A PROPOSED CLASSIFICATION OF CORROSIVE SOILS IN THE GULF COAST REGION.

F. W. Stones.

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Considerable trouble is experienced with pipe line corrosion in the gulf coast regions and it is not infrequent to find lines penetrated two years after they have been laid. However, until recently, apparently no thought has been given the problem of classification of these corrosive soils.

K. H. Logan of the Bureau of Standards has investigated the rate of corrosion of various soils thruout the country and has attempted to correlate rate of corrosion with pH values of the soils.

(Report of the Committee on Metals and Report on Soil Corrosion Investigation to the American Foundrymens' Association. Preprint # 447)

Logan has plotted the rate of corrosion vs. the pH values of the different soils. As noted by Speller, there is no correlation. The plot shows that the pH value is not the controlling factor in soil corrosion and would indicate that the soil components which affect the equilibria of ferrous and ferric ions also comes into play. For example, Buttonwillow, Cal. white alkali shows a very high rate of corrosion while the pH value is 8 - 9. We know that a high pH value does not favor corrosion. This would indicate that the alkaline solution could not precipitate a protective coating of the ferrous or ferric oxide on the pipe because of the formation of the soluble bicarbonate.

Logan has buried several specimens of pipe covered with different kinds of coatings thruout the country. By measuring the potential between the soil and the pipe, pH values, etc., he expects to obtain some valuable data in a few years.

Logan's method seems to be faulty in that he uses such terms as "clay, loam, sandy," etc., which are entirely without significance for purposes of comparison, for one should not expect two soils of the same physical nature to have the same chemical properties to the same extent.

Attempts at classification by chemical analysis have not been successful.

W. H. Walker (J.A.C.S. 28, 1, 251), W. R. Whitney (J.A.C.S. 25, 394 - 406 - (1903), W. D. Bancroft (J. Phys. Chem. 28, 785 - 871 (1924) and others have firmly established the electrolytic theory of corrosion. Frank N. Speller has recently discussed corrosion in general in detail from the engineering point of view. (Speller - Corrosion - Causes and Prevention) and the following have been established as factors in underground corrosion:

- I. Physical and Chemical Characteristics of the Soil.
 - (a) Water retaining capacity.
 Soluble solids and gases in soil water.
 - (b) Electrical conductivity.

Dissolved electrolytes and degree of subdivision of the soil. The more finely divided the soil the longer is the path of the current between two points.

- (c) Effect produced by different solid substances in contact with the pipe.
- (d) Power of adsorption on the metal.
- II. Depolarization of Atomic Hydrogen on the Metal Surface.

 Depolarization takes place chiefly because of dissolved oxygen in the soil water.
- III. Solution Pressure of the Metal.
- IV. Adsorbed Protective Films.

V. Composition of the Metal.

It has been established that the composition of the metal, within the range of practical limits, has no effect on the rate of corrosion underground. (Speller - Pg. 90 - 137)

A number of people have postulated that the reason a piece of metal corrodes underground is because the adsorbed film of atomic hydrogen on the metal is depolarized.

It was supposed that a correlation might result if the rate of depolarization of this film could be estimated. To do this, a cell was set up consisting of a saturated calomel electrode and a quinhydrone ectrode in contact with the soil samples suspended in distilled water. The soils were analysed for water and then 5 gm. samples were suspended in amounts of water varying from 5 cc. to 30 cc. The pH values were obtained as well as possible and plotted vs. cc. water added to the sample. By extrapolation of this curve, the pH value of the original soil water was obtained.

During these determinations, time was plotted vs. potentiometer reading. It was thought that the slope of this curve would indicate the rate of depolarization of the atomic hydrogen and if this were the case the method could be modified using an iron electrode and thereby obtain the correlation desired.

Neither of these curves were of particular value. The time of attaining equilibrium varied considerably for the same sample. It was possible to obtain the pH curve fairly well. For example, one soil containing 21% water had a pH value running from 7.2 with 5g. in 5 cc. water to 7.9 with 5g. in 30 cc. water. The curve between was nearly a straight line. Extrapolation of this curve gave 7.15 for the pH of the original 21% water in the sample. This is, of course, too nearly neutral to be the cause of any considerable corrosion. The

soil was shown to be quite corrosive by later tests.

It has been reported that if a solution of sodium chloride in carbon dioxide free water is shaken with Fuller's earth and the mixture filtered, the filtrate will be acid due to the preferential adsorption of the base from solution. On the basis of this and other work, Weiser (Weiser - The Hydrous Oxides. pg. 409) postulates that the soil acidity is due to the preferential adsorption of bases in solution in the soil water by the soil colloids.

In view of these statements, experiments were made to determine whether or not there could be such a thing as a clay adsorbing a base so strongly from solution that the film of water adjacent to the pipe could be acid. No phenomenon such as described with Fuller's earth could be obtained either with clay or Fuller's earth. However, a similar thing was observed upon letting freshly precipitated barium sulfate settle from solution. The supernament solution was acidic or basic depending on whether sodium or potassium sulfate was used to precipitate the barium. Such a condition would never be obtained in the case of soil colloids around a pipe because these colloids have been precipitated and adsorption risen to a maximum value attainable with solutions as dilute as those in soil water long before man ever laid a pipe line.

Acid soils are said to be rare. However, almost any soil will turn lithus from #### ## blue to red if a piece of the blue paper is pressed against the moist sample. The change will be very decided and will take place in about five minutes. This is probably due to the preferential adsorption of one form of the dye and not the other, the two being in equilibrium. In support of this, a clay which turned blue lithus red had a pH value so nearly 7 that any corrosion from this point would be out of the question.

Another scheme to get at the rate of depolarization was based on the following reasoning. There are many organic compounds in the soil some of which are capable of reacting with atomic hydrogen.

Considering the methods of organic analysis, one would say that these compounds could be detected by titration with alkaline permanganate.

Electrometric titrations were made using a pyrolysite electrode. Fifty gram samples of the soil were suspended in water and stirred mechanically and titrated with 0.005 N premanganate solution. The end points were fairly sharp, showing that the electrode was functioning properly. However, tho the curves were plotted with reasonable accuracy, the points on the curves could not be checked very well. for The end points of the different curves obtained off the same sample checked fairly well. The amount of permanganate used was negligible. One sample of 50 g. took up 0.36 cc. of 0.005 N permanganate.

After examining some specimens of corroded pipe it was concluded that there must be a cathode and an anode in short circuit to produce a pit. The anode might be in the metal itself or it might be some substance in contact with the pipe, or it might be a concentration cell which was short circuited. In any event, there appeared to be a short circuited cell in the vicinity of the pit, and if this were true the controlling factors should lie in the resistance of the intervening soil.

R. O. E. Davis has done some work on the electrical resistance of soils (Trans. Am. Electrochem. Soc. 17, 391 - 403-1910) and he concluded his article with these statements;

"From previous work we know that the condition of the soil has a marked influence on corrosion and from a study of soil conditions it has been observed that soil containing water adds to the corrosive influence".

"Again, since corrosion is electrolytic, the solution in the soil - an electrolyte - facilitates corrosion.

The measurement of soil resisitivty shows:

- (1) Dry soil has a very high resistivity.
- (2) At a depth of two feet or more, the conductivity for a given soil is approximately constant.
- (3) Conductivity is almost directly proportional to the water content.
- (4) Conductivity of soils saturated with water is directly proportional to the salt content.
- (5) Below saturation, the resistivity of the soil increases as the surface area. (sq. cm./gm.) At the saturation point and beyond, the surface area does not have so much effect.
- (6) Sodium carbonate has the effect of greatly increasing the conductivity.
- (7) Humus decreases the conductivity.
- (8) Sandy soil will probably afford the least electrolyte and clay soil the most."

Davis' work and results seemed to warrant an attempt to classify corrosive soils by their conductivity.

F. K. Cameron of the Bureau of Standards designed a slide wire bridge and rubber cup with electrodes in the surface with which to measure the resistance of soils. For this work, instead of using a round rubber cup with platinum electrodes, a cell was made as follows; A discarded automobile battery cell box was sawed off about 3" from the bottom and the plate supports broken out with pliers. Those portions of the plate supports which could not be removed with pliers were removed with a hot steel spatula.

Electrodes were cut from sheet copper and dry cell terminals soldered to the center. These electrodes were fastened in the ends of the cell, using the terminals for bolts and also for making electrical connection with the plates.

A Ford coil was used as the source of A. C. and a students' potentiometer was connected for use as a Wheatstone bridge.

This apparatus worked very nicely and was compact enough to be transported with ease. It had the advantage that the cell could be replaced almost anywhere in the field in case of breakage.

The technique of obtaining the resistance of a sample of soil was as follows. The electrodes were cleaned with emery cloth from the film which was formed during the previous run. This was found to be a necessary procedure. The electrodes were then wiped off and the soil to be tested placed in the box in layers and each layer saturated with distilled water as it was put in. The soil was then pressed down with a pestle until it was uniformly packed. If water came to the top during the packing of a layer it was arbitrarily said to be saturated and no more water was added as long as any appeared during the packing process. This was continued until the electrodes were covered and the resistance measured and converted to specific resistance by means of a pre-determined cell constant. With a little practice the soil can be made just saturated when the cell is full and checks can be obtained to within about 3%.

When in the field, the amount of corrosion on pipe had to be estimated for the sake of making reasonable speed. The pipe was laid bare and the surface scraped with a knife and the pits dug out. The corrosion was reported as being between certain limits and with or without pits, e.g. corrosion general, scales off sides and bottom 1/32 - 1/16 inch thick, pits on sides and bottom 1/32 - 1/16 inch deep.

Of course, such measurements do not warrant very accurate resistance determinations.

The table given is on a 5 year basis and a measuring temperature of 20 C. In listing the data in the table, measurements taken too close together were thrown out. Also, much data was not used because it was taken on lines where experiments were in progress and the lines had been disturbed and the protective coatings changed.

Data as to replacements of short pieces of pipe were not easily available and this leads to some uncertainty in some instances as to the length of time the pipe had been in the ground.

In estimating whether a soil will be corrosive, the resistivity of the area considered must be used rather than the resistivity of one spot for there will be individual exceptions. If an area of low resistivity has a spot of high resistivity in it, the chances are that the high resistance spot will be as corrosive as the rest of the area and vice versa. Of course, one cannot say that there is a definite dividing line between corrosive and non-corrosive soils. Nor can not say that soils of a certain resistivity produce a certain amount of corrosion because it was found that the resistivity of a particular sample will vary 100 ohms from the average given in the tables, or obtained from the curve.

In plotting the curve, the points were placed halfway between the estimated corrosion limits.

In view of the following facts, the correlation has worked out quite well.

- (1) Soil corrosion is admittedly a very complicated problem which has many factors entering into it.
- (2) Conductivity is only one or at best a group of closely related factors.
- (3) The estimation of the amount of corrosion is very rough.
- (4) Reliable data as to repairs, replacements of small sections,

etc., were often missing and the best information available was the word of the line rider.

(5) The correlation is in threement with about of for the individual readings, considering the above mentioned variation of 100 ohms either way.

RESULTS

to the 5 year basis. In making this calculation, it was assumed that the rate of corrosion was constant.

Data which were obtained with pipes with experimental coatings were omitted. Data which were extremely far off were omitted from the averages and such data are marked with an asterisk in the table.

The values in the body of the table are resistance of the soil in ohms per centimeter cabe, while the columns are headed with the type and amount of corrosion as estimated.

The cell constant was 1.41

None	Slight general	Scale& pits 1/32"- 1/16	Scale & Pits 1/16" - 1/8"
4160	775	246	381
5500	3250	* J170	245
3520	223 0	J 17	
1170	675	2 63	313 average.
23200	945	483 average	
2330	1445		
3420	635	d170 omitted	
27900	1125		
19750	936		
	14100		
	930		
	7900		
	3100		
			

Average of these two columns not taken because of asymptotic nature of the curve.

Scale & No Pits 1/32" - 1/16"	Scale and To Pits 1/16" - 1/3"	Pits only 1/32"-1/16"	1/16"-1/J"	1/o"- pen.
2 6J	230	1190	213	245
403	343	1550	5 1 5	*935
Average 334	*705	508	452	250
Average 754	Average 326 705 omitted	423	*1270	160
		Average 918		*1460
	-		дverage 395	7.vers.ge 218

Averaging all the data, except those mentioned, the following results are obtained and these are shown on the curve.

Basis: 5 years.

Slijht general	o25	ohms	per	cm3.
1/32" - 1/16"	57ა	ti	ti	ti
1/16" - 1/6"	345	Ħ	11	Ħ
1/3" - pentration	213	11	11	tt

I should like to point out that so far as I am aware, no one seems to have investigated the problem of catalysis in underground corrosion. It may be that the best protective coating would contain a substance which poisons the iron, the catalyst for the formation of molecular hydrogen from atomic hydrogen.

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Bibliography.

Corrosion - Causes and Prevention. Smeller.

The Electrolytic Theory of Corrosion. N. D. Bancroft.

J. Phys. Chem. <u>28</u>, 785 - 371 (1924)

Report of the Committee on Corrosion of Metals and Report on Soil Corrosion Investigation. Am. Foundrymen's Assn. Preprint $_{\it H}$ +47. Apparartus for Soil Conductivity Measurements. F. K. Cameron.

Trans. Am. Electrochem. Soc. <u>15</u>, 559 (1909)

W. H. Walker J. Am. Chem. Soc. 28, 1, 251. (1906)

The Effect of Moisture and of Solutions upon the Electric

Conductivity of Soils. R. O. E. Davis. Trans. Am. Electrochem.

Soc. <u>17</u>, 391 - 403 (1910)

Thompson and Crocker. Trans. Am. Electrochem. Soc. 27, 166, (1915)

