PROPERTIES OF RADIOACTIVE WASTES
AND WASTE CONTAINERS

PROGRESS REPORT No. 6
JULY - SEPTEMBER 1977

P. COLOMBO AND R.M. NEILSON, JR.

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SUMMARY

Although the waste container is generally given no credit for the containment of activity in burial, the integrity of the waste container should be considered since it can provide an important barrier to the migration of activity from the burial site. Corrosion is one of the primary causes of the loss of integrity of the waste container in burial. Corrosive failure is due to the interaction of the burial environment (soil) and/or the interaction of the waste form with the waste container.

In this report, a survey has been made of the available literature on the corrosion of steels in soil environments. The effect of the physical and chemical properties of the soil on the rate and type of corrosion of steels has been evaluated. The corrosion rates of ferrous alloys are influenced primarily by the soil environment; alloy compositional and microstructural considerations are secondary. However, as the steel is made more resistant to uniform corrosion it becomes more susceptible to pitting corrosion. The various tests and criteria proposed to measure the corrosiveness of soil have been reviewed.

I. INTRODUCTION

Solidified radioactive wastes are currently contained and buried in either 55 gallon mild carbon steel drums or large vaults (50-200 ft.³) made of mild steel or concrete. The purpose of the container is to provide ease of handling, minimize personnel exposure and prevent the loss of activity from the waste package prior to burial. Current waste management philosophy gives no credit to the container for containing the activity in burial. However, since the migration of activity from the trenches at the burial sites is of prime importance in the evaluation of the site, the ability of waste container, as well as the waste form, to contain the activity should be considered. If the integrity of the container could be maintained for greater lengths of time during burial, it could provide an important barrier to migration of activity from the burial site.

Container failure can occur by either mechanical failure or corrosion. Corrosion attack of the container could result due to chemical interactions with the environment and with the waste form. However, corrosion from the external environment during interim storage and transportation is usually low and, therefore, can be neglected. The primary concern of attack by the environment is in burial, where the container is in contact with the soil for a long period of time. The mean lifetime of the container in the burial environment is of interest, and to this end a survey of the available literature on the corrosion of steels in soil environment is presented.

II. CORROSION IN SOILS

Corrosion of metals in soils is electrochemical in nature and, therefore, the mechanism of electrochemical reactions can be used to explain the rate of corrosion in soils. For electrochemical corrosion to occur, there must be a potential difference between two points that are electrically connected and immersed in an electrolyte. A current flows from the anode area through the electrolyte to the cathode area and then through metal to complete a circuit. The anode has a more negative potential than the cathode, and is corroded by the loss of metal ions to the electrolyte. The anodic reaction is:

Simultaneously the cathodic reaction is either:

in acidic solutions, or

in neutral and basic solutions containing air.

The rate of metal loss is determined by the current flow through the complete circuit. The anodic reaction can be controlled by the type of metal or alloy exposed. The cathodic reaction generally depends on the pH of the electrolyte and the availability of oxygen at the cathodic site. The rate of the reaction is also dependent on the electrolyte which provides the resistive path for the flow of current. The rate of corrosion of the metal can be controlled by controlling any one of these factors.

The various factors not only control the rate of corrosion but, also the kind of corrosion attack, whether it is uniform or the pitting type of corrosion. Uniform corrosion is the loss of the metal over the completed exposed area. This form of corrosion is exhibited by normally active materials and it is generally

low in soil environments. Uniform corrosion is important for underground structures that are primarily load bearing, such as steel pilings.

Pitting is the corrosion of the metal at localized areas, while the rest of the metal is not attacked. This type of corrosion is of major importance in structures used for containment, such as pipelines, waste barrels, etc. As the composition of the metal is changed to make it less active, i.e. passive, the rate of uniform corrosion decreases, however, the material is now susceptible to pitting corrosion. Localized attack may also occur due to buildup of local corrosion product concentration, or differences in aeration because of variations in the packing of the soil.

Soil as a corrosive environment is probably of greater complexity than any other environment. Therefore, it is difficult to make absolute predictions of the rate of corrosion of metals in soils. Only some generalizations regarding soil types and corrosion can be made. The following sections discuss the characteristic features of the soil as a corrosive environment, however, it must be remembered that the absolute corrosion rate will depend on the interaction of the climate, rainfall and the various soil reactions.

It has been found that the measured corrosion rate in soils is dependent on whether the material was buried in undisturbed soil, such as immersion of pilings, or in disturbed soils, such as trenches or excavations which are dug and refilled. In general, the corrosion in undisturbed soil is lower than in disturbed soils. This difference is mainly attributed to the aeration of the soil. The disturbed soils have a higher oxygen content which generally leads to higher corrosion rates. The results reported in this report have been obtained from disturbed soils and thus closely simulate the conditions in radioactive waste burial sites.

Corrosion rate is generally expressed as the average uniform corrosion rate in $\text{mg/dm}^2/\text{day}$ (mdd), which expresses the loss of weight of the material, or mils per year (mpy), which gives average rate of penetration of the metal by the corrosion process. (Conversion of mdd to mpy: $\text{mpy} = \text{mdd} \times 1.44/\text{density (g/cm}^3\text{)}$ of the material). In the case of pitting, the maximum penetration of the metal by pitting in mils for the total exposure period is given.

III. MATERIAL CONSIDERATION

In a major investigation by the National Bureau of Standards,¹ to determine the corrosion of metals in soils, a large number of samples of wrought steels, low alloy steels and high alloy steels were exposed for over 12 years in various types of soils in the United States. It was concluded that the differences in the soils was so great that the average rate of corrosion of a given steel for all soils would have little value. In the case of various wrought steels exposed to the same soil the corrosion rate was similar with respect to the weight loss and the pit depth distribution. However, the same steel exposed to different soils was attacked differently. Therefore, the soil type was judged as a better criteria to determine the corrosion rate of steels. Generally, the rate of uniform corrosion of alloyed steels is less than ordinary steels, but the alloy steels are more susceptible to pitting corrosion.

IV. CHARACTERIZATION OF SOILS

Soils are commonly classified according to the general size range of their inorganic particulate matter; sand (0.07 to 2 mm), silt (0.005 to 0.07 mm), and clay (< 0.005 mm). The proportion of the three size groups will determine the soil type. Figure 1 represents the commonly used terminology for the various proportions of sand, silt and clay.²

Since soils contain organic matter, moisture, gases, and living organisms as well as mineral particles, it is apparent that the relative size range does not determine the whole nature of the soil structure. In fact, most soils contain an aggregate of particles within a matrix of organic and inorganic colloidal matter. This aggregate determines the physical and chemical properties of soil such as the moisture content, aeration, biological activity and alkali accumulation.

The soil characteristics at a given site may also vary as a function of the depth below the surface. Corrosion surveys based on surface observation give little information as to the actual environment of the buried material. For example, Figure 2 shows that the resistivity of one soil (one of the parameters used to measure the aggressiveness of the soil is its resistivity) changes from 2,000 Ω -cm at 60 cm (2 ft.) from the surface to 200 Ω -cm at 450 cm (15 ft.) from the surface, and could lead to an increase in the corrosion rate with depth. The various strata of the soil above the buried material is also important, since they determine the accessibility of the air and moisture to the soil surrounding the buried material.

The clay content of a soil is the most important inorganic constituent of the soil. The sand and the silt in the soil generally remain inert, but the weathering of the clay can cause various changes in the physical and chemical properties of the soil. These changes can have significant effect on the corrosion of buried metals.

Figure 1. Proportions of sand, silt and clay making up the various groups of soils classified on the basis of particle size (Ref. 2).

Figure 2. Variation of soil resistivity with depth for a light brown clay aggressive to ferrous metals (Ref. 10).

A. Physical Properties

The physical properties of soils that affect corrosion are chiefly those that determine the permeability of the soil to air and water. The particle size distribution is the most important factor which influences both the aeration and the moisture content of the soil. In general, sandy soils have a free circulation of air and a low water holding capacity. Therefore, the corrosion rate in these soils is low and approaches the atmospheric type. Clayey and silty soils are characterized by a fine texture, high water holding capacity, poor aeration and poor drainage. These soils give higher corrosion rates and represent conventional aqueous corrosion. Clay particles are highly plastic and become sticky and impervious when saturated with water. Such soils shrink and crack on drying and swell on rewetting. This process of shrinkage and cracking on drying and swelling on rewetting gives a greater rate of corrosion.

1. Aeration

Aeration, i.e. the availability of oxygen at the burial site plays a direct role on the type and rate of corrosion of the metal. The effect of oxygen is, however, dependent on other properties of the soil, such as the acidity and the moisture content. Generally, poor aeration and high values of acidity and salt content increase the corrosion rate.³ Well aerated alkaline soils are typically not corrosive.

In well aerated soils a protective oxide film may form on the metal and this would prevent further degradation of the metal. However, the protective film may be punctured due to local chemical changes in the soil and lead to pitting of the metal. The rate of pit growth is also dependent on the aeration of the soil. In well aerated soil the rate of pitting, although initially high, falls off rapidly with time. On the other hand, in poorly aerated soils, the rate of pitting decreases slowly, if at all, with time. The effect of time on the average pit depth is shown in Figure 3 for selected soils.

In addition, it appears probable that aeration of soils may affect

Figure 3. Pit depth versus time (Ref. 1) for wrought ferrous pipes in various soils.

corrosion not only by the direct action of oxygen in forming protective films, but also indirectly through the influence of oxygen reacting with and decreasing the concentration of the organic complexing agents or depolarizers naturally present in some soils which greatly stimulate local-action cells. In this regard, the beneficial effect of aeration extends to soils that harbor sulfate-reducing bacteria, because these bacteria become dormant in the presence of dissolved oxygen.

Local differences in the packing of the soil and its moisture content may develop oxygen concentration cells. The area of the metal which is not accessible to oxygen is anodic, i.e. it corrodes, to the areas which are readily accessible to oxygen. The rate of corrosion is dependent on the relative size of the anode and the cathode. A small size ratio gives rise to rapid pitting. The presence of oxygen concentration cells has been cited as one of the major reasons for local corrosion of pipelines.⁴

2. Moisture Content

The principle function of the soil moisture is to furnish the electrolyte for carrying the current and promote the electrochemical corrosion process. The moisture content controls the amount of dissolved salts, which determines the soil resistivity of the electrolyte, as well as the acidity or alkalinity and the development of the chemical reactions between the primary products of metallic corrosion and the electrolyte.

The resistivity of soil is extensively used as the main single parameter to predict the corrosiveness of a soil.¹ Combined with resistivity, absolute moisture content values have also been used to determine the aggressiveness in soils. In fact, Tomashov and Mikhailovsky⁵ and Stratfull⁶ regard the water content as one of the most important factors controlling the rate of corrosion of metals in soils.

The moisture content and the oxygen content of the soil are inter-related. A porous soil may retain moisture over a long period of time or may

allow optimum aeration and both these factors tend to increase the initial rate of corrosion. The wet-dry alteration, either temporal or spatial, leads to higher corrosion rates than would be obtained with a constant environment. This same fluctuation also leads to greater variation in biological activity in soils.

B. Chemical Properties

A large number of chemical elements exist in soils, but most are combined in insoluble compounds which exert little direct chemical influence on corrosion. These inert compounds of soils are chiefly oxides of silicon, aluminum and iron. Chemical analysis of soils, for corrosion studies are usually limited to determinations of constituents that are soluble in water.

The development of acidity in soils is a result of the natural process of weathering under humid conditions. The acidity is expressed as the pH value. Most soils have a pH of from 4.5 to 10. It should be emphasized that the pH value is a measure of the existing hydrogen ion concentration and not the total quantity of ionizable hydrogen in the soil, which is referred to as the total soil acidity. Because the pH and total acidity depends on the type of clay, amount of organic matter, exchangeable bases, and salts, the relationship between pH and total acidity is not constant for all soils at all times. Generally, soils rich in organic matter are well buffered and retain greater amounts of acidity or alkalinity than sandy soils. Such buffered soils resist changes in soil pH and prevent development of low pH and very corrosive conditions.

The chemical properties of soils may also vary with time due to bacterial action.

1. Inorganic Matter

The main inorganic ions in soils are positively charged cations, such as Ca^{++} , Mg^{++} , Na^+ and K^+ , and negatively charged anions such as Cl^- , SO_4^{--} , CO_3^{--} , and HCO_3^- . As a result of disintegration of rocks and micro-organic reaction, some metasilicic acid $(\text{H}_2\text{SiO}_3)_n$ may be present. Depending on the surrounding geological structure, traces of iron, copper, lead and zinc may also be found

in the soil.

The effect of soluble salts on corrosion is shown in Table 1. It is observed that in general, the corrosive soils have large soluble salt contents. However, the absolute concentration of the various constituents cannot be used to determine the corrosiveness of the soil because of the inconsistencies shown in the rate of corrosion at locations where the chemical composition is not markedly different.¹ It should be remembered that only the salts that are soluble in the soil at a given time play a role in the corrosion process and the amount of dissolved salts is controlled by the moisture content of the soil. Since the soluble ions contribute to the conductivity of the soil, the relation between the conductivity and the corrosion rate of the soil does give an indirect indication of the effect of inorganic matter on the corrosiveness of soils.

2. Organic Matter

There are two types of organic matter found in soils; (i), non-living matter derived from decay of vegetable matter from drainage and in waters from marshy land, and (ii), living, microscopic organisms such as bacteria and algae. The non-living organic matter do not directly interact in the corrosion process; they generally just change the chemical composition of the soil. The living organism can affect the corrosion behavior in the following ways:

- a. Influence the anodic and cathodic reactions.
- b. Influence the protective films.
- c. Influence the environment.

Micro-organisms are classified according to their ability to grow in the presence or absence of oxygen, (i) aerobic - organisms that require oxygen in their metabolic process, and (ii) anaerobic - organisms that grow most favorably in environments containing little or no oxygen.

The most important anaerobic bacteria which influence the corrosion behavior of buried steels are sulfate reducing. These reduce the sulfate to sulfide by reacting with the hydrogen in the soil. The presence of sulfide ions

Table 1

Relation of Water Soluble Salts to Some Other
Properties and to Corrosivity of Certain Soils (Ref. 1)

SOIL		COMPOSITION OF WATER EXTRACT, mg-eq per 100 g of soil ¹						ACIDITY		Electrical Resistivity at 60°F	CORROSIVITY
Type	Na+K	Ca	Mg	CO ₃	HCO ₃	Cl	SO ₄	pH	Total acid- ity, mg-eq per 100 g of soil		Max. pit depth in Bessemer steel after 12 years
LEAST CORROSIVE											
										ohm-cm	Mils
Unidentified silt loam-----	0.67	0.72	0.39	0.00	0.88	0.06	0.48	7.6	3.0	1,770	29
Keyport loam-----	----	----	----	----	----	----	----	4.5	19.1	5,980	50
Ruston sandy loam-----	----	----	----	----	----	----	----	4.5	4.6	11,200	47
Merrimac gravelly sandy loam--	----	----	----	----	----	----	----	4.5	12.6	11,400	31
Miami silt loam-----	0.27	0.50	0.31	0.00	0.70	0.03	0.12	7.3	2.6	2,980	39
Everett gravelly sandy loam---	----	----	----	----	----	----	----	5.9	12.8	45,000	40
Norfolk fine sand-----	----	----	----	----	----	----	----	4.7	1.8	20,500	45
MOST CORROSIVE											
Fargo clay loam-----	1.42	1.72	2.55	0.00	0.71	0.01	4.43	7.6	(2)	350	119
Unidentified alkali soil-----	8.15	3.70	0.70	0.00	0.24	0.18	11.98	7.4	(2)	263	137
Muck-----	2.15	1.92	1.55	0.00	0.00	1.69	2.36	4.2	28.1	1,270	146
Peat-----	1.52	7.30	4.06	0.00	----	2.27	2.13	6.8	36.0	800	103
Montezuma clay adobe-----	1.50	0.06	0.18	0.00	0.12	0.99	0.89	6.8	(2)	408	153
Merced silt loam-----	8.38	0.38	0.22	0.02	1.87	1.12	5.57	9.4	(2)	278	173

1 Analyses by I.A. Denison; mg-eq = milligram equivalent.

2 Alkaline.

markedly increases the anodic reaction. The corrosion product in this reaction is iron sulfide which deposits on the steel.

Aerobic bacteria react with sulfur to produce sulfuric acid. These bacteria thrive in low pH environments and can sometimes produce localized sulfuric acid concentration of up to 5% by weight. Thus, these bacteria can produce locally very corrosive environments.

Sulfate-reducing and sulfur-oxidizing bacteria can operate in a cyclic fashion when soil conditions change. Sulfate-reducing bacteria grow rapidly during rainy seasons when the soil is wet and air is excluded, and sulfur-oxidizing bacteria grow rapidly during dry seasons when air permeates the soil. In certain areas, this cyclic effect has caused extensive corrosion damage of buried steel pipelines. Also, it is evident that the presence of micro-organisms can accentuate conditions of differential aeration in soils.

Other organisms, such as iron bacteria, assimilate ferrous iron from the solution and precipitate it as ferrous or ferric hydroxide in sheets surrounding their cell walls.⁷ The growth of iron bacteria frequently results in tubercles on steel surfaces that tend to promote crevice attack. Certain bacteria are capable of oxidizing ammonia to nitric acid. Dilute nitric acid corrodes iron and most other metals. In most soils, the amount of available ammonia is not high enough to cause an appreciable accumulation of nitric acid; however, these bacteria may be important where extensive use of synthetic ammonia fertilizers have been employed on cultivated fields above buried materials. Finally, most bacteria also produce carbon dioxide, which can contribute to the formation of carbonic acid and increase corrosivity. Some of the more important micro-organisms and their characteristics are listed in Table 2.⁸

No detailed study of the effect of organic matter on the life of steel structures has been made. The most important aspect of this form of corrosion is that it is localized and, thus, can have a significant effect on the integrity of a containment vessel.

Table 2
Physiological Properties of Microorganisms (Ref. 8)

Group and Type	Oxygen Requirement	Soil Components Reduced or Oxidized	Major End Products	Habitat	Approximate Optimum Reaction pH	Temperature limits, C°
I. Sulfate reducing, (Desulfovibrio, Desulfuricans)	Anaerobic	Sulfates, thiosulfates, sulfites, sulfur, hypsulfides	Hydrogen sulfide	Water, muds, sewage, oil wells, soils, bottom deposits, concrete	Optimum: 5.-7.5 Limits: 5.-9.0	Optimum: 25-30 Maximum: 55-65
II. Sulfur oxidizing (Thiobacillus thiooxidans)	Aerobic	Sulfur, sulfides, thiosulfates	Sulfuric acid	Soil composts, sulfur and rock phosphates, soils containing incompletely oxidized sulfur compounds	Optimum: 2.0-4.0 Limits: 0.5-6.0	Optimum: 28-30
III. Thiosulfate oxidizing (Thiobacillus thio-parus)	Aerobic	Thiosulfates, sulfur	Thiosulfate to sulfate and sulfur Sulfur to sulfate	Widely distributed, sea and river water, mud sewage, soil	Optimum: Close to neutral Limits: 7.0-9.0	Optimum: 30
IV. Iron bacteria (Crenothrix and leptothrix)	Aerobic	Ferrous carbonate, ferrous bicarbonate, manganese bicarbonate	Ferric hydroxide	Stagnant and running water containing iron salts and organic matter		Optimum: 24 Limits: 5-40

3. Influence of pH

The influence of pH on the corrosion behavior of iron is very characteristic, as shown in Figure 4. In an acid solution iron dissolves freely and evenly with the evolution of hydrogen. With the increase in pH, i.e. decrease in acidity and hydrogen ion concentration, the corrosion rate decreases regularly until a pH value of about 4.0 is reached. When the influence of oxygen reduction at the cathode begins to be appreciable. In the pH range 4.0-9.5, the rate of attack is almost constant and is generally controlled by the supply of oxygen. With further increase in the pH value the corrosion rate decreases more sharply to a minimum at about pH 12.0. On further increase in the pH value the corrosion rate starts to increase again with the formation of ferroates.

Since the pH of most soils is within 4.0 to 9.0, the corrosion rate is expected to be similar. Although the overall attack may be reduced by increasing the pH value there is a real danger that the attack will be concentrated at a localized area and the depth of pitting may become very severe, particularly in the presence of aggressive ions such as chlorides.

The pH of the soil as a single parameter of the soil corrosiveness is not a good indicator since, unless the soil has constituents that act as buffers, the pH changes as the corrosion reaction proceeds. Probably the total soil acidity may be a better gauge. It has been found that for a fixed amount of oxygen present in the soil the rate of corrosion is proportional to the total acidity rather than the pH. Denison and Ewing⁹ showed that the corrosivity of Northern Ohio soils could be expressed as:

$$P = 7500 \frac{A-5}{R}$$

where

P = number of pipes repaired
A = total acidity, $\frac{\text{milligram equivalent of H}_2}{100 \text{ gms soil}}$
R = resistivity, ohms-cm

V. TESTS AND CRITERIA FOR SOIL AGGRESSIVENESS

It should be obvious from the preceding discussion that corrosion of metals in soils depends on a large number of interrelated parameters. The heterogeneity of the soil and the complex nature of the corrosion process suggests that a single parameter would not give a good predictive value of the aggressiveness of the soil. However, on the basis of laboratory tests and field experience, many investigators in various countries have attempted to formulate tests that would measure a single or combination of parameters to predict the corrosiveness of soils.

It was found by preliminary tests and experience with buried metals that in the case of ferrous metals the corrosion rate did not depend significantly on the composition or heat treatment of the ferrous alloy. The corrosion rate was mainly dependent on the soil characteristics. Early investigations had also determined that although the chemical properties played a major role in the corrosion process, they could not be used as a reliable measure of the soil corrosivity. Generally, the tests and criteria should be simple, relatively rapid, capable of field use, and give results predicting relative corrosion rates.

Some of the major criteria developed are listed below.

A. Resistivity

Romanoff¹ stated that the most reliable parameter to estimate the corrosivity of soils is its resistivity. The resistance depends on the temperature, moisture content, dissolved salts, compactness of the soil and presence of inert material, all the major elements controlling the rate of corrosion. The resistance of the electrolyte is one of the main factors that affect the flow current associated with corrosion. It is also a parameter that can be easily measured. Table 3 shows a direct relation between soil resistivity and corrosion rates. Based on an extensive study in the United States, of various metals buried all over the country, soil aggressiveness has been characterized by separate resistivity ranges. This has been graphically shown for ferrous metals in Table 4.

Table 3

Corrosion of Pipelines as Affected (Ref. 9)
by Soil Acidity and Resistivity

Influence of Acidity - Soil Resistivity 4,000 to 5,000 ohm-cm		
Soil Type	Total Acidity	Proportion of Pipeline Requiring Repairs
	mg-eq ^a	Percent
Wauseon fine sandy loam-----	7.5	6.3
Caneadea silt loam-----	12.2	13.3
Miami silt loam-----	16.8	22.8
Mahoning silt loam-----	18.1	20.9
Trumbull clay loam-----	21.1	20.0
Crosby silt loam-----	22.0	30.8
Influence of Resistivity - Total Acidity 15 to 18 mg-eq ^a		
Soil Type	Total Acidity	Proportion of Pipeline Requiring Repairs
	ohm-cm	Percent
Lordstown fine sandy loam---	11,450	3.3
Wooster loam-----	8,002	6.0
Volusia silt loam-----	5,473	13.6
Mahoning silt loam-----	4,903	20.9
Miami silt loam-----	3,982	22.8
Nappanee clay loam-----	1,009	57.0

^a Milligram-equivalents of hydrogen ion per 100 g of soil.

Table 4

Matrix of Pit Depth Versus Years of Exposure Depicting the
Soil Corrosion of Ferrous Alloys for Different Resistivity Soils (Ref. 17)

24: > 1,000 mpy

29: 220 mils

The resistivity of the soil gives a rapid qualitative indication of the aggressiveness of the soil. A weakness of the resistivity procedure is that it neither indicates variations in aeration and pH, nor biological activity in the soil.

B. Resistivity + pH

Stratfull⁶ developed a new test method to estimate relative corrosiveness of the soil by combining the relative influences of the hydrogen-ion concentration (pH) and the "minimum" resistivity of the soil. It establishes the relative soil corrosivity by plotting these combined values on a chart as shown in Figure 5. It will be noted that the corrosion rate in alkaline soils (pH > 7.0) is influenced much more by the resistivity than by pH. In acidic soils the corrosion is controlled by the combined effect of pH and resistivity of the soil. In the discussion of such a plot the authors state that the resistivity of the soil is dependent on the moisture content and the resistivity will decrease to a minimum value as the moisture content increases and then increases again as more moisture is added, Figure 6. The resistivity would, therefore, change with the weather conditions and whether the soil is in a slurry form (such as in marshy land) or in a dry area. A better criterion would, therefore, be the minimum resistivity. The authors state that probably the total acidity would be a more dependable indicator than pH. However, the feasibility of using the total acidity instead of pH was not determined in their study.

In the case of certain Ohio soils, Denison and Ewing⁹ showed that there is a direct relation between the proportion of pipeline repairs and the total acidity and resistivity of the soil, Table 3.

C. Resistivity + Redox Potential

G.H. Booth and co-workers,^{10,11,12} on an extensive study of soil systems in the United Kingdom recommended a criterion for the aggressiveness of soils:

Figure 5. Chart for estimating corrosion rate of steel pipe (Ref. 6).

Figure 6. Effect of moisture content on the resistivity of soil (Ref. 6).

	<u>Aggressive</u>	<u>Non-Aggressive</u>
Resistivity, Ω -cm	<2,000	>2,000
and/or		
Redox-potential at pH=7, (V(N.H.E.))	<0.400 or <0.430 if clay	>0.400 or >0.430 if clay
Borderline cases to be resolved by:		
Water content % w/w	>20	<20

The resistivity would generally give an indication of the uniform corrosion of metal while the redox potential would be indicative of the risk of bacterial corrosion. A summary of the results to support their criteria is given in Table 5. Based on their prediction they have plotted the results of their survey as histograms, Figures 7, 8 and 9. Figures 7 and 8 have been subdivided into aggressiveness and non-aggressiveness, according to whether the attack was attributed to low resistivity or to low redox potential. It should be noted that the limiting value of 2,000 Ω -cm for the resistivity is in very close agreement with value suggested by Schwerdtfeger,¹³ and the value of 0.430V as a critical value of the redox potential approximates closely to the minimum value for non-aggressiveness put forward by Starkey and Wight,¹⁴ Table 6, for anaerobic corrosion of iron in soils. In the borderline case the soil is considered aggressive if the water content is greater than 20%. This critical value of 20% water has also been cited by Tomashov and Mikhailovsky⁵ as being the value at which 100% of the buried metal surface becomes electrochemically active.

D. Polarization of the Metal

Since it was recognized that corrosion in soils is electrochemical in nature, many investigators attempted to measure the actual corrosion currents. 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. The currents may also be suppressed by polarization films and corrosion products. Denison¹⁵ developed a cell for the measurement of corrosion

Table 5

Properties of Some Soils in the U.K., their Predicted
Aggressiveness and the Measured Corrosion
Rate of Mild Steel (Ref. 11 and 12)

DESCRIPTION OF SOIL	#	SITE	RESISTIVITY, Ω - cm	REDOX- POTENTIAL, V at pH = 7 (N.H.E.)	pH	WATER CONTENT, %	ASSESSMENT FOR FERROUS MATERIAL	RATE OF CORROSION OF MILD STEEL AFTER 4 YEARS mg/dm ² /day
Fine loam, stones and chalk	1	Turville	21,800	0.512	7.8	19.0	Non-aggressive	1.7
Fine sandy loam	2	Ripley	21,450	0.500	7.5	11.7	Non-aggressive	2.7
Brown clay	3	Brixton	3,900	0.527	7.6	19.9	Non-aggressive	3.1
Fine loam with fine gravel	4	Teddington	33,400	0.460	4.0	10.3	Non-aggressive	3.3
Fine loam	5	Eversley	17,100	0.528	6.7	14.5	Non-aggressive	3.5
Heterogenous clay	6	Cricklewood	2,100	0.543	7.5	23.5	Non-aggressive	4.7
Light brown clay and ballast	7	Botany Bay	19,200	0.527	5.6	15.6	Non-aggressive	11.8
Mixed clay and loam	8	Greenform	1,500	0.490	7.5	25.5	Aggressive	---
Clay-sand mixture	9	Basildon	2,800	0.365	7.5	26.5	Aggressive	4.7
Brown clay	10	Rayleigh	740	0.380	7.6	25.3	Aggressive	6.3
Homogenous brown clay	11	Canvey Island	1,700	0.520	8.6	22.6	Aggressive	8.1
Clay	12	Broughton	2,000	0.468	7.6	26.0	Aggressive	16.9

Table 6

Classification of Corrosiveness of Soils Based
on Redox Potential Measurements to Determine
the Anaerobic Corrosion of Iron (Ref. 13)

Range of Soil Redox Potential	Classification of Corrosiveness
Below 100 mv	Severe
100 to 200 mv	Moderate
200 to 400 mv	Slight
Above 400 mv	Noncorrosive

Figure 7. Electrical resistivity of soils (a) non-aggressive, (b) aggressive - probably due to bacteria, (c) aggressive - not due to bacteria (Ref. 11).

Figure 8. Redox potential of soils (a) non-aggressive, (b) aggressive - probably due to low resistivity, (c) aggressive - with high resistivity (Ref. 11).

Figure 9. Water content of soils (a) non-aggressive, (b) aggressive (Ref. 11).

currents in the laboratory which has since been refined by Schwerdtfeger.¹⁶ The cell consists essentially of two electrodes, a cathode in the form of a metal screen or perforated disc and the anode (metal to be tested) in the form of a solid disc of the same metal separated by a layer of moist soil that constitutes the electrolyte. The principal measurements made were the open circuit potentials, short circuit currents, and simultaneous values of current and potential under various conditions and at different time intervals. Table 7 gives a scale of the corrosiveness of soils based on electrical measurements and loss in weight of the anode material. At the conclusion of a two-week test period the results show that there is a definite correlation between the weight loss and both the current at corrosion potential and the maximum short circuit current. Schwerdtfeger¹⁶ also showed that there is good correlation between the weight loss of the anode in the Denison cell for six months and the weight loss of the samples exposed for 10 years in the same soils in the field.

E. Polarization and Resistance

Tomashov and Mikhailovsky⁴ developed an electrochemical evaluation method for the corrosiveness of the soil to measure both the uniform corrosion and the localized corrosion of the buried metal. They developed a cell, which could be forced into a soil at the site under consideration, and an electronic device that could measure the soil resistivity, open circuit potential, and the currents produced by the application of anodic and cathodic potentials to the sample. The uniform corrosion rate is then given by:

$$I_{\text{corr}} = 160 \frac{I_a \cdot I_c}{I_a + I_c}$$

where:

I_{corr} = Corrosion rate g/m^2 year.

I_a = Anodic current.

I_c = Cathodic current

and the classification of the soil aggressiveness is given below

Table 7

Corrosiveness of Soils as Indicated by Electrical
Measurements and Loss in Weight of Anodes (Ref. 16)

Soil		Resis- tivity at 60°F	Maxi- mum open circuit volt- age ^a	Corro- sion poten- tial ^b	Current at cor- rosion po- tential	Maxi- mum short- circuit cur- rent	Loss of weight ^c
No.	Type						
		ohm- cm	v	v	ma	ma	(mg/cm ²)/ yr
1	Docas clay -----	62	0.31	0.34	2.72	2.19	1,475
2	Billings silt loam-----	81	.30	.32	3.86	2.85	1,230
3	Unidentified alkali soil-----	263	.38	.29	2.55	2.20	1,230
4	Lake Charles clay-----	406	.37	.29	2.92	1.64	1,150
5	Imperial clay-----	102	.38	.31	2.90	1.70	1,130
6	Merced clay adobe-----	128	.30	.35	2.00	1.70	1,040
7	Merced silt loam-----	278	.34	.22	1.88	1.05	722
8	Acadia clay-----	190	.12	.31	1.20	.80	708
9	Fargo clay loam-----	350	.12	.37	.78	.55	580
10	Fresno fine sandy loam-----	51	.16	.21	1.20	.60	534
11	Bell clay-----	684	.14	.33	.90	.54	504
12	Unidentified soil-----	2,120	.14	.24	.50	.42	370
13	Allis silt loam-----	1,215	.14	.22	.60	.23	244
14	Summit silt loam-----	1,320	.07	.26	.40	.20	214
15	Mahoning silt loam-----	2,870	.20	.30	.67	.32	202
16	Miami clay loam-----	1,780	.01	.32	.005	.003	16

^a Potential (H scale) between anode and cathode of corrosion cell on open circuit.

^b Potential (H scale) at intersection of current-density-potential curves.

^c Calculated from results in a 2-week run.

$\frac{I_a \cdot I_c}{I_a + I_c}$	Soil Corrosiveness
0 - 0.1 mA	Low
0.1 - 1.0 mA	Moderate
1.0 and higher	High

The rate of penetration due to localized corrosion is given by:

$$D = A \frac{I_c}{\rho}$$

where:

D = Depth of penetration in mm.

A = Constant.

I_c = Cathodic current.

ρ = Specific resistivity of the soil.

Based on a survey of soils in the U.S.S.R. the authors obtained preliminary results to show direct relations between the electrochemical measurements by their apparatus and the rate of general and localized corrosion in steels. The usefulness of this procedure has not been completely established, however, it represents an attempt to integrate some of the complex factors controlling corrosion rates in soils.

VI. CONCLUSIONS

Corrosion of metals in soil environments is electrochemical in nature, therefore the principles of electrochemical corrosion can be used to study corrosion attack in soil and estimate the rate of metal degradation.

In the case of ferrous alloys, minor composition and structure changes in the steels are not important for its corrosion resistance. Similarly, cold working and different heat treatments do not have a significant effect on the rate of corrosion in soils. However, as the steel is made more resistant to uniform corrosion, i.e. passivated, it becomes more susceptible to pitting corrosion.

The corrosion behavior of steels in soils is generally dependent on the soil type. Both the physical and chemical characteristics of the soil affect the type and rate of corrosion. General comments on the soil properties and the metal corrosion have been made, although it must be remembered that the absolute corrosion rate will depend on the effect of the climate factors, such as the amount of rainfall, temperature, air movement and sunlight on the soil.

The various tests and criteria proposed to measure the soil corrosiveness have been critically reviewed. The tests can be categorized into two main groups, (i) measurement of the properties of the soil and estimation of the corrosion rate from past experience of exposure of metals to the various soils, and (ii) measurement of the electrochemical polarization of the metal in a given soil. Both types of tests have been used successfully to evaluate the corrosion behavior of steels in soil. The tests based in the properties of the soil give a qualitative indication of the general corrosiveness of the soil, while the electrochemical tests, if further developed, could be used to predict the absolute corrosion rate of a metal in a given soil. The criteria could be used to predict the corrosion behavior of mild steel drums used for containment of solidified radioactive wastes.

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