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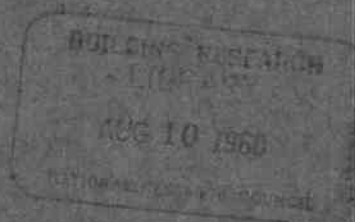
CANADA

MECHANISM AND EVALUATION OF CORROSION IN SOILS
A LITERATURE REVIEW

BY
J. D. SCOTT

ANALYZED

TECHNICAL PAPER NO. 100
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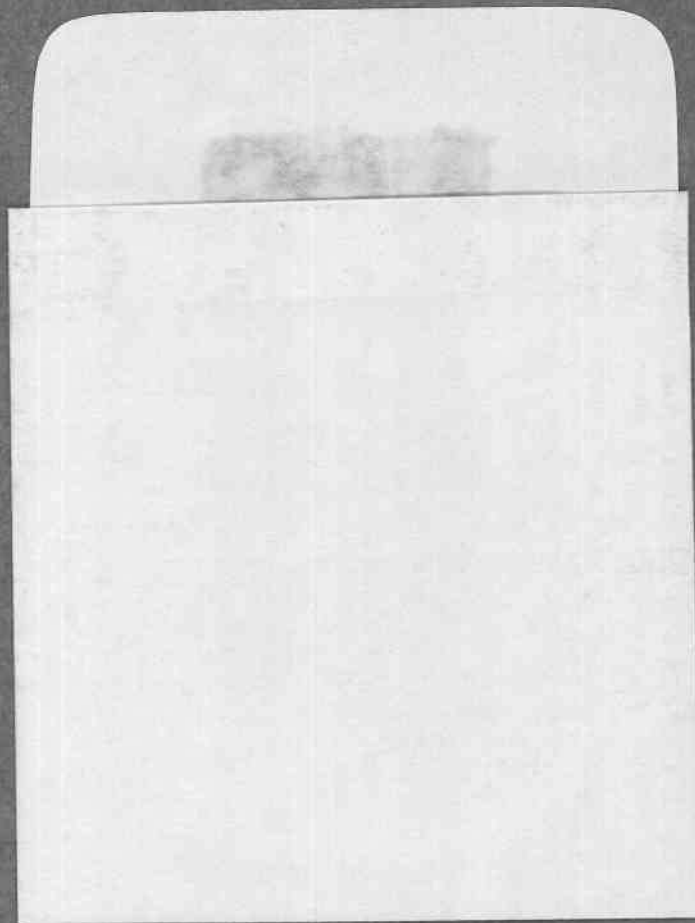


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Technical Paper No. 100
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Division of Building Research

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PREFACE

Several investigations carried out by the Soil Mechanics Section of the Division of Building Research have demonstrated the economic importance and also the technical complications of corrosion of metals buried in soil, such as steel pipes and piles. Close association with the staff of the Norwegian Geotechnical Institute, who have carried out extensive studies of this problem, has intensified interest in the matter.

The Division is therefore glad to be able to make available in this form the results of a careful survey of the existing literature, generally in English, on the subject of underground corrosion. The study was made by Mr. J.D. Scott, a graduate of Queen's University, with field experience in British Columbia, now a post-graduate student at the University of Illinois. Mr. Scott spent his summer vacation of 1959 working in the Soil Mechanics Section of the Division.

No single reference could be found which treated all the factors known to be involved, nor even the tests which are now available for use in the field and laboratory. Accordingly, search was made for all useful references in the literature; those found were carefully reviewed, the following report being the result of this critical assessment. Only those references that were considered to be significant have been mentioned. A discussion of the more fruitful references is included as a guide to further reading.

The Division hopes that this report upon Mr. Scott's "desk research" will be of use to others who are concerned with underground corrosion, just as it will provide also the essential background necessary for work in this field that the Division hopes to undertake.

Ottawa
May 1960

Robert F. Legget
Director

MECHANISM AND EVALUATION OF CORROSION IN SOILS - A LITERATURE REVIEW

by

J. D. Scott

Mechanism of Corrosion

It has been fairly well established (18) that in all cases of corrosion in the presence of moisture the mechanism of the corrosion reaction between metal and environment is electrochemical. Corrosion in moist soil may then be defined as the destruction or deterioration of metal by electrochemical reaction with its environment. It occurs because, in many environments, most metals are not inherently stable and tend to revert to some more stable combination of which the metallic ores, as found in nature, are familiar examples. The corrosion products consist mainly of oxides (usually more or less hydrated), carbonates, and sulphides.

The electrochemical principles, upon which the theory of the mechanism of corrosion is based, are fairly simple although their application is apparently complex. The element iron, like all other metals, when placed in contact with water or a solution, has an inherent tendency to go into solution in the form of electrically charged particles (iron ions) but, since the solution must remain electrically neutral, these positive ions can enter solution only if an equivalent number of positive ions of some other element are somehow displaced. In the ordinary case of iron immersed in water, the element immediately plated out is hydrogen which gathers on the iron surface as a thin film.

The tendency for the iron ions to go into solution is accentuated if a difference in electrical potential is formed

between two points on the iron. (Factors causing potential difference are discussed later.) This potential difference causes a flow of electrons from the point where the iron ions go into solution (the anode) through the metal to the area where the hydrogen ions congregate (the cathode). At the same time, a transfer of ions takes place from the anode through the soil water (the electrolyte) to the cathode. This action is the same as that which takes place in a battery, the soil water and points on the metal forming the battery and the piece of buried metal acting as the external lead which joins the electrodes of the battery. In a battery, the electrode from which ions transfer into the electrolyte will be destroyed by the loss of ions.

The above discussion should not be confused with the electrical engineering convention in which an "electric current" is assumed to flow from the positive electrode through the external lead to the negative electrode, the opposite direction to the actual flow of electrons. The electrochemical process is shown in Fig. 1. An iron atom at the anode, which has the most negative potential, loses two electrons (oxidation) and becomes a positive ion which is dissolved into the electrolyte. The electrons, which remain in the metal, travel to the cathode where they are accepted by the hydrogen or other ions (reduction).

The electrochemical theory of corrosion thus is simply that corrosion occurs through the loss of metal ions at anodic points or areas. Correlation of this theory with actual or potential corrosion of metals underground is, however, complicated and difficult because of the many factors that, singly or in combination, affect the course of the electrochemical reaction.

These factors not only determine the amount of corrosion and the rate at which it occurs but also the kind of corrosion, whether it is uniformly distributed or is localized as the pitting type of corrosion.

Consequently, for electrochemical corrosion to occur, there must be a potential difference between two points that are electrically connected and immersed in an electrolyte. The anode and cathode can be close together (local or micro cell) or far apart (macro cell). The quantity of current that passes through the cell is directly proportional to the amount of metal that is removed by corrosion (Faraday's law). Anything that affects the flow of the current therefore affects the rate and amount of corrosion.

The chemical reactions that take place during the corrosion process tend, because of their by-products, to bring the corrosion process to a halt. At the anode, where the iron ions accumulate in the electrolyte, the rate of diffusion is slowed down as the ions increase in number at the surface of the metal. The concentration of the dissolved metal increases the potential of the anode and the potential difference at the cell is decreased. The anode becomes stifled or polarized. At the cathode, the hydrogen builds up as an insulating layer on the iron and the cathode becomes polarized. The hydrogen layer also decreases the positive potential of the cathode, decreasing the potential difference of the cell. As the anodic chemical reaction can take place very much faster than the cathodic chemical reaction, the polarization of the cathode is much more effective in reducing corrosion than the polarization of the anode. In other words, the change of potential of the cathode as a result of polarization is usually much greater than the change of the potential of the anode.

If corrosion is to proceed, the hydrogen film on the cathode must somehow be removed. This depolarization or removal of the hydrogen film at the cathode may take place by a number of methods: (a) by the combination of hydrogen with oxygen dissolved in the soil water to form water; (b) by escaping as bubbles of hydrogen gas; (c) by electrochemical means or by chemical reactions with the electrolyte or salts in the electrolyte; (d) through activity of certain anaerobic bacteria; and (e) by combination with the products of microbial development.

In all these cases the removal of the film permits the original reaction to progress. More iron goes into solution, more hydrogen plates out; this process continues at a rate determined mainly by the rate at which the hydrogen film is removed. This effect of depolarization may decrease with time and the initial rate of corrosion is usually much greater than the rate after a short period of time.

In acid solutions the reaction is identical, but the film is removed mainly as bubbles of gas. This happens because the tendency of the hydrogen to plate out from a solution increases with the degree of acidity of the solution to such an extent that the pressure in the gas film suffices to form bubbles. This accounts directly for the fact that corrosion is generally more rapid in acid solutions than in alkaline solutions.

The rate of corrosion of ferrous materials, as determined by either loss of weight or depth of pits, depends to a minor extent only upon the type of metal. Ordinary iron and steel, within the common variations found commercially, corrode at approximately the same relative rate and have the same general type of corrosion pattern in a specific environment (6). Other conditions being equal, the ratio of the area of the cathode to the area of the anode is a controlling factor in the rate of corrosion. The

smaller the anodic areas in relation to the associated cathodic parts, the greater is the rate of penetration of corrosion at the anodic points (18).

Factors Influencing Corrosion in Soil

The factors that influence corrosion in soil may be divided into primary factors, those which determine the tendency of the metal to corrode and thus influence its initial rate of reaction, and secondary factors, those which influence the rate of subsequent reactions and allow the initial reaction to continue (18). The secondary factors often have more influence on the ultimate amount and rate of corrosion than do the primary factors. The factors may be further subdivided corresponding to the properties of the metal, the soil, and the water.

The metallic properties are generally considered to be primary factors, while the soil and water properties can be both primary and secondary factors. No attempt is made to list these factors in the order of their relative importance since under different conditions different factors become dominant.

Metal

1. Non-uniformity of the metal
2. Stress concentrations
3. Dissimilar metals (galvanic corrosion)
4. Stray electrical currents
5. Electrical resistance of the metal

Soil and Water

1. Physical properties: grain size, grain-size distribution, void ratio, permeability

2. Chemical properties: water soluble salts in the soil, pH, total acidity
3. Resistivity
4. Aeration (availability of oxygen)
5. Micro-organisms.

Corrosion cells can be classified according to the factors that cause the potential difference between the electrodes. Natural soil corrosion or self-corrosion is caused by non-uniformity of the metal or differences in the physical or chemical properties of the environment. Concentration cell corrosion is the name often given to corrosion cells caused by the differences in the environment.

Metal

1. Non-uniformity of the metal

Non-uniformity of the metal can often be responsible for the potential difference that may exist between two points in the metal. Any departure from complete homogeneity of structure and composition of the metal may cause potential differences.

(a) Factors in the metal proper. - (i) heterogeneous structure, as in grey cast-iron; (ii) differential thermal or metallurgical treatment, as in metal from different heats; (iii) non-uniformity of the structure, as in metal which is normally manufactured by mixing and fusing several different basic metals and other materials.

(b) Factors on the metal surface. - (i) surface roughness or non-uniform finish, scratches, or cut edges. The scars, scratches and edges (such as threads) usually become anodic with resultant rapid corrosion because of the large surrounding cathode areas (3, 18); (ii) mill scale. A continuous and unbroken film of mill scale retards soil corrosion, but a discontinuous film permits

excessive corrosion where the iron is exposed (17).

Graphitic corrosion of cast iron is caused by electro-chemical action originating between the constituents of the metal itself. Cast iron is a non-homogeneous metal since it contains free graphite in a matrix of metal. The carbon is quite inert and cathodic to the iron and, as a result, the iron is selectively dissolved leaving a porous mass of carbon that can readily be cut with a knife. The metal may show no outward signs of deterioration, but it has lost its strength. White cast iron does not show this effect because free carbon is not present. This type of corrosion appears to take place where the soil water contains calcium sulphate or chloride (18).

2. Stress concentrations

Stress concentrations may occur during manufacture of the metal, during construction, or during use. The most strained parts become anodic to areas that are less strained (18).

3. Dissimilar metals

The connection of two metals differing in electro-chemical potential has frequently been the cause of severe galvanic corrosion. The least noble metal (lower in the galvanic series) will become the anode and corrode. If copper or bronze are connected to steel or iron, the steel or iron will become anodic to the copper or bronze and protect it from corrosion while being corroded itself. Fortunately most iron-copper connections in water distribution systems are made between large iron pipes and small copper pipes. The anodic area is then large compared to the cathodic area and corrosion of the iron is slow. If the copper member becomes large, however, the corrosion of the

iron may be severe.

4. Stray electrical currents

It is common practice with direct current circuits, such as used in electric street railways, electric bus lines, electrified mines, and manufacturing plants of one sort or another, to make use of the ground as a return path for the current. If the ground current travels through any metallic structure, the area where the ions leave the structure, being the anode, will corrode rapidly because of the large current usually occurring with this type of system. Alternating currents, which are more generally used, are not particularly harmful (3). The replacement of direct with alternating current and the adoption of better insulation has reduced the difficulties due to stray current corrosion (7).

5. Electrical resistance of the metal

The resistance of the metal as it forms one arm of the electrochemical circuit will have an effect on the rate of corrosion. As its resistance is so small compared with that of the soil water, however, its effect is negligible. Use of this property can be made, where macro cells occur, since the corrosion current can be interrupted by the use of insulated joints.

Soil and Water

The soil and water properties determine the environment that exists around a buried metal. Any difference in environment between two points on the metal may cause a potential difference between these two points. The same properties which could cause this potential difference and therefore be primary factors may also affect the rate of corrosion and be secondary factors. No sharp distinction can therefore be made between some properties and they will appear in the discussion more than once.

The presence of water is absolutely necessary if corrosion is to take place. As pure water free from dissolved oxygen does not corrode iron appreciably at normal temperatures, the corrosive character of a soil depends primarily upon the presence of dissolved materials or bacteria in the soil water (18).

1. Physical properties

The physical properties of soil that are of importance in corrosion are those that affect the flow of air and water through the soil. Therefore, grain size, grain-size distribution, void ratio, and permeability are important. The swelling and shrinking properties are also important because of the manner in which they affect the permeability of the soil and the distribution of stress in the metal.

A change in the texture or structure of the soil surrounding the metal usually changes the amount of water, air, or dissolved oxygen in contact with the metal and these factors may cause a potential difference in the metal. These changes in the soil properties can occur when the metal passes through different soil strata or soil horizons or when the backfill around a metal structure is composed of hard lumps (from the desiccated crust) mixed with softer material. In such cases, the areas with the lowest permeability usually become anodic and corrode. Differences in moisture content can cause severe pitting such as in the case of the bottom of pipes resting on heavy, moist, undisturbed soil at the bottom of an excavation, while the rest of the circumference is in contact with the drier backfill (3).

Severe corrosion has occurred when cinder backfill is used. When steel is placed in intimate contact with cinders, the dissimilarity is one of materials. The cinder is one material, the cathode; the metal structure is the anode. The acids leached out of the cinders contaminate the soil and increase its activity. No hydrogen film collects on the cinder cathode and the cell remains active, resulting in rapid corrosion of the metal (3).

The permeability of the soil affects the rate of corrosion in two ways: it will control the rate of diffusion of the corrosion products and it will control the rate at which oxygen can reach the corroding metal.

2. Chemical properties

Although a large number of chemical elements exist in soils, most of them are combined in compounds, not easily soluble, that exert little chemical influence or corrosion. The soluble constituents of soils affect corrosion because they control the potentials of the anodes and cathodes and the resistance of the path of the corrosion current. The soluble constituents, especially the salts, furnish most of the ions that carry the current. As a rule, soils containing considerable quantities of salts in solution are corrosive (10).

Corrosion is also affected by the reactions between the soluble salts and the primary products of corrosion, the effect on the rate of corrosion depending on whether the reaction products are precipitated and on whether the deposited products are close to the anode and cathode of the corrosion circuit. In general, if the reactions result in the formation of soluble products, or if the products are precipitated at a distance from the electrodes, corrosion continues (10).

Difference of potential and therefore corrosion may be brought about by solutions of different substances (acids, bases, salts, or gases) in contact with adjoining parts of the same metallic surface. The same effect may be produced by two solutions of a single substance which vary in concentration, the anode being at the weaker solution (18).

Soils made alkaline by an abundance of calcium carbonate are called calcareous, and soils containing appreciable amounts of exchangeable sodium (or sodium plus potassium) are called alkali soils. The degree or intensity of acidity or alkalinity of a soil is expressed as its pH value. A pH value of 7 indicates neutrality; lower values, acidity; higher values, alkalinity. The pH value is a measure of the degree or intensity of the existing hydrogen-ion concentration, and not of the total quantity of ionizable hydrogen in the soil, which is referred to as the total soil acidity. Because the pH value and total soil acidity are influenced by the kind of clay, the kind and amount of organic matter, exchangeable bases present, and the soluble salts present in a soil, the relationship between pH and total acidity is not constant for all types of soils. Generally, soils rich in organic matter retain greater reserves of acidity and alkalinity than sandy soils or other soils low in organic matter (14). An acid soil with a low pH value and a high total acidity would be expected to be more corrosive than a soil having a lower pH value and a lower total acidity because of the greater tendency of high total acidity to prevent the formation of protective films (10).

The chemical properties of a soil may vary with time because of bacterial action. Certain types of bacteria are capable of "fixing" atmospheric nitrogen and of converting

nitrogenous material in the soil to forms useful to plant life. Other bacteria convert sulphur and sulphides to sulphates, and still other bacteria accomplish the reverse reaction.

3. Resistivity

The electrical resistance of the soil has been found to be one of the important factors in the soil corrosion process. As it is one of the most easily measured properties of a soil it is frequently used as an indication of soil corrosiveness. As the mineral grains of the soil have a relatively high electrical resistance, the electrical conductivity depends mainly on the quantity of soil water present and the concentration of salts or other electrolytes in solution. As the temperature also has an effect on the resistivity, seasonal temperature changes may be a factor, frozen soil having a very high resistivity (14).

A high salt concentration reduces the electrical resistivity and promotes electrolytic action, so that it is not surprising that some correlation between soil resistivity and corrosion has been found in areas showing relatively low resistance. Measurements of this factor, therefore, may afford a useful indication of corrosive areas when the results are used in connection with other soil characteristics.

A moderately high soil resistivity is usually, but not necessarily, caused by the absence of salts or by the relatively insoluble salts such as lime, magnesia, and gypsum. The lower resistivities are caused by higher concentrations of more soluble salts such as chlorides, sulphates, and carbonates of potassium and sodium (6).

4. Aeration (availability of oxygen)

The availability or non-availability of oxygen has been considered one of the most important factors in determining the rate and magnitude of soil corrosion.

It has been found that the corrosion rate in most natural waters is determined by the rate of depolarization at cathodic areas and, therefore, by the rate at which dissolved oxygen reaches these portions of the metal surface (an exception being when anaerobic bacteria are present). The effective oxygen concentration at the metal surface is determined by many factors such as: (a) the concentration of oxygen in the solution as a whole which is influenced by the partial pressure of oxygen in the atmosphere above the solution, the area of contact with the atmosphere, the rate of solution and diffusion of oxygen, the viscosity and amount of motion of the solution, the depth of immersion, and the presence of other substances in the solution; (b) the temperature, which also affects many of the conditions mentioned under (a); and (c) the degree of permeability of films or coatings on the metal surface (18).

As well as being an important secondary factor in corrosion, the distribution of oxygen is also an important primary factor. The unequal distribution of oxygen on buried metal surfaces appears to be one of the chief sources of potential differences. Under such conditions, areas deficient in oxygen are anodic with respect to those areas having a greater supply of oxygen. The supply of oxygen varies with the depth, with moisture content, with the topography, with the height of the water table, and with the permeability of the soil. All such non-uniform conditions give rise to corrosion currents (17). Since many of the above conditions

vary with the season of the year the rate of corrosion due to differential aeration will show a similar variation.

In well-aerated soils the rate of pitting of ferrous materials is initially very high because of the abundant oxygen supply at the cathodic areas. Oxidation and consequent precipitation of the corrosion products in close contact with the anodic areas cause a marked reduction in the rate of corrosion, with the result that the ultimate depth of pitting is relatively slight. On the other hand, in poorly aerated soils the rate of pitting, although low because of the deficiency of oxygen at the cathodic areas, is relatively unchanged with time, because the corrosion products in the reduced conditions are precipitated at points remote from the anodic areas. Consequently, the depths of the deepest pits after a long period are usually considerably greater in poorly aerated soils than in well aerated soils (10). This phenomenon appears to be the reason why corrosion in soil where the water is freely draining (and therefore supplying large quantities of oxygen to the metal) is less than in soil where the water is stagnant.

The optimum conditions, therefore, for corrosion propagation by differential aeration occur when part of the metallic structure is in well aerated soil and part in poorly aerated soil. The well aerated portion becomes the cathode which is depolarized rapidly and the poorly aerated portion becomes the anode which is rapidly corroded as the corrosion products are removed in the reduced condition. This corrosive action has been found between different sections of a pipe a mile apart (18).

5. Micro-organisms

Studies of certain micro-organisms have shown that they may have a great influence on the amount and rate of soil corrosion.

Micro-organisms contribute to corrosion by one or more of the following factors, each of which is dependent upon the physiological characteristics of the micro-organism (21):

- (a) Direct influence on the rate of anodic or cathodic reaction
- (b) Change of surface metal film resistance by their metabolism or products of metabolism
- (c) Creation of corrosive environment, and
- (d) Establishment of a barrier by growth and multiplication so as to create electrolytic concentration (aeration) cells on the metal surface.

To develop and grow, most micro-organisms must have available certain inorganic and organic chemical compounds to supply the oxygen, carbon, nitrogen, hydrogen, or sulphur necessary to their metabolic processes. These compounds are subject to considerable variation in regard to both chemical composition and the relative quantities of each required by a specific bacterium. The micro-organisms associated with corrosion should not be considered in any sense as being restricted to a soil or soil type. Availability of various inorganic and organic nutrients in a given environment together with other factors, such as pH, oxygen concentration, and temperature, will determine whether or not microbiological development can take place. It is possible, in so far as corrosion is concerned, to select any non-corrosive washed silica sand and make this sand severely corrosive by suitably adjusting both the chemical and associated environmental conditions (21).

Micro-organisms can be grouped according to their ability or inability to grow in an environment containing atmospheric oxygen. Aerobic micro-organisms readily grow in such environments, whereas anaerobic micro-organisms develop most favourably in environments in which the concentration of dissolved oxygen approaches zero (21).

The micro-organisms which have been found associated with soil corrosion are sulphate-reducing bacteria which occur under anaerobic conditions. These anaerobic bacteria are considered responsible for much of the severe soil corrosion which takes place in the Eastern United States (14), Great Britain (22) and Holland (2).

All species and strains of the sulphate-reducing bacteria have one common characteristic in that they utilize hydrogen to reduce sulphate. This results in the formation of hydrogen sulphide, which, in turn, further reacts with the ferrous metal to form ferrous sulphides. The sulphate-reducing bacteria are apparently able to utilize either bound or cathodic hydrogen; hence the hydrogen required by these micro-organisms for the reduction of sulphate may be obtained from either organic compounds or the aqueous electrolyte at the cathodic interface of the metal. Corrosion then occurs when the cathodic hydrogen resulting from the electrochemical corrosion process is removed and utilized by these bacteria. As corrosion proceeds more cathodic hydrogen is formed and the microbiological depolarization process continues, thus permitting corrosion to proceed apace in the absence of oxygen (18).

The above corrosion process is a secondary process and it may be necessary that a soil be corrosive from other factors before the anaerobic bacteria can prolong corrosion

by cathodic depolarization. It appears probable, however, that the anaerobic bacteria can cause differential aeration cells to form on the metal surface by removing the soil oxygen at local points where organic matter is being decomposed (8). This results in the unaerated portion of the metal becoming anodic to oxidized portions in the more aerated soils.

Environmental conditions which are necessary for the growth of the anaerobic sulphate-reducing bacteria are the absence of oxygen, an adequate concentration of sulphate, and adequate amounts of nutrients including organic matter. The bacteria develop best close to neutrality and fail to grow in laboratory media at reactions below pH 5.5 or above pH 8.5. On the basis of laboratory and field results, it has been concluded (19) that anaerobic corrosion is unlikely to occur in soils more acid than pH 5.5 and that corrosion is generally most severe close to neutrality.

The soil factor which has been found (19) to be most significant as an index of anaerobic corrosion is the degree of soil reductiveness, which can be measured as the oxidation-reduction potential, otherwise known as the redox potential or E_h . Since the sulphate-reducing organisms are anaerobes, they grow under strongly reducing conditions where the redox potential is low. There are changes in the pH and E_h of some soils during the year and these changes will be reflected in the activity of the anaerobic bacteria. The principal factor responsible for the changes is precipitation but the variations are not the same for all soils (19).

The sites where anaerobic corrosion has most frequently occurred are flat, low-lying lands, swamps or areas adjacent to

water which maintains the water table at a high level. Dense soils such as clays and clay loams which are poorly drained and poorly aerated are most commonly involved. Peat and mixtures of peat and sand are frequently anaerobic. Decaying organic matter favours the rapid multiplication of the sulphate-reducing bacteria (4). Even in soils of high oxygen content, however, a sufficient degree of anaerobiosis may frequently occur at isolated points and permit the active development of these bacteria. A decrease in the oxygen concentration at such a point, due to biochemical reducing reactions particularly cellulose fermentation, or even the presence of reducing metal ions, is often sufficient to permit the development of the sulphate-reducing bacteria (21).

The only certain way of determining the presence of anaerobic bacteria is to secure a sample of the soil and develop a bacterial culture from the sample (3). Although it is desirable to determine the presence of the bacteria from sites in which anaerobic corrosion might occur, their absence, or presence in low numbers, does not necessarily mean that this form of corrosion will not take place. These bacteria tend to migrate to the site of corrosion and multiply there (4).

Methods for Estimating Soil Corrosiveness

From the discussion of the factors that affect the corrosiveness of the soil, it is obvious that present knowledge of the action and the interaction of these many factors is not sufficient to determine rigorously how corrosive a soil will be. All that can be attempted is an estimate of the average relative corrosiveness of a soil. If soils are separated into four or five classes with respect to corrosiveness it can then be

estimated to which particular class a soil will belong. Fortunately, this is all that is usually required, as it is impractical to provide more than a few degrees or kinds of protection when it has been determined that a soil will be corrosive.

It has been found in general that soils which are corrosive are poorly drained, heavy (clayey), high in organic matter, high in dissolved salts, low in resistivity, high in total acidity, high in natural potential, and/or have an environment favourable to anaerobic bacteria. Methods for estimating soil corrosiveness then usually entail the measurement of one or several of these factors. Measurements of more than one or two of the factors are not usually economically justified as the properties of a soil may change every few feet and the testing of even a small area would consume an excessive amount of time.

The available test methods may be separated into the two general classes of laboratory tests and field or in situ tests. Laboratory tests are usually chemical tests which attempt to determine the one or more constituents or properties of the soil which give it its corrosive properties, and from which an estimate of the corrosiveness of the soil can be made. In field tests, electrical methods are usually employed in which no attempt is made to determine the cause of the soil's corrosiveness, but the magnitude of the electrical measurement is used to estimate the severity of the corrosiveness.

The results of all of these tests have had to be correlated with corrosion by some empirical method. Usually, tests have been made on soil the corrosiveness of which is known

from examination of buried test pieces or pipe lines. It should be kept in mind that although test results may have correlated fairly well with the actual corrosion in some soils, they may not do so in all soils.

Laboratory Tests

1. Soluble salts

There is no doubt that corrosion of metals in soils is affected by the chemical composition and the soluble salts of the soil. Chemical compositions have not, however, been used to any great extent for determining the corrosiveness of soils because of the variations that exist among sampling points and because of inconsistencies shown to exist in the rates of corrosion at locations where the chemical compositions of the soils are not markedly different (14).

2. Hydrogen-ion concentration and total acidity

The measurement of the pH of the soil may be done both in the laboratory and the field. Although no definite relationship has been noted between pH and corrosion, it has been found that, all other factors being equal, there is a relationship between total acidity and rate of corrosion (14). The methods of determining total acidity are described in references 10 and 14.

3. Resistivity

The resistivity of a soil depends largely on the nature and amount of dissolved salts in the soil, and also on the temperature and moisture content, compactness of the soil, and presence of inert materials such as stones and gravel.

If direct current is used in the measurement of resistivity, polarization of the electrodes will affect the results; if alternating currents are employed, the apparatus must compensate for inductive and capacitive effects. Since two samples of soil are seldom identical, and since the factors other than resistivity are rarely constant, an approximate value of resistivity is usually sufficient. The resistivity is usually measured as the number of ohms resistance across one cubic centimetre of soil (ohm-cm).

Since laboratory measurements of resistivity are taken on disturbed samples of soil, it is doubtful whether they are similar to the resistivity of the same soils in the field. The U.S. Bureau of Soils has devised a cell in which the soil is placed after being saturated, the electrical resistance is then measured between two electrodes using a Wheatstone bridge and 1,000 cps current (14). The disturbance and saturation may considerably change the resistivity for some soils.

4. Electrolytic-bridge or soil alkali bridge (6, 10, 14).

The electrolytic-bridge designed by the U.S. Department of Agriculture may also be used to measure the resistivity of samples of soil. Since the soil sample is mixed with distilled water until it is saturated after it is placed in the measuring cell, it is questionable whether the resistivity is representative of actual field conditions. By use of tables and nomograms prepared by the U.S. Department of Agriculture, the salt content in the soil can be estimated from the results of the measurements of resistance and temperature. The instrument is manufactured by several electrical instrument companies.

5. Putman's decomposition potential tests (6, 14).

A laboratory test developed by Putman and which has been used extensively in the Western United States constituted one of the earliest attempts to determine soil corrosivity and to associate corrosion with the electrical condition of the corroding metal. A subsequent modification takes account of the resistivity and acidity of the soil and of polarization.

The soil at its natural water content is compacted into a cell under a pressure and its resistivity found with an alternating current Wheatstone bridge. The current flow between the electrodes under a specified potential difference is then measured. These values, together with the pH, were correlated with the U.S. National Bureau of Standards soil-corrosion records on buried specimens.

6. Williams-Corfield or nipple-and-can test (6, 14).

The Williams-Corfield or nipple-and-can test has probably been used more in practice than any other test (6). A 4-inch length of 3/4-inch sand-blasted iron pipe is carefully weighed and placed in the centre of a pint can, and the space between the pipe and the can is filled with a water-saturated sample of the soil to be tested. The pipe is connected to the positive side of a 6-volt storage battery and the can to the negative pole. After 24 hours the pipe is removed, cleaned, and re-weighed. The corrosivity of the soil is indicated by a "corrosion index" as determined by the loss in weight.

Corrosion Index
(weight loss of pipe)

Corrosiveness of soil

3 gm or over

Very severe

2 to 2.99 gm

Severe

1 to 1.99 gm

Moderate

less than 1 gm

Good

Although this test has little theoretical justification, it is easy to run and has wide correlation with field experience. It appears to give an accurate estimate of the typical soils in the western part of the United States but is not readily adaptable to the more generally acid soils of the East (14).

7. Denison electrolytic corrosion cell (10, 14, 16)

Denison's cell test simulates actual soil conditions more nearly than do the tests so far discussed and yields more reproducible results (10). On the other hand, it requires greater care, more apparatus, and more time than the other tests. It has the advantage that the behaviour of different soils and metals can be investigated under uniform conditions of moisture and aeration, and the current through the cell can be regulated at will.

The cell consists essentially of two electrodes, a cathode in the form of a metal screen or perforated dish and an anode in the form of a solid disc of the same metal, separated by a layer of moist soil that constitutes the electrolyte. The cell is assembled in such a manner that the perforated cathode is more accessible to air than is the solid metal anode. An electromotive force is therefore developed in the cell by means of differential aeration between the two electrodes.

The cell, as modified by Schwerdtfeger (16), requires six months as the minimum time to determine soil corrosiveness. The laboratory results at the conclusion of the tests are based on the weight losses of the cell electrodes. Tests have shown that good correlation exists between laboratory data and the actual field weight losses (16). Equations have been set up whereby weight losses and maximum pit depths as indicated by the laboratory

corrosion cell can be extrapolated to any desired area of specimen and period of exposure within reasonable limits.

8. Presence of sulphides

The presence of anaerobic bacteria cannot be determined by any chemical test, but as the action of the bacteria responsible for corrosion is to reduce sulphates to hydrogen sulphide, the presence of sulphide in the corrosion products will indicate that bacteria are present. If the corrosion products are treated with a dilute solution of hydrochloric acid, the presence of sulphide is readily detected by the odour of hydrogen sulphide. A positive test for sulphides is that lead acetate paper will turn black when exposed to the evolved gas.

Field Tests

1. Identification of soil types (6,10, 14)

A method of establishing which soils are corrosive that has long appealed to investigators of soil corrosion is soil classification. Pedology, the science of soils, has classified soils according to their physical and chemical properties, the same properties which help to determine the corrosiveness of the soil. If the corrosiveness of a soil type or a soil series can be determined, then an estimate of possible corrosion can be made wherever this soil type or series occurs. As pedological soil maps are available for parts of the country, they may be an aid in determining the soil corrosivity in these areas.

Unfortunately, however, the corrosiveness of only a small percentage of the soil types or series has been actually

determined. In general, therefore, the corrosiveness of a soil series must be inferred from its chemical and physical characteristics, and by association of the characteristics of soils of unknown corrosivity with those of soils of known corrosivity. If the soil types are known in the area to be examined, then tests for corrosiveness may be limited to several tests for each soil type.

2. Shepard soil resistivity meter or cane apparatus (6, 10, 14)

Of the several pieces of apparatus used for determination of soil resistivity by corrosion engineers, Shepard's apparatus is probably that most widely used (6). It is portable, inexpensive, and a large number of observations can be made in a few hours either in the walls and bottoms of trenches or in holes driven in the ground. The apparatus consists of two insulating rods, such as bakelite rods, about 3 feet long, on which are mounted two iron electrodes connected to leads running through the centre of the rod. Because polarization of iron electrodes is largely a cathode effect, the amount of polarization has been reduced by making the cathode larger than the anode, thereby decreasing the current density on the cathode. The circuit is energized by a 3-volt battery (two flashlight cells) and the positive pole is connected through a switch to the anode. The batteries, indicating meter, and appropriate switches are mounted on one of the rods. With this instrument, the soil resistivity is measured between the two rods which are stuck in the ground about 8 inches apart. The apparatus cannot be used in very dry or rocky soil. The main disadvantage of the instrument is that its maximum depth of penetration is limited to about 2 feet.

The reading obtained is determined almost entirely by the

soil in the immediate vicinity of the anodic rod, and several readings are required to measure the average resistivity of the soil throughout the test area because the apparatus measures the resistivity of only a small volume of soil. Several manufacturers produce the instrument for sale. The polarization errors in the Shepard resistivity meter may be avoided by using alternating current instead of direct current. A meter similar in appearance to the Shepard meter, but using alternating current, has been designed (6).

The degree of corrosive action of the soil is generally estimated from the resistivity in the following manner:

<u>Resistivity</u>	<u>Corrosiveness of Soil</u>
ohm-cm.	
0-500	Very high
500-1000	High
1000-2000	Over normal
2000-10,000	Normal
over 10,000	Low

3. Wenner's four terminal method or McCallum earth current meter or megger apparatus (6, 10, 14).

The average resistivity of a large volume of earth can be obtained from the surface of the ground by the use of this apparatus. Four electrodes are placed in the earth spaced at equal distances in a straight line. An alternating or periodically reversed direct current is caused to flow between the outer electrodes, and the resulting differences of potential between the inner electrodes is observed. From these results, the resistivity can be calculated.

The advantages of this instrument are that no holes have to be dug and the resistivity to considerable depths can be found. The degree of corrosive action of the soil is estimated from the resistivity in the same manner as with the Shepard apparatus. Commercial models are available. Modifications of this apparatus have been used in geophysical work to determine boundaries of soil or rock strata from the surface.

4. Radio balance or radio frequency absorption (10, 14).

Another method for measuring soil resistivity, which however, requires further development for dependable results, is based on the radio balance that was originally intended for use in locating pipelines or other buried metal. The assembly consists of a six-tube, portable, impedance-coupled radio receiver and a two-tube oscillator. The apparatus operates on the principle that conducting materials act as a shield to the propagation of high-frequency waves, and consequently, the presence of conducting materials can be detected by properly designed apparatus. The instrument can be calibrated by making successive determinations of a number of soils of known resistivity. The equipment has the advantages of requiring no excavation and of giving a continuous reading across a site. It will measure the average resistivity, however, to a depth of only 4 feet. It is especially useful in locating approximately the boundaries of low resistance soils, which are usually corrosive.

5. Columbia rod (6, 10, 14).

The currents that are associated with corrosion depend not only on the resistivity of the soil but also on the potential of the metal with respect to the adjacent electrolyte and on the suppression of the corrosion currents by polarization films and corrosion products. The Columbia rod was designed to take account of these factors.

It consists of a $1\frac{1}{2}$ -inch rod tipped with a cone which is composed of a copper electrode and a steel electrode insulated from each other and connected to leads which pass through the rod. As no battery is used, the galvanic potential between these dissimilar metals constitutes the only source of current. The rod is driven into the bottom of a previously drilled auger hole. When the rod has been placed in position the circuit is closed through a microammeter and the current is read every 10 seconds for a period of 40 seconds. During the 40-second interval the current decreases and appears to approach a steady value. The instrument is calibrated by readings taken in soils of known corrosivity.

The Columbia rod has not been fully developed and has not been used extensively (10). Some tests have been made where the resistivity as well as the current have been measured between the electrodes. These tests have indicated that the current readings of the rod are affected more by the resistance of soil than by the potential of the metal (6). The amount of soil whose properties are measured in a single test is, of course, very small.

6. Norwegian Geotechnical Institute corrosion sounder (1, 15).

The Norwegian Geotechnical Institute has developed a probe which might be considered a refinement of the Columbia rod. This sounding device, in contrast to all the other corrosion apparatus developed to date, can be used to estimate the soil corrosiveness to considerable depth for structures such as steel piles.

The probe consists of a $1\frac{1}{4}$ -inch steel tube with a magnesium point insulated from the tube. Leads pass from the magnesium anode and from the bottom section of steel pipe up the pipe to the surface. No hole has to be drilled for the use of this sounding device since it is driven or pushed from the surface with measurements being made at any desired depth.

The resistivity of the soil is measured between the point and the tube by using a 600-cycles/sec alternating current and a Wheatstone bridge arrangement. The galvanic current between the magnesium point and the steel tube is then measured with a sensitive ammeter. These two measurements, resistance and current, can be used to calculate the electromotive force (emf) or potential difference between the magnesium anode and the steel cathode. The instrument has been calibrated by comparing the measured resistivity and electromotive force of soils from which old steel piles could be pulled for inspection of corrosion.

As the galvanic current is influenced by the rate at which the cathode and anode can be depolarized by oxygen or other depolarizing agents in the soil, the electromotive force can be expressed by the degree of depolarization. This value can be obtained by dividing the emf by the maximum possible value of the emf measured in salt water saturated with oxygen.

The classification of the corrosiveness of soil when using the probe is as follows (1, 15):

<u>Group</u>	<u>Corrosiveness of Soil</u>
1	Very low corrosivity
2	Low corrosivity
3	Intermediate corrosivity (app. 0.001 in./yr)
4	High corrosivity
5	Very high corrosivity

<u>Resistivity</u> (ohm-cm)	<u>Effective Electromotive Force (mv)</u>				
	350	350-450	450-550	550-650	650
50	2	3	4	4	5
50-250	2	3	3	4	5
250-1250	2	2	3	3	4
1250-6250	1	2	2	3	3-4
6250	1	1	1	2	2-3

<u>Resistivity</u> (ohm-cm)	<u>Degree of Depolarization (%)</u>			
	0-40	40-60	60-80	80-100
50	2	3-4	4	5
50-250	2	3	4	5
250-1250	2	2-3	3	4
1250-6250	1	2	3	3-4
6250	1	1	2	2-3

The amount of soil that influences any one measurement is very small and the differences in values which occur in a horizontal or vertical direction should be kept in mind when estimating soil corrosiveness.

7. Russian soil corrosion probe (20).

A probe has been developed in the U.S.S.R. which attempts to measure more soil corrosion factors than does any other apparatus developed to date. Measurements are made of the soil resistivity with no polarization, galvanic potential difference between electrodes with no polarization, and polarization of electrodes under an external direct current.

The probe apparatus consists of a thick-walled pipe 2 meters long and 20 mm in diameter made of separate portions screwed together. The head of the rod carries two iron electrodes, each 20 sq cm in area, isolated from the metal rod by ebonite washers and with miniature copper-sulphate reference electrodes. Both iron electrodes are used as anodes or cathodes of cells and for measuring electrical resistivity of the soil. An iron bar, forced into the soil at a distance of 1.5 to 2.0 meters from the rod, serves as an auxiliary electrode for polarization. Leads from the electrodes pass through the rod to the surface.

The rod is forced into the soil and the soil resistivity between the iron electrodes measured with a 1000 cycles/sec alternating current. The galvanic current between the iron and copper-sulphate electrodes is then measured, the copper-sulphate cathodes ensuring that cathodic polarization will not take place. Cathodic polarization is measured at the two iron electrodes by imposing an 0.8-volt potential between the distant iron bar and the electrodes. The final value of the cathode current, which becomes steady within 20 minutes, is measured. Anodic polarization of both iron electrodes is then produced by a potential difference of 0.2 volt and the current measured after 10 minutes, a time considered sufficient for partial stabilization of the electrode process.

By consideration of the above measured values the corrosivity of the soil is estimated. The instrument was calibrated by comparing measured values for different soils with the corrosive losses of steel samples buried in those soils. Although the apparatus has the advantage that a fairly large volume of soil is included in the polarizing circuit, it has the disadvantage of all the other instruments except the Norwegian probe, in that it was designed for use with pipelines and can only make measurements to shallow depths.

8. Redox soil probe (5, 14, 19)

An in situ test to determine whether a soil environment is favourable for the development of anaerobic bacteria has been developed by the American Gas Association (5). The degree of soil aeration can also be indicated with this test.

Anaerobic sulphate-reducing bacteria thrive in poorly aerated neutral soils. These soils become reduced to varying degrees and the degree of reduction can be measured by determining the oxidation-reduction (redox) potential. These potentials are influenced by the hydrogen ion concentration, so the pH must be determined to evaluate the significance of the soil redox potentials.

The apparatus devised can measure soil E_h (redox potential) in the field to a depth of 4 feet. It consists of a plastic tube with a tapered point. Two platinum electrodes are fixed in the slope of the tip and a calomel reference cell is contained within the 6-inch lower section of the probe tube. A porous ceramic plug is used for the electrolyte solution bridge from the calomel cell to the soil contact surface. Leads from the electrodes pass up the tube to the surface.

A sample of soil is obtained from the desired depth for a test of the pH. If the pH is in the range pH 5.5 to 8.5 the possibility of bacterial corrosion occurring is evident and a test is made with the redox probe. A hole is made with a crowbar or soil auger to the desired depth and the redox probe with freshly cleaned electrodes is inserted to the bottom of the hole and the tip pressed into the undisturbed soil. Two readings are made, one with each platinum electrode.

Survey work with the soil probe in the Eastern United States gave good correlation between E_h values of the soil and pipe inspections. The following scale was formulated for estimating soil corrosiveness from soil redox potentials:

<u>Range of Soil E_h</u> millivolts	<u>Corrosiveness of Soil</u> (from anaerobic corrosion)
below 100	Severe
100-200	Moderate
200-400	Slight
over 400	None

Discussion of Test Methods

In practice, soil corrosion investigations are seldom made, and when they are, are often of doubtful value. The following references give an indication of the present practice in the oil and gas industries.

McHardy and Windebank (11) describe an investigation for a proposed 350-mile gas pipeline in Pakistan. At 5-mile intervals the soil resistivity was measured at depths of 1, 3, and 10 metres

by means of an earth megger using the four-pin method. Representative soil samples were also taken at points where changes in soil conditions occurred. A chemical and microbiological analysis of numerous soil samples confirmed survey observations that the entire route was generally corrosive to a greater or lesser degree.

Parker (13), in discussing the fundamentals of corrosion studies on existing pipelines, states that soil resistivity measurements should be made with the four-terminal instrument so that the resistivity may be determined at the approximate depth of the pipe. When analysing the results of the resistivity survey it may be assumed that: soils over 10,000 ohm-cm are rarely corrosive; soils under 1000 ohm-cm are almost always corrosive; and soils between these two values are only corrosive in narrow strips of relatively low resistivity.

Kulman (9) in interviewing 28 gas companies in the United States found that they identify corrosive soil by one or more of the following methods: measurement of soil resistivity; observation of wetness or dampness; measurement of soil pH; presence of dense soil. The author points out that none of these methods gives a quantitative measure of the oxygen content or aeration of the soil. All companies were in agreement that better methods of measuring soil corrosiveness were needed.

Carrière and Lobry de Bruyn (2), in discussing soil corrosion in Holland, give the methods recommended by the Dutch Corrosion Committee for determining soil corrosiveness. In the lower parts of the Netherlands where the water table is close to the surface, the water often brackish, and anaerobic bacteria

play an important role in the corrosion process, the investigations consist of the following determinations: chemical analysis of the soil, acidity by pH measurement, electrical conductivity with the Shepard apparatus, and state of oxidation with respect to reduction of the soil by measurement of the redox-potential.

Other organizations use some of the other test methods which have been discussed in addition to the methods given in the above references. The use of different tests in different localities is entirely justified. It can be said in general that each of the different tests can identify certain corrosive conditions in the soil, but that no single test can identify all places where corrosion is likely to occur. It is probable that their relative effectiveness will differ in different localities. What is required is a series of laboratory and field tests on soils in different localities and correlation of these tests with the amount of corrosion observed on samples or pipes laid in the same soils.

Two series of such tests have been reported and are discussed below. The first problem of such a comparison is that the results will depend to a certain extent upon what criterion is adopted for judging the amount of corrosion a sample has undergone. Maximum pit depth, holes per unit length, average weight loss, or average pit depth can be used for this purpose. The element of time must be taken into account because corrosion does not, as a rule, proceed at a uniform rate.

It should also be noted that almost all tests and correlation of tests to date have been made on disturbed soil for the purpose of estimating the corrosiveness of the soil

on pipelines or similar buried structures. The use of these tests for the estimation of corrosion of steel piles which are in relatively undisturbed soil is not reasonable until better correlations are made between these tests and corrosion in undisturbed soil.

In 1937, the Magnolia Pipeline Company uncovered 25 miles of 8-inch asphalt-coated steel line that had been buried for 16 years in south-eastern Texas (10). As a measure of the corrosive action, the depths of the three deepest pits and the number of punctures, if any, in each 20-foot length of pipe were recorded. The Shepard resistivity apparatus was used to determine soil resistivity at pipe depth at 200-foot intervals along the right-of-way. The soils were identified according to the U.S. Department of Agriculture classification system, and soil samples taken at pipe depth were sent to the laboratories of the National Bureau of Standards for determinations of hydrogen-ion concentration, total acidity, resistivity at normal moisture content, Columbia rod test (modified for laboratory use), Putman test, nipple-and-can test, and the original Denison electrolytic cell test.

It was not possible to correlate the tests on a single soil sample with the amount of corrosion on the pipe adjacent to it. However, when the pipeline area was divided into five arbitrary zones, according to corrosivity or pit depths, it was found that all of the methods used showed, in a general way, the corrosiveness of the soils, but that no test correctly determined the corrosivity of every soil series and some correctly classified only two of the soils. As a result of this study, it was concluded:

- (a) The soil types of a soils series usually do not differ greatly in corrosiveness.
- (b) Some degree of correlation with corrosivity can be established for single property determinations of selected soils.
- (c) No single property determination can be correlated with corrosiveness of all the soils encountered.
- (d) The Denison cell test has the best potentialities for correlation with soils in general, because it is, in effect, an accelerated corrosion test rather than a determination of a single property of the soil.
- (e) Correlations can be established better on the basis of an area or zone than on a particular spot.

Kulman (8) reported on a series of tests on soils adjacent to corroded steel gas mains in New York City. The tests were made during the ten year period up to 1949 and an analysis of tests at 472 excavations was given. The soil texture, colour, aeration, and drainage were described, a hydrochloric acid test for sulphide in the corrosion product was made, and soil resistivity and pH were measured. A description of the pipe corrosion (pitting, scale, etc.) and measurements of the pit depths were made.

The study showed that the most severe corrosion usually occurred in a dense, anaerobic, clay containing soils in which organic matter was present. Severe corrosion in the sandy soils was less frequent and when it did occur it was generally manifested as oxidation and slabbing. The average soil resistivity of soils associated with severe corrosion was 12,200 ohm-cm; with moderate

corrosion, 25,600 ohm-cm; and with slight corrosion, 40,000 ohm-cm. The hydrochloric acid tests on corrosion products gave evidence of ferrous sulphide in 81 per cent of the cases of severe corrosion, 54 per cent of the cases of moderate corrosion, and 46 per cent of the cases of slight corrosion. Although other factors were present, the results indicated a correlation between pipe corrosion and anaerobic conditions, together with the possible activity of anaerobic bacteria. It was not possible to obtain a satisfactory correlation between pipe corrosion and soil pH.

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DISCUSSION OF REFERENCES

1. CORROSION - GENERAL

Speller, 1951 (18), has a clear, detailed discussion of the electrochemical mechanism of corrosion. This is an excellent book on corrosion.

Uhlig, 1948 (21), is a condensed summary of corrosion information with articles by many authors. Has a good section on micro-organisms.

Fontana, 1957 (7), is a compilation of monthly columns written over ten years. Good, simple description of practical corrosion problems but has little on soil corrosion.

2. UNDERGROUND CORROSION - GENERAL

Logan, 1945 (10), and Romanoff, 1957 (14), are the best all round books on soil corrosion. They contain, however, little theory

and are mainly the results of the U.S. National Bureau of Standards tests. They have good descriptions of all the different test apparatus except for the newer probes. Circular 579 (14) is a revised edition of circular 450 (10) but circular 450 has more detail on some of the test apparatus. Logan has 206 references and Romanoff 407 references.

Ewing, 1938 (5), is a good, general book on soil corrosion. Has a good description of test apparatus.

Columbia Gas System, 1952 (3), is a good simple description of underground corrosion processes written in a popular style for the layman.

Mudd, 1945 (12), is a fairly good general article on soil corrosion.

3. FACTORS AFFECTING SOIL CORROSION

No one reference is outstanding in the discussion of all the factors affecting soil corrosion. References 3, 6, 7, 10, 14, 17, 18, and 21 all discuss various factors.

4. METHODS OF DETERMINING SOIL CORROSIVENESS

Logan, 1945 (10), Romanoff, 1957 (14), and Ewing, 1938 (6), all discuss most of the test methods and apparatus.

Schwerdtfeger, 1953 (16), has the best reference to the Denison cell.

Starkey and Wight, 1945 (19), have the best discussion of the redox probe.

Bjerrum, 1957 (1), and Rosenquist, 1956 (15), discuss the Norwegian probe.

Tomashov and Mikhailovsky, 1959 (20), discuss the Russian probe.

5. ANAEROBIC BACTERIA

References 19 and 21 have the most comprehensive discussions of anaerobic bacteria. Additional information is also available in references 4, 8, and 22. Reference 5 discusses the redox probe.

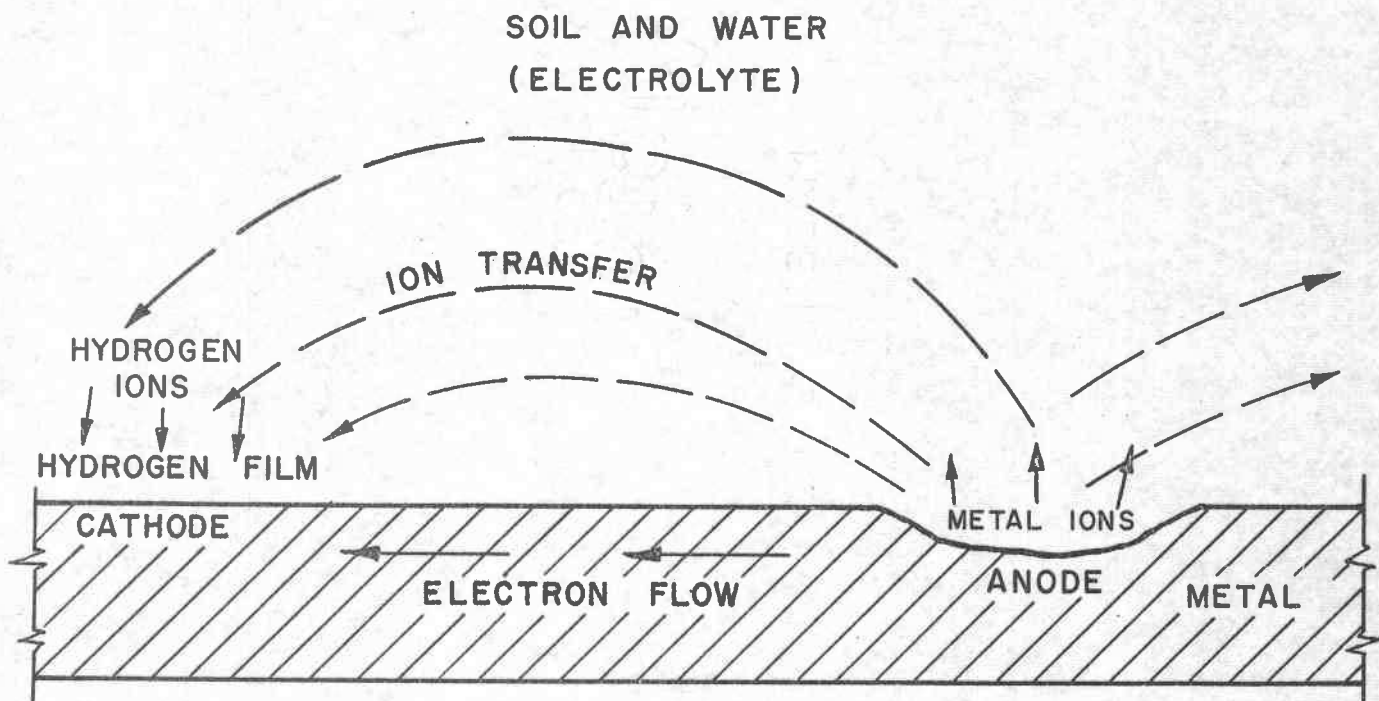


FIGURE 1

ELECTROCHEMICAL THEORY OF SOIL CORROSION