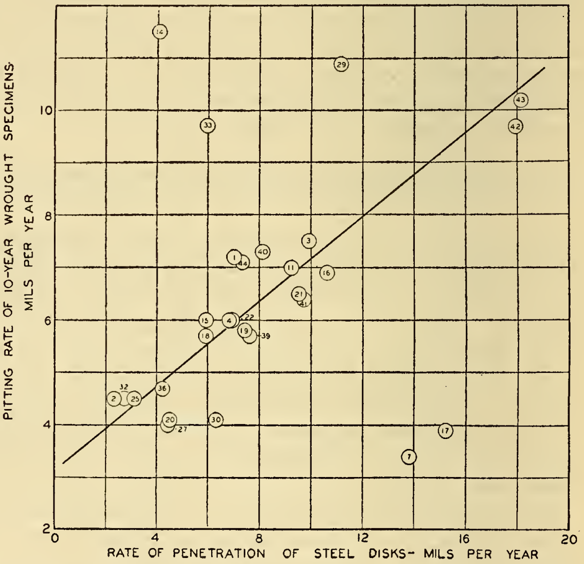

FIGURE 5.—*Relation between rates of pitting of 10-year wrought specimens and rates of corrosion of steel in laboratory test.*

value, at least to determine whether some form of protection against corrosion is needed.

The laboratory corrosion test indicates roughly whether the average penetration over the surface of the buried specimens would be large or small; but no correlation is evident or to be expected between the rates of average penetration of the field and laboratory specimens. A close correlation between rates of average penetration in the field and in the laboratory could occur only if the corroded areas of the two sets of specimens were always in the same ratio. This is known not to be the case. Corrosion occurred more or less generally over the surface of the disks, but the corroded areas of the field specimens varied greatly, from the relatively small area occupied by sharp pits on certain specimens to the entire surface of others. As will be shown later, the corroded area of the specimens is influenced largely by the physical characteristics of the soils in the field. When the soils are brought into the laboratory and prepared for testing, these characteristics are necessarily modified.

V. DISTRIBUTION OF CORRODED AND UNCORRODED AREAS AS INDICATED BY THE PITTING FACTOR

It has been observed in inspecting underground pipe lines that corrosion may take widely different forms, from the production of sharp isolated pits to a uniform attack of the metal surface. This range in the form of corrosion is illustrated by photographs of sections of operating pipe lines (fig. 6). In figure 6 (A) in which pitting is especially pronounced, it will be observed that the corroded area is relatively small, whereas in figure 6 (D) there is very little pitting, although practically the entire surface has been attacked.

The variation in the type of corrosion which may occur in soils is exhibited especially well by the specimens of ferrous materials which have been removed from the National Bureau of Standards test sites. Figure 7 illustrates corrosion patterns on steel specimens ranging from a uniform attack of the metal surface with entire absence of pitting (7 A) to a highly localized attack in the form of deep, well-marked pits (7 F). It will be especially noted from table 2, in which the essential data relative to figure 7 are shown that, although the weight of metal lost from the specimens is roughly the same, the maximum depth of pits ranges from zero to 107 mils. Accordingly, the pitting factor, defined as the ratio of the maximum depth of pit to the average penetration, varies from 1 to 24.5.

Table 2.—*Variation of maximum pit and pitting factor at the same stage of corrosion*

Number	Soil number	Soil type	Loss of weight	Average penetration	Depth of maximum penetration	Pitting factor
			Oz/ft²	*Mils*	*Mils*	
1	47	Unidentified silt loam	2.11	3.2	3.2	1
2	27	Miller clay	3.73	5.7	36	6.3
3	20	Mahoning silt loam	2.99	4.6	34	7.4
4	16	Kalmia fine sandy loam	4.23	6.5	60	9.3
5	3	Cecil clay loam	3.43	5.3	63	11.8
6	14	Hempstead silt loam	2.86	4.4	107	24.5

The fact that the ferrous specimens removed from any one soil exhibit essentially the same corrosion pattern regardless of the nature of the material, suggests immediately that the physical or chemical properties of the soil control the character of corrosion. It has been observed, for instance, that the specimens which have been in contact with poorly drained soils for a number of years are usually corroded uniformly, but those in well-drained soils show a greater tendency toward localized attack. These observations indicate a relation between the type of corrosion and the permeability of the soil.

In order to correlate the ratio of corroded and uncorroded areas on the specimens with the physical characteristics of soils, it is necessary to have a suitable measure or index of these areas. Unfortunately, it was not practicable to measure the corroded and uncorroded areas on all of the specimens, but as will be shown, the pitting factor may be employed as a rough index of the ratio of these areas.

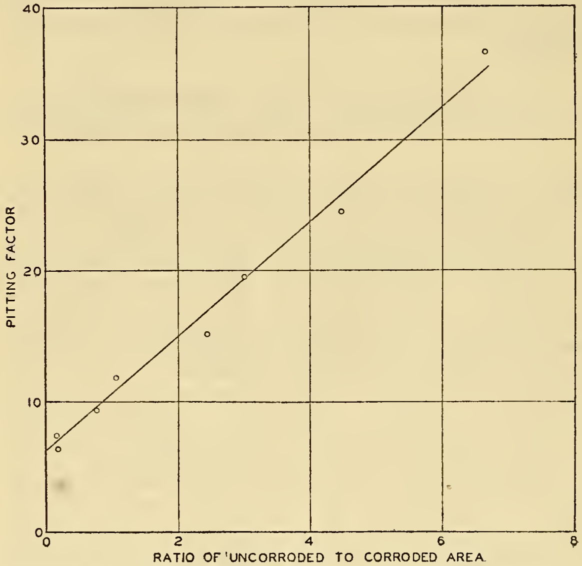

FIGURE 8.—*Relation between pitting factor and ratio of uncorroded to corroded area.*

As the pitting factor is defined as the depth of the deepest pit divided by the average depth of penetration, if a single pit of uniform depth (and no other corrosion) occurs on a specimen of unit area, the area of the pit can be readily calculated from the pitting factor. In this case the pitting factor would correspond to the depth of the pit divided by its volume, and the area of the pit, which would be equal to the volume divided by the depth, would therefore be the reciprocal of the pitting factor.

It is evident that this simple relation cannot be used to calculate the corroded area of actual specimens because pits have irregular shapes and because the average depth of all the pits on a specimen is unknown. However, since visual examination of the corroded specimens indicates a possible relation between the pitting factor and the ratio of uncorroded and corroded areas, it seemed worth while to devise a method which would test this relation experimentally. The method consisted in making on paper impressions in ink of a group of corroded specimens and measuring the total area covered by ink, which corresponded to the uncorroded area. The corroded area was then obtained by subtraction from the total area. If the corroded area was small, it was directly measured and the uncorroded area was obtained by difference. The areas were measured by placing transparent coordinate paper over the ink impression and counting the number of squares covering the black or white areas.

In order to produce a firm pressure as the specimen was rolled over the paper a 2-foot (60-cm) length of 1½-inch (38-mm) pipe was attached firmly to the specimen in such a manner that the projecting ends of the pipe could be used as handles. It was found that sharp outlines of the pits could be obtained by making the impression on paper resting on a resilient rubber pad. Seven steel specimens with pitting factors from 6.3 to 36.6 were employed. In figure 8 it is seen that the pitting factors are roughly proportional to the ratio of the uncorroded to the corroded areas.

In order to account for the distribution of the corroded and uncorroded areas on the test specimens it may be assumed that they coincide respectively in a general way with the anodic and cathodic areas set up by the action of the soil. It is recognized that there may have been a certain shifting of the anodic and cathodic areas as a result of changes in soil moisture and aeration, but these temporary effects probably produced only a superficial roughening of the specimens.

Figure 9 shows the change with time of the pitting factors for typical acid soils. After about 8 years these pitting factors become approximately constant; that is, the ratios of the rates of average and maximum penetration remain the same. These constant pitting factors (based on 10 years' observations) are listed in table 3 for most of the soils considered in this investigation.

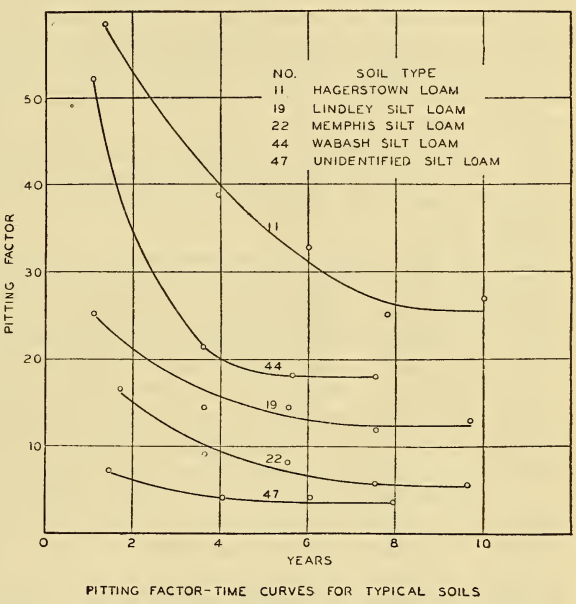

FIGURE 9.—*Pitting factor time curves of various soils.*

TABLE 3.—*Pitting factors of acid soils*

Soil number	Pitting factor	Soil number	Pitting factor	Soil number	Pitting factor
1	5.7	17	4.5	33	5.5
2	7.5	18	12.5	35	7.5
3	10.0	19	12.5	36	13.5
4	5.5	20	5.5	37	6.0
5	4.7	21	10.0	39	7.5
6	11.7	22	5.5	40	6.5
7	4.5	24	10.0	41	8.0
8	10.0	25	12.5	42	8.0
10	5.3	27	5.0	43	5.0
11	25.5	29	5.0	44	18.0
14	15.0	30	6.0	47	3.0
15	6.0	31	11.0		
16	9.8	32	10.5		

VI. RELATION OF THE PHYSICAL PROPERTIES OF SOILS TO CORROSION

The influence of the physical properties of soils on their corrosiveness has not hitherto been systematically studied, although the importance of physical factors in soil corrosion has been recognized. The relation of the mechanism of the corrosion of lead in soils to the size of soil particles has been explained by Burns and Salley (12). These investigators found that the rate of corrosion increased with increase in particle size. The corrosion was attributed to the operation of oxygen concentration cells, which originated from partial or complete exclusion of oxygen at the points of contact of the metal and the soil particles. Such areas became anodic to the surrounding parts of the metal surface that were more accessible to air. (Potential differences of approximately 1 volt have been obtained by Shepard in this laboratory with iron under conditions involving differential aeration.) Burns and Salley point out that the ratio of cathodic to anodic area on a metal surface is determined by the total area of contact between soil and metal, and that this area is in turn determined by particle size. Since a decrease in particle size permits contact of a greater number of particles per unit area, the area of contact increases, and hence the ratio of cathodic to anodic area decreases with decrease in particle size.

In their explanation of the mechanism of corrosion Burns and Salley point out that the resistance and potential difference in the cell under consideration are independent of particle size. Hence the cathodic current density and the degree of polarization must vary inversely with particle size. Since the rate of corrosion depends upon the rate of depolarization by oxygen, the amount of oxygen required to maintain any given rate of corrosion per unit area increases with decrease in particle size, and conversely, any given concentration of oxygen produces increasing rates of corrosion with increase in particle size.

This explanation by Burns and Salley was reached from a laboratory study of the effects on corrosion of mineral particles of a limited range of size. In applying this explanation to corrosion in soils under natural conditions it is necessary to consider that the units of structure in soils are not individual particles but relatively large masses or aggregates of particles. These aggregates range in physical condition from dense, compact masses impermeable to air and water to porous masses through which water and air penetrate readily. According to the mechanism of corrosion just described, in dense, impermeable soils, in which air would be excluded from a relatively large area, the area of contact between soil and metal would be large and the anodic area would be relatively great, hence corrosion would take the form of large uniformly attacked areas. Since the cathodic current density and polarization would be relatively great because of the small cathodic area, and the oxygen concentration would be low because of the denseness of the soil, it follows that the rate of penetration by corrosion would be low. On the other hand, in porous, highly permeable soils, the area from which oxygen is excluded would necessarily be small, and hence the anodic area would also be small. Since the cathodic current density and the polarization would be low, the rate of penetration by corrosion would be relatively great, unless it was reduced by the accumulation of corrosion products. Under these conditions corrosion would take the form of pitting.

From the foregoing considerations it is evident that the permeability of soils to air determines to a large extent the rate of corrosion and the distribution of corroded areas on the metal surface. Hence it should be possible to correlate those properties of soil which determine their permeability with expressions of the distribution of corroded areas, such as the pitting factor.

It is well known that the permeability of a soil is largely dependent on its texture, illustrated by the excessive drainage of sands and the poor drainage of many heavy clay soils. With decreasing size of particles the size of the capillary spaces in soils tends to diminish, so that considerable resistance may be offered to the movement of fluids, especially in the usual moist condition of soils several feet below the surface. It has been shown by previous investigators that over a definite range of size of spherical particles the volume rate of flow varies directly with the square of the average diameter of the particle (other conditions being the same). This simple relation, however, cannot be applied generally to soils, partly because the particles of clay and silt are not spherical and are not of approximately uniform size.

Although, as previously stated, heavy clay soils tend to be impermeable, some soils containing a high percentage of clay are porous and well aerated. Impermeable clay soils are usually characterized by the presence of a clay fraction which, in the presence of water, shows characteristic colloidal properties such as high dispersability and absorptiveness and a marked tendency to swell. In relatively permeable clays, these properties are not pronounced. Because of the marked retentiveness of highly colloidal soils for water the interstitial spaces are largely filled with water, and offer considerable resistance to the movement of air.

The permeability of a soil is influenced not only by the texture (i.e., the size distribution of the particles) and by the colloidal behavior, but also by the degree of compactness or denseness of the soil, which is determined by the average diameter of the pores.

1. METHODS OF MEASURING PHYSICAL PROPERTIES OF SOILS

The physical properties of soils which influence their permeability have been recently studied by Slater and Byers (13). It was found that the relative permeability of soils was indicated by measurements of several physical properties and also by expressions derived from these measurements. Thus the percentage of silt, the dispersability of the silt and clay and an expression obtained by dividing the percentage of readily dispersed silt and clay by the colloid-moisture equivalent ratio were correlated with the measured permeability of undisturbed cores of various surface soils. None of these properties, however, appeared to be correlated with the observed percolation rates for the subsoils. It is evident that the swelling of a mass of soil which is associated with the dispersiveness of the individual particles would tend to reduce the size of interstitial spaces, thereby increasing the resistance to the movement of air.

Since the rate of movement of air in soils is controlled largely by the total space through which air may diffuse, it was thought that comparison of the relative volumes occupied by air under specified conditions in the different soils might provide an index to their permeability. Such measurements to have the greatest significance should be made under conditions which simulate the natural condition of the soil with respect to moisture content and degree of packing as indicated by the apparent density. By means of centrifugal force the moistened samples of soil were compacted until their volume weights approached closely the volume weights of undisturbed lumps of soil from the corresponding test sites. The moisture contents of the centrifuged samples also approximated the average moisture contents of the soils at the test sites so far as these values could be determined. The volume of the compressed sample which is occupied by air will be referred to in the succeeding discussion by the term "volume of voids", following the practice of Boyd (14).

1. Mechanical analysis including colloid content was made by the method now employed at the Bureau of Chemistry and Soils of the United States Department of Agriculture (15). This method depends upon the relation of settling velocity to particle size, as given by Stokes' formula for the fall of a solid sphere in a viscous fluid.

2. Water-holding capacity was determined by the method employed by Slater (13). A 30 g sample of soil contained in the screen-bottom box also used for the moisture equivalent determination was saturated with water, centrifuged for 40 minutes at 1,000 times gravity to produce a standard packing and again saturated with water. After draining for 18 hours in a saturated atmosphere the box containing the soil was wiped dry, weighed, dried in an oven at 105 C and reweighed. The loss in weight was expressed as percentage of the weight of the oven-dried soil.

3. Moisture equivalent (16), defined as the moisture retained by a moist soil under a centrifugal force of 1,000 times gravity, was determined on the samples of soil which had previously been compacted to various degrees corresponding to the volume weights of undisturbed lumps of soil from the same test site. Because of the previous treatment of the samples the values obtained were lower in the case of most soils than the values for the moisture equivalent as conventionally determined.

4. *Volume weight* (*apparent specific gravity*).—The volume weight of the compacted soil was determined at the moisture equivalent and after drying in the oven at 105 C. To do so sufficient mercury was added to the soil contained in the moisture-equivalent box to fill the box, and the box containing the soil and mercury was weighed and the volume of the soil was calculated. The volume weight of undisturbed lumps from the test sites was determined by immersing the dry lumps in a dish filled with mercury, calculating the volume of the lump from the weight of the mercury displaced. The value selected for volume weight of lumps of each soil was the average of 6 to 8 closely agreeing determinations made on lumps selected at random.

5. *Volume of voids.*—The term "volume of voids" means the total space occupied by air in a mass of soil compacted by a definite force and having a definite moisture content. It was calculated by subtracting from the volume of moist soil the volume occupied by the soil particles plus the volume of water contained in the soil, and is expressed as percentage of the volume of the moist soil. The volume of the dried soil particles was calculated from their specific gravity as determined by the pycnometer method. The volume of the moist soil was determined on samples which had been compacted centrifugally in an attempt to reproduce for each soil the degree of compaction

indicated by the volume weight of the undisturbed samples from the test sites. The centrifugal force applied ranged from 1,000 to 2,000 times gravity, the samples being alternately saturated and centrifuged. In all soils the final centrifuging was made at 1,000 times gravity in order to insure that the moisture contents at the determination of the volume of voids would be comparable.

Comparison of the volume weights of the centrifuged samples with the volume weights of the soil in the field condition (table 4) shows that, with few exceptions, the latter were higher. However, in most of the soils the measured volume of voids was so low that, even if the material had been compressed to its field condition, the results would not have been significantly different.

6. Dispersiveness of silt and clay was determined by a slight modification of the method described by Middleton (17). A 10-g sample of soil contained in a 1-liter glass cylinder was moistened with distilled water and after 18 hours was suspended in 1 liter of water by shaking end over end 20 times. The suspension was then allowed to settle for 3 minutes and 45 seconds, when a 25-ml sample was pipetted at a depth of 30 cm. (Previous studies have shown that then the sample consisted of particles with a maximum diameter of 0.05 mm.) From the dry weight of the residue obtained by evaporating the pipetted fraction, the total weight of silt and clay in the suspension was calculated. This quantity, expressed as percentage of the weight of the sample, has been designated by Slater and Byers as the "suspension percentage." The ratio of the silt and clay so determined to the total silt and clay obtained by mechanical analysis is called the "dispersion ratio" (17). This value has been calculated for the clay soils in order to determine the relative dispersability of the silt and clay in these soils.

In view of the fact that the moisture equivalent is dependent upon the proportion of the finer capillary spaces to the total pore space, it was assumed that the relative permeability of the soil might be roughly indicated by the ratio of the saturation capacity of the soil (corresponding to the total pore space) to the moisture equivalent. Accordingly, these ratios were calculated and are shown in table 4.

TABLE 4.—*Comparison of physical properties of soils with pitting factor*

Soil no.	Soil type	Depth	Mechanical analysis				Water-holding capacity	Moisture equivalent of compacted soil	Volume weight		Volume of voids	Ratio of water-holding capacity to moisture equivalent	Suspension percentage	Dispersion ratio	Pitting factor
			Sand	Silt	Clay	Colloid			Field	Laboratory					
		Inches	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*			*Percent*		*Percent*		
47	Unidentified silt loam	36	9.0	44.9	46.1	27.7	25.8	21.1	1.72	1.74	1.1	1.22	45.5	50.0	3.0
7	Fairmount silt loam	40	10.3	26.1	63.6	55.0	39.2	36.4	2.02	1.79	3.7	1.08	41.2	45.9	4.5
17	Keyport loam	36	9.6	38.6	51.7	39.6	32.8	27.7	1.72	1.60	4.4	1.18	43.5	48.1	4.5
5	Dublin clay adobe	30	25.6	38.6	35.8	30.2	29.2	27.5	2.00	1.85	4.9	1.06	40.8	54.8	4.7
27	Miller clay	30	1.4	10.8	87.8	71.5	48.6	44.6	2.01	1.78	1.9	1.09	30.2	30.6	5.0
4	Chester loam	36	29.3	53.0	17.7	9.9	34.5	22.9	1.78	1.66	7.0	1.51	27.9	----------	5.5
20	Mahoning silt loam	50	19.6	44.1	36.3	23.7	22.9	18.6	1.90	1.83	3.8	1.23	37.7	46.9	5.5
22	Memphis silt loam	33	1.2	76.5	22.3	18.3	43.5	28.4	1.67	1.64	9.6	1.53	38.7	----------	5.5
1	Allis silt loam	90	9.8	37.7	52.5	31.1	23.7	20.2	--------	1.83	1.1	1.18	38.0	42.1	5.7
15	Houston black clay	36	4.4	25.2	70.4	62.0	53.2	50.5	2.08	1.83	5.7	1.05	28.3	29.6	6.0
30	Muscatine silt loam	36	2.1	65.5	32.4	26.1	30.3	24.0	1.81	1.68	7.2	1.26	25.7	26.3	6.0
40	Sharkey clay	30	2.5	50.4	47.1	32.8	42.8	31.0	1.78	1.73	2.3	1.38	24.9	25.5	6.5
2	Bell clay	40	17.2	37.9	44.9	40.4	41.4	35.2	1.95	1.93	2.0	1.18	19.1	23.0	7.5
35	Ramona loam	36	35.9	37.3	26.0	19.3	20.4	15.8	1.88	1.77	10.9	1.29	22.2	----------	7.5
39	Sassafras silt loam	36	42.1	42.6	15.3	8.7	27.4	18.3	1.72	1.76	7.5	1.39	18.9	----------	7.5
41	Summit silt loam	36	3.0	56.7	40.3	35.0	36.7	28.1	1.61	1.61	6.9	1.31	24.7	25.5	8.0
42	Susquehanna clay	30	30.1	24.1	45.8	40.9	36.5	24.8	1.79	1.48	14.9	1.47	11.8	16.9	8.0
16	Kalmia fine sandy loam	30	50.4	23.1	26.5	21.8	21.3	16.5	1.65	1.66	12.0	1.29	11.1	----------	9.8
3	Cecil clay loam	32	29.0	24.9	46.1	37.8	47.6	29.9	1.60	1.32	18.2	1.59	4.4	6.2	10.0
21	Marshall silt loam	36	3.2	65.9	30.9	27.1	34.9	24.8	1.66	1.57	10.8	1.41	26.0	26.9	10.0
8	Fargo clay loam	48	2.2	27.7	70.1	50.7	50.8	34.8	1.56	1.57	8.7	1.46	20.2	20.6	10.0
32	Ontario loam	48	42.1	42.1	15.8	8.2	18.4	11.8	1.85	1.81	11.7	1.56	15.9	----------	10.5
19	Lindley silt loam	36	15.7	50.1	34.2	29.3	35.8	26.3	1.76	1.73	3.9	1.36	15.9	18.9	12.5
18	Knox silt loam	48	1.3	78.4	20.3	15.0	46.8	22.0	1.26	1.43	16.6	2.13	24.2	----------	12.5
25	Miami clay loam	36	21.0	43.0	36.0	21.8	22.4	18.6	1.95	1.81	9.5	1.31	24.8	31.4	12.5
36	Ruston sandy loam	36	60.6	21.8	17.6	14.8	32.1	14.9	1.62	1.62	16.0	2.15	17.0	----------	13.5
14	Hempstead silt loam	60	56.6	29.5	13.9	9.5	20.3	12.2	1.76	1.77	14.4	1.66	19.8	----------	15.0
44	Wabash silt loam	30	2.4	66.4	31.2	25.8	33.8	25.3	1.55	1.56	7.2	1.34	22.1	22.6	18.0
11	Hagerstown loam	60	25.8	21.1	53.1	45.9	49.8	31.3	1.49	1.41	15.5	1.59	7.9	10.6	25.5

SOILS CONTAINING LESS THAN 10 PERCENT OF CLAY

10	Gloucester sandy loam	30	64.0	29.4	6.6	2.8	22.8	9.0	1.58	1.58	27.8	2.53	16.4	----------	5.3
37	St. Johns fine sand	30	90.6	4.9	4.5	4.3	35.9	7.0	1.30	1.30	41.4	5.13	3.3	----------	6.0
24	Merrimac gravelly sandy loam	33	72.0	22.4	5.6	2.7	32.2	9.7	1.40	1.40	34.7	3.32	10.4	----------	10.0
31	Norfolk sand	24	97.3	2.1	.6	----------	21.9	2.3	1.55	1.55	38.1	9.52	1.8	----------	11.0
6	Everett gravelly sandy loam	36	69.0	23.8	7.2	3.5	24.7	9.5	1.50	1.50	40.6	2.60	12.2	----------	11.7

2. CORRELATIONS BETWEEN PHYSICAL PROPERTIES OF SOILS AND PITTING FACTOR

The data obtained from the various physical determinations are shown in table 4. In order to facilitate comparison with the pitting factor the data for the various soils have been arranged in the order of increasing pitting factor.

A comparison of the values for the pitting factor with the data on the physical properties of the soils containing more than 10 percent of clay indicates that the pitting factor is very largely determined by the permeability of the soil. It will be noted that increase in the pitting factor is generally accompanied by an increase in the volume of voids and the ratio of water-holding capacity to moisture equivalent. It will also be observed that there is a rough inverse relation between the pitting factor and the quantity of easily dispersed silt and clay, and also between the pitting factor and the dispersability of the clay and silt in the clay soils as indicated by the dispersion ratio. It will also be observed that there is a tendency for the pitting factor to increase inversely with the volume weight of the soils in the field condition, as might be expected.

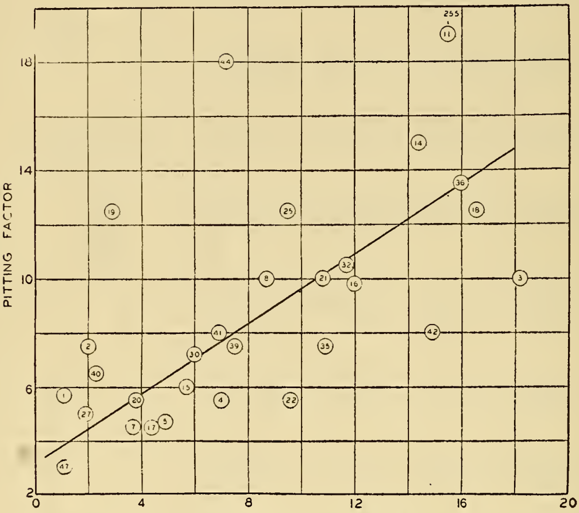

Figure 10.—*Relation between volume of voids in soils and pitting factor.*

In figure 10 the correlation between the pitting factor and the volume of voids is shown graphically. The significance of this relation may be best appreciated if it is assumed that the pitting factor is roughly proportional to the ratio of the cathodic to anodic areas on the specimens, as has been suggested. According to this assumption, a low volume of voids, which is associated with a relatively impermeable soil, would indicate a large anodic area corresponding to general corrosion of the metal surface. Conversely, a large value for the volume of voids, associated with a permeable soil would indicate a small total anodic area and hence localized corrosion or pitting. Furthermore, by reason of the large cathodic surface and the corresponding low cathodic current density, the concentration of oxygen required to maintain any given degree of depolarization would be small and deep pitting would result in the absence of interference from the accumulation of corrosion products or other inhibiting factors.

In view of the fact that the values for the volume of voids is determined by the moisture content of the soil, it is apparent that the goodness of fit of the line drawn through the points (fig. 10) depends largely upon how well the moisture content of the soil at the time of measurement corresponds to the average moisture content of the soil in the field. Secondly, the gross structural features of the soil, such as the natural occurrence of cracks and fissures, affect the permeability to an extent which cannot be evaluated by the methods employed.

As previously indicated, a definite proportionality exists between the pitting factor and the ratio of water-holding capacity to moisture equivalent. The coefficient of correlation for this relation is 0.723 which according to the level of significance of Fisher (18) gives, for 30 observations, a probability somewhat better than 0.99 that the relation is significant. This value compares with 0.722 which is the coefficient of correlation calculated for the pitting factor volume of voids relation shown in figure 10.

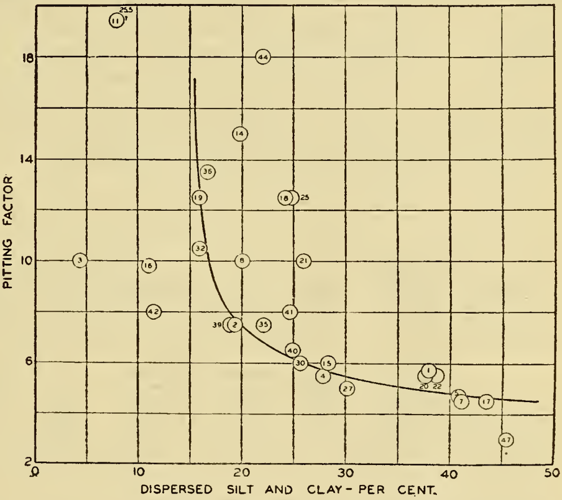

Figure 11.—*Relation between dispersed silt and clay in soils and pitting factor.*

The correlation observed between the pitting factor and the moisture ratio may be explained as follows. In a soil having a moisture ratio approaching unity it is evident that the amount of water retained by the soil under a force of 1,000 times gravity is nearly equal to the quantity required for saturation. Since the moisture is held so completely it follows that the capillary spaces through which air might move must be exceedingly fine and, therefore, offer high resistance to the diffusion of air. Under such conditions, which might amount to virtual exclusion of oxygen over a large part of the metal surface, the anodic area must be relatively great and the pitting factor correspondingly small. On the other hand, large values of the moisture ratio indicating large capillary spaces through which air may diffuse would be expected to produce relatively large cathodic areas, which would be indicated by high pitting factors.

The correlation between the quantity of silt and clay which is readily dispersed in water and the pitting factor is shown graphically in figure 11. As indicated by the figure, low pitting factors are associated with high concentrations of silt and clay, the pitting factor decreasing rapidly with the quantity of dispersed material. The explanation of the observed correlation evidently lies in the fact that dispersion of the soil material with the resultant swelling of the colloidal material results in diminution in size of the capillary spaces within the soil. The increased resistance to the diffusion of oxygen produced in this manner would then tend to increase the anodic area with respect to the cathodic area.

It is apparent that the correlation shown in figure 11 becomes less satisfactory as the quantity of dispersed material decreases and at values below 10 to 15 percent it is probably without significance. It is likely that some minimum quantity of dispersed material is necessary for corrosion to be produced by differential aeration since concentration of dispersed silt and clay on parts of the metal surface may be essential to the effective exclusion of oxygen and so to the development of anodic areas. This observation may possibly have a bearing on the fact that relatively slight pitting has occurred in acid soils containing less than 10 percent of clay.

From the relation which has been developed between the permeability of the soil and the pitting factor, and explanation may now be offered for the failure of certain very acid soils to induce serious pitting. It will be recalled in this connection (fig. 3) that soils 7 and 17, although very acid, produced lower rates of pitting than any of the other acid soils. The physical characteristics of these soils are shown in table 5 for comparison with the characteristics of soils 3 and 11 which conform to the acidity relation.

TABLE 5.—*Comparison of physical properties of soils with pitting rate*

Soil number	Average pitting rate for 10 years	Total acidity	Clay content	Volume of voids	Saturation, moisture equivalent ratio	Suspension percentage	Permeability
	Mils/yr	*m.e.*	*Percent*	*Percent*		*Percent*	
7	3.4	29.8	63.6	3.7	1.08	41.2	Impermeable.
17	3.9	19.1	51.7	4.4	1.18	43.5	Do.
3	7.5	11.5	46.1	18.2	1.59	4.4	Permeable.
11	7.0	10.8	53.1	15.5	1.59	7.9	Do.

From the data shown in table 5 it is apparent that the two groups of soils which differ so widely in their rates of pitting differ also with respect to the physical characteristics which determine their permeability. By the criteria which have been employed, soils 7 and 17 are relatively impermeable, whereas soils 3 and 11 are permeable. It has been seen that highly impermeable soils tend to restrict the accessibility of oxygen over a large part of the metal surface and thus to produce relatively large anodic areas. Since the cathodic current density and hence the degree of polarization must be comparatively high, because of the small cathodic areas, it follows that in the absence of corrosive factors, such as high acidity or high salt content, the rate of penetration by corrosion under conditions of poor aeration would be expected to be low. This conclusion is confirmed by the low rates of pitting which have occurred in soils 7 and 17. These conditions are completely reversed in soils 3 and 11 where, because of their high porosity, air has ready access to the greater part of the metal surface, corrosion being confined to small anodic areas. Because of the large cathodic surface and resulting low current density, depolarization by oxygen is readily accomplished, and the rate of pitting is limited only by the accumulation of corrosion products. It is perhaps significant to note in connection with the present discussion that soil 47, which, by the criteria employed is the least permeable of all the soils, also has the lowest average pitting rate, approximately 1 mil per year.

So far as the data from the other soils are concerned, it is not possible to demonstrate a relation between permeability of the soil and rate of pitting. This might be taken to indicate that, except in very impermeable soils, differences in permeability do not have a marked effect on the pitting rate. However, it is more reasonable to assume that the available data on pitting rates are not suitable for testing this effect, since too few data are recorded for soils of the same acidity but differing permeability.

VII. SUMMARY

The corrosiveness of acid soils toward ferrous metals was studied by means of a laboratory corrosion test and by comparing corrosion data on specimens removed from the National Bureau of Standards test sites with certain physical and chemical properties of soils. The corrosion data from the field tests include measurements of loss of weight and depth of pits on specimens of a variety of ferrous materials removed after 8 and 10 years' exposure to 37 acid soils.

In a preliminary study of corrosion in a synthetic "soil" composed of pulverized quartz and agar it was found that the loss of weight of the test specimens increased markedly with increasing acidity within the range of acidity shown by soils. The low rate of corrosion in the range of mild alkalinity was attributed to the action of an adherent film or layer of ferrous and ferric hydroxides which tended to diminish the accessibility of oxygen to the cathodic surface. The high rate of corrosion in the acid range was explained by assuming that the metal ions diffused readily outward into the soil and that the acidity of the soil neutralized hydroxyl ions as they were formed at the cathode, thereby preventing the formation of a protective rust layer.

Comparison of the average rates of pitting of the field specimens at 10 years indicated that the rates of pitting at practically all of the test sites were determined chiefly by the total acidity of the soil. A similar correlation between the loss of weight of specimens and total acidity was obtained when samples of soils from the test sites were employed in the laboratory corrosion test. The correspondence between the field and laboratory data suggests the use of the laboratory test as a convenient means of testing the corrosiveness of acid soils. However, because of the effect of pipe-line currents it may be necessary to employ supplementary tests, such as the measurement of soil resistivity.

The pitting factor, defined as the ratio of the maximum depth of pit to the average penetration, diminishes with time and appears to approach a fairly constant value after 8 or 10 years. The pitting factor is shown to be roughly proportional to the ratio of the uncorroded to corroded area on a metal surface. This relation was employed in studying the influence of certain physical properties of the soil on the distribution of corrosion.

Measurements of several physical properties of the soil which determine its permeability to air were made in order to relate permeability to the rate of pitting and the distribution of corroded areas. These measurements included the following: (1) Percentage of the total volume of moist soil which is occupied by air; (2) ratio of the moisture required for saturation to the moisture equivalent; and (3) dispersability of silt and clay. Definite correlations were obtained between the values for these properties and the pitting factor, indicating that the greater the permeability of the soil, exclusive of sands, the greater is the tendency for corrosion to be confined to pits, other conditions being the same. An explanation is suggested for the failure of certain very acid and impermeable soils to induce pitting.

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