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The undersigned, acting as a Committee of
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CORROSIVE ACTION OF SOILS ON IRON AND LEAD

A Thesis submitted to

the Faculty of the Graduate School of the

University of Minnesota

by

Laurence A. Stenger

in partial fulfillment of the requirements for the

Degree of Master of Science

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CORROSIVE ACTION OF SOILS ON IRON AND LEAD

One of the features of industrial conditions little noticed by the average person is the multiplicity of pipe lines, cables, conduits and various other metallic structures found in the subsoils of cities. These structures, with the exception of earthenware sewers and conduits and bituminized fiber conduits, are all constructed from iron, cast, wrought, pure ingot iron, steel and lead. The irons and lead are used for water pipes, irons for electrical conduits and gas pipes, lead is used as a protective covering for electric power and telephone cables, usually containing two per cent of tin. Rails of street railways may be included with these structures, also steel foundations of buildings and steel tunnel linings.

Usually these pipes, etc., are placed in the soil with the idea they will not be affected, at least to the point of destruction, by any corrosive agencies. Attempts are sometimes made to paint or coat the metallic surfaces for protection, more often not.

An enormous amount of work has been done investigating the causes of corrosion of iron and lead in air and methods for their adequate protection. Comparatively little has been done investigating and preventing corrosion of these metals in soils.

There have been several theories advanced to explain the corrosion of iron⁽¹⁾. These are the electrolytic⁽²⁾, the carbon dioxide or acid, the hydrogen peroxide, the oxidation and the biological or bacterial. From the results of work on this subject, together with a study of the writings of Whitney, Cushman, Gardner⁽³⁾, Walker⁽⁴⁾, and many others on corrosion in general, it is believed that practically all corrosion, of both iron and lead, is electrolytic in action.

The general study of the subject was begun with field observations of underground structures in different places. Extensive work of this type was done at Havana, Cuba, in 1911, by Mr. S. T. Dodd and the writer. At that time a new sewer system was being installed, the excavations for which offered a rare opportunity for observing the many piping systems buried in the ground. There it was found the corrosive action of the soil on iron was severe. The most damage was done to the smaller iron gas and water service pipes. From reliable information from several sources, it was found their life was from three to seven years, for either wrought iron or steel pipes. A poorly galvanized pipe would corrode as badly as a black pipe. A good heavy galvanized coat was an effective protection. Corrosive action was very

- (1) Friend, Corrosion of Iron and Steel, p. 34.
- (2) Whitney, Jour. Amer. Chem. Soc., 1903, 25, 394.
- (3) Cushman and Gardner, Corrosion and Preservation of Iron and Steel.
- (4) Electrolytic Theory of the Corrosion of Iron and Steel and its Application. Jour. Iron and Steel Inst., 1909, 79, p.69.

marked also on cast iron pipe. Careful work was done to find leakage electric currents where this corrosion occurred. None were found. The street railway rails carry no current, the double trolley system being in use. The rails of two electric lines entering the city carried current, these were the only sources of leakage current in the city, and, owing to the good soil conductivity, damage from that current would be localized closely to the lower potential points of the tracks. No damage had been reported from this cause. Furthermore, corrosion had been common in that city before electricity had been used at all, therefore it is absolutely certain the pipes were corroded by reactions between soil constituents and the metal.

In Indiana, there was laid in 1891 an eight inch steel gas pipe with screwed wrought iron couplings. This pipe extended from the Grant County gas fields to Crawfordsville, where it ended about one-half mile from an electric railway. This pipe was taken up in 1911. It was corroded in local areas over the pipe, many places through the walls, and generally over the whole length of line. It was buried three to five feet deep, lying in moist yellow clay soil. This corrosion was also due to reactions between soil constituents and iron and none other.

In Pierre, South Dakota, cast iron water pipes have been replaced account of damage due to soil corrosion only. No source of direct current leakage is in the city.

Small iron service pipes were corroded to leakage in six years. The soil there is a clay and gumbo, it is popularly termed alkaline.

Cast iron and steel pipes have been found in Minneapolis and St. Paul, corroded to destruction in black peat soil, cinder fills and clay. The soils were found to be actively corrosive.

Commercial lead is very long lived under ordinary circumstances. In Havana it was found that lead covers of insulated electric cables laid in earthenware conduits were destroyed in three years. This occurred where running water was in the conduits and only indirectly was caused by soil action. The lead water service pipes buried in clay were in an excellent state of preservation, all observations and information indicated there was no damage done to them.

Consideration of these facts and others leads to the classification of corrosive effects in two types. One, called electrolysis, is the resultant of an outside generated electrical current flowing from the metal by an electrolytic conduction path. The other has been termed auto-electrolysis, it is electro-chemical in nature - nearly all corrosive effects on subsoil structures, not caused from electrolysis, are produced by it.

These two types are to be clearly differentiated, although it has been found their effects are similar.

Electrolysis from leakage currents (6) from the rails of electric lines manifested itself by corroding underground pipes in the early days of electric traction development. At that time, little attention was paid to track bonding and methods of conducting the electric currents from the rails. These points, together with other factors tending to reduce the leakage current flow, have been carefully studied, whence electrolysis has been ^{reduced} to almost a negligible amount. It might be expected the rails would be quickly destroyed, as leakage currents tend to leave them at the higher potential points, where they are in contact with the soil, which usually is an electrolytic conductor. If it were dry, the leakage current would be reduced to zero, the rail would be insulated. In practice, it is not found necessary to remove rails because of electrolysis, it is insignificant. Usually a small local area of rail base edge just under the spike head is corroded, and spikes in wet ties will be sharpened. This is especially noted in zinc chloride treated ties, which should not be used, as they lessen the effective resistance to leakage currents. The electric current leaving other underground structures is a small fraction of that leaving the rails, so corrosion caused exclusively by leakage is small in amount (7).

If an underground structure is discharging a leakage current, it will be at a considerably higher potential than the

- (6) McCullom and Logan, Leakage of Currents from Electric Railways, Bureau of Standards Bul. 63, 1916.
(7) J.G. and R.G. Cunliffe, Jour. Proc. Institution of Elect. Engrs., Vol. 43, part 197, 1909.

immediately surrounding ground, even if the current density is very small, due to the counter electromotive forces⁽⁸⁾ set up at the iron surface, contact resistance, reduced area of soil in the near vicinity of the metal, and the usually quite high specific resistance of the ground. If this electromotive force with structure positive to the ground is found to exceed one volt, with unidirectional fluctuating values, and variable current is found flowing in the structure, with opportunity to leave it through electrolytic conducting soil for a lower potential metallic structure in the near vicinity, electrolysis may occur from the railway leakage current.

On account of the number of variable factors found affecting corrosion rates, among them some that may be called factors of indefiniteness, it becomes rather difficult to isolate factors and study them effectively. Considering the metal alone, the factors affecting its corrosion rates are constitution, properties of components, segregations, foreign substances including gases, states of strain, solution tension and conditions of surface.

External factors, involving the soils and conditions outside of and in contact with the metal are moisture content, gases, composition, electrical conductivity and components. The latter may be chemically corrosive, electronegative to the metal and catalytic in action. Also, porosity or density, homogeneity, concentrations, bacterial conditions, temperature and pressure are to be included.

(8) Irving Langmuir, The Relation Between Polarization and the Corrosion of Iron by Stray Currents. Stevens Institute Indicator, Oct., 1907.

Soils, embodying the external factors of corrosion, are mixtures of more or less inert solids, colloids and electrolytes in varying concentrations. Electrical conduction, as before mentioned, in soils would in most cases be electrolytic, as the dry soil is an insulator.

At the beginning of the laboratory work some experiments were carried out, electrolyzing cast iron and sheet steel in solutions. Results of some of these are given on charts accompanying. They show that the iron goes into solution at a rate of 1.042 grams per ampere hour, approximately. This is with a valence of two. Then further work was done using various irons in different soils, to compare all effects under the various conditions, and to find the corrosion rates both by electrolysis and auto-electrolysis. Results of some of these experiments are tabulated.

For getting the data of Table I., the following procedure was used: Each kind of soil was air dried, crushed and sieved through an eight-mesh screen. The moisture was determined, then pure water added to make up the percentage shown. The soils were packed into 250 c.c. beakers. The electrodes were No. 22 mild steel sheet, analysis 4, cut 1 x 2.25 inches, well cleaned, each stamped with a number and a copper wire terminal soldered to one corner. One electrode per cell was dried and weighed, it was to be the anode. The soldered joint was covered with paraffine, a rubber tube slipped over the copper terminal, and two electrodes were wet in distilled

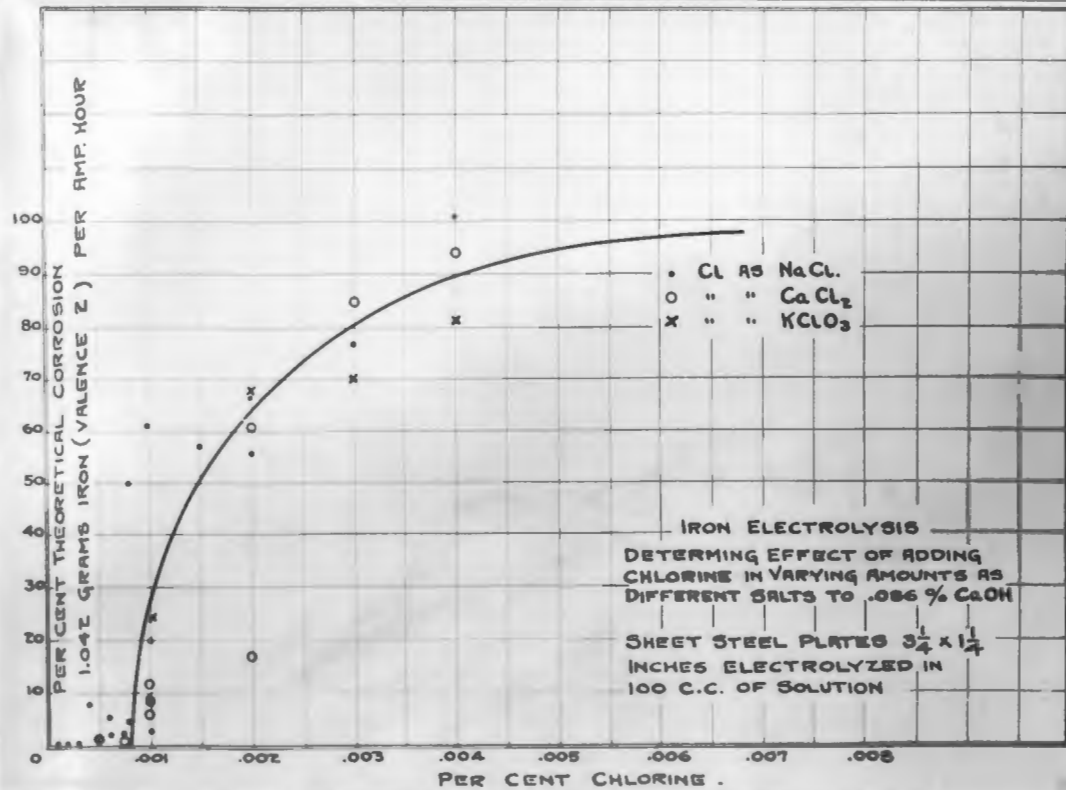


Chart 1

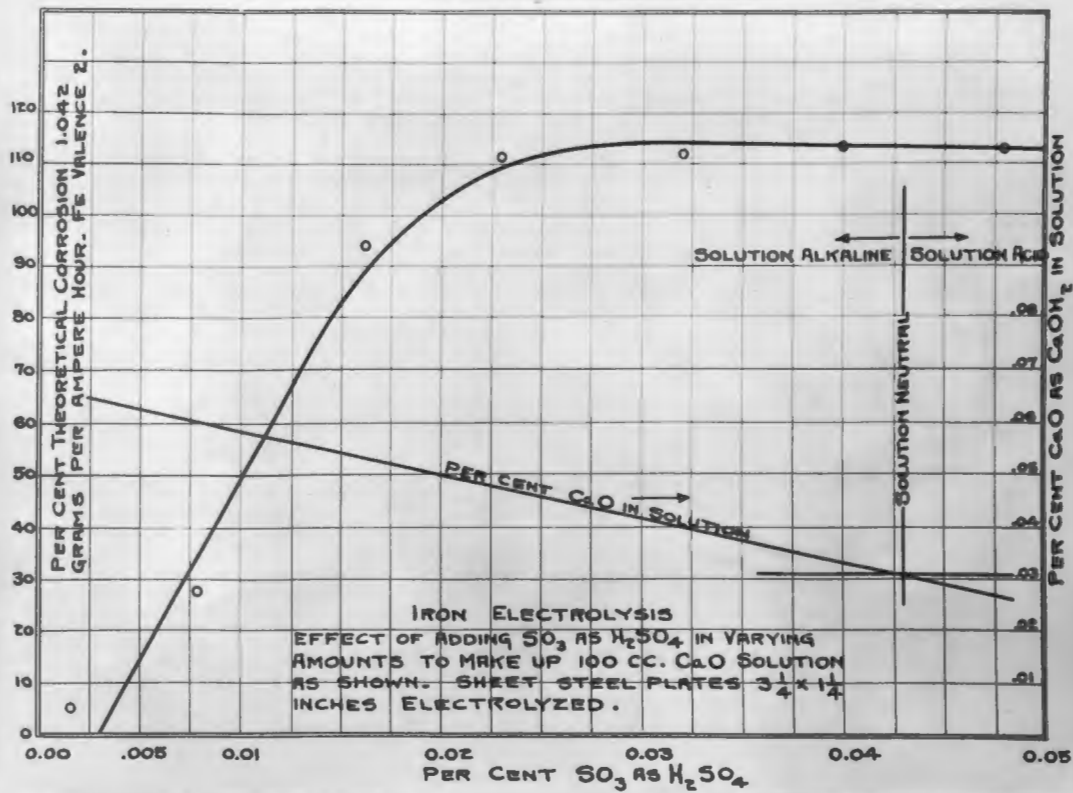


Chart 2

7 b

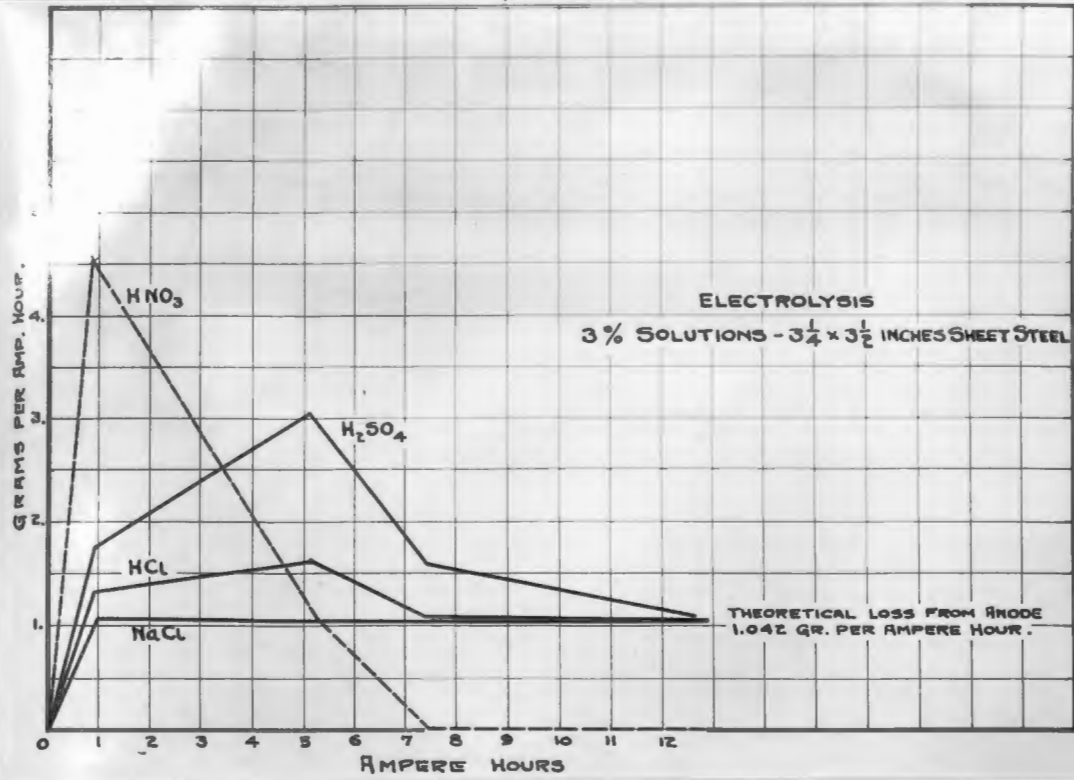


Chart 3

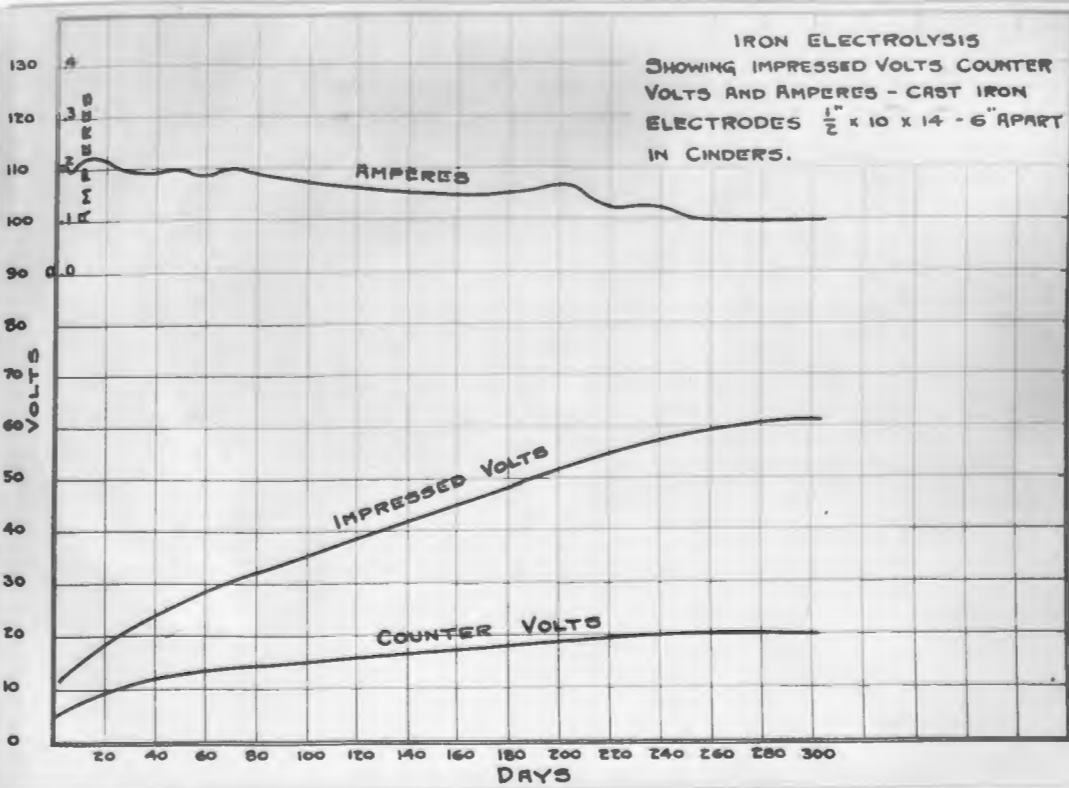


Chart 4

water and placed in each cell, about one inch apart. Each cell was weighed for the purpose of detecting moisture loss during the course of the experiment. If any was observed upon reweighing after several days, it was restored by the addition of pure water. Each cell was then placed on a 0.75 x 2 inch flat cork in a 700 c.c. beaker containing some water and a strip of filter paper up the inside to keep the air moist. A watch glass cover was put on. The cells were allowed to stand at room temperature for 550 hours, no terminal connected. Anodes were then removed, brushed clean, rubber tubing and paraffine taken off, dried and weighed, to get the natural corrosion. They were then replaced in the cell, and all cells were connected in series with copper coulometers and milliammeter, and constant current of .000233 ampere passed for 550 hours. The anodes were then removed, cleaned, dried and weighed as before.

The corrosion to be charged to the electric current is the total loss from an anode less its natural loss in the same time without outside generated current. The efficiency of electrolysis then is, in per cent,

$$\frac{\text{grams total loss} - \text{natural loss} \times 100}{1.042 \times \text{ampere hours}} \quad (9)$$

In this work, care was used in all points, especially

(9) McCullom and Logan, Electrolytic Corrosion of Iron in Soils. Bureau Standards Bul. 25, 1913.

TABLE I. ELECTROLYSIS

| Kind of soil | % Water in soil | Grams loss natural | Total loss under Elect. | Difference | Eff'y. of Elect. | Volts on Cell |
|-----------------|-----------------|--------------------|-------------------------|------------|------------------|---------------|
| Yellow clay | 8.3 | .001 | .033 | .032 | 24 | 1.3 |
| | 12.0 | .0007 | .1470 | .146 | 110 | 0.7 |
| | 16.2 | .0692 | .2097 | .140 | 105 | 0.45 |
| | 20.0 | .1007 | .2095 | .160 | 120 | 0.4 |
| | 26.6 | .1192 | .2797 | .160 | 120 | 0.34 |
| | 29.5 | .1953 | .2350 | .042 | 32 | 0.25 |
| | 32.4 | .2550 | .2245 | -.030 | | 0.05 |
| Blue clay | 17.9 | .0540 | .1593 | .1053 | 79 | 0.6 |
| | 22.6 | .102 | .1803 | .0783 | 58 | 0.5 |
| | 26.9 | .166 | .2368 | .0708 | 52 | 0.5 |
| | 32.2 | .1238 | .1907 | .0669 | 50 | 0.3 |
| | 9.5 | .00 | .0530 | .0530 | 40 | 0.7 |
| Blue clay flaky | 16.0 | .00 | .0372 | .0372 | 28 | 0.6 |
| | 27.6 | .1712 | .1638 | -.0074 | | 0.55 |
| | 36.3 | .2699 | .2443 | -.0256 | | 0.53 |
| Yellow clay | 16.7 | .0012 | .2443 | +.2431 | 180 | 0.41 |
| | 38.0 | .0403 | .2047 | .1644 | 123 | 0.01 |
| Black peat | 68.0 | .249 | .3728 | .1238 | 93 | 0.06 |
| | 77.0 | .303 | .3165 | .0135 | 10 | 0.10 |

TABLE II. ELECTROLYSIS

Electrolysis of cast iron anode placed between two sheet steel cathodes in cells similar to those of table I. Duplicate cells without current used to determine natural corrosion loss.

Amperes .001, run 1800 hours, 1.8 ampere hours.

| Soil | % Water | Grams Natural loss | Total Loss | Efficiency of Electrolysis | Voltage on cells end of test |
|--------|------------|--------------------------|---------------|----------------------------------|------------------------------------|
| | 14 | .454 | 1.013 | 31 | 1.7 |
| Yellow | 17 | .851 | 2.485 | 90 | 1.5 |
| clay | 23 | .558 | 2.274 | 91 | 0.7 |
| A. | 29 | .203 | 1.039 | 46 | 0.9 |
| | 31 | .231 | 1.868 | 90 | 0.7 |
| | 15 | 1.162 | 2.461 | 71 | 2.0 |
| Havana | 22 | 1.236 | 2,615 | 76 | 0.4 |
| clay | 29 | .698 | 2,157 | 80 | 0.2 |
| | 35 | .305 | 1.9055 | 88 | 0.3 |

Cells same type, placed on variable voltage, taken from a railway return circuit, 0.7 ampere hour.

| | | | | | Volts at .001 amp. |
|--------|----|------|-------|------|-----------------------|
| | 14 | .454 | .7380 | 40.6 | 2.1 |
| Yellow | 17 | .851 | 1.303 | 44 | 1.2 |
| clay | 23 | .558 | 1.350 | 99 | 0.4 |
| A. | 29 | .203 | .989 | 98 | 0.2 |
| | 31 | .231 | 1.099 | 109 | 0.55 |

TABLE III. ELECTROLYSIS

Soils in natural condition as taken from earth, two cleaned plates placed one-eighth inch apart in soil, cells as before. Plates marked + and - were electrolyzed as anode and cathode, electrolyzed cells in series, .000324 amperes adjusted daily to constancy, 646 hour run, 0.209 ampere hour. Remaining cells not connected electrically, plates subject to natural corrosion only. Figures given for all data involved.

Clean gray colloidal clay from 40th St. & Blaisdell Ave., Minneapolis

| Pure Ingot Sheet #16 1.3 x 2.5 inches. | | Mild Sheet Steel #22 Anal- ysis 4. 1.3 x 2.5 inches. | |
|--|-------------------------------------|---|-------------------------------------|
| | Grams | | Grams |
| No. 1 + | 24.9123 24.5795 <u>0.3337</u> | + 11 | 13.2436 12.9035 <u>0.3401</u> |
| 2 - | 25.6720 25.6350 <u>0.0370</u> | - 12 | 13.5755 13.4850 <u>0.0905</u> |
| 5. | 23.6920 23.5471 <u>0.1449</u> | 15. | 12.7650 12.6122 <u>0.1528</u> |
| 6. | 25.3750 25.1880 <u>0.1870</u> | 16. | 12.9608 12.8047 <u>0.1561</u> |
| <u>Black Peat from near Lake Harriet, Minneapolis, Analysis G.</u> | | | |
| + 3 | 25.3740 24.9575 <u>0.4165</u> | + 13 | 13.4216 12.9815 <u>0.4401</u> |
| - 4 | 25.3215 25.2967 <u>0.0248</u> | - 14 | 13.5450 13.4997 <u>0.0453</u> |
| 7. | 24.4678 24.3700 <u>0.1178</u> | 17. | 12.2483 11.9620 <u>0.2863</u> |
| 8. | 24.5292 24.4272 <u>0.1020</u> | 18. | 13.0097 12.6788 <u>0.3309</u> |

TABLE III. A.

Electrical data on cells of table III. Voltage and counter voltage of cells measured with the Lippman electrometer. The counter voltage is read when electrolyzing current is interrupted momentarily.

| Cell No. | + 1 - 2 | + 3 - 4 | + 11 - 12 | + 13 - 14 | | | | |
|---------------------------------|---------|---------|-----------|-----------|-----|------|------|------|
| Age of cell, hours | Volts | C.V. | V. | C.V. | V. | C.V. | V. | C.V. |
| 0.0 + | .19 | - | .03 | - | .23 | - | .21 | - |
| 24 | .15 | | .03 | | .25 | | .20 | |
| 72 | .18 | | .07 | .02 | .27 | | .22 | .07 |
| 240 | .09 | | .30 | .20 | .30 | .10 | .35 | .15 |
| 408 | .08 | .05 | .27 | .17 | .40 | .18 | .50 | .25 |
| 646 | .30 | .20 | .60 | .35 | .75 | .25 | .80+ | .40 |
| Efficiency of electrolysis % | 77 | | 140 | | 85 | | 60 | |

ELECTROLYSIS TABLE IV.

Shows losses from electrolysis and auto electrolysis for metals and soils specified. Treated 556 hours, amperes .000439, 0.244 ampere hours.

| | <u>Soils</u> | <u>Clay A</u> | <u>Sand</u> | <u>Peat D</u> |
|---------------------------|------------------------------|---------------|---------------|---------------|
| | Per cent water | 21.5 | 8.78 | 51.3 |
| Cast Iron | | .3222 | .4463 | .6473 |
| | | .0810 | .3153 | .3935 |
| | | <u>.2412</u> | <u>.1310</u> | <u>.2538</u> |
| | Efficiency % electrolysis | 95 | 51.6 | 100 |
| Sheet steel with scale | | .3010 | .3582 | .4628 |
| | | .06 | .2286 | .2282 |
| | | <u>.2410</u> | <u>.1296</u> | <u>.2346</u> |
| | Efficiency | 95 | 51.6 | 92.5 |
| Commercial sheet lead | | .7745 | 1.0920 | 1.1237 |
| | | .0348 | .0013 | .0234 |
| | | <u>.7397</u> | <u>1.0907</u> | <u>1.1003</u> |
| | Efficiency | 88 | 130 | 131 |
| Lead cable cover | | .6894 | 1.3108 | 1.1485 |
| | | .0178 | .0280 | .0613 |
| | | <u>.6716</u> | <u>1.2828</u> | <u>1.0872</u> |
| | Efficiency | 80 | 152.5 | 129.5 |

in measuring the small currents, and in cleaning and weighing the electrodes. Several sets were run, using different soils, and electrodes of lead and various irons and steels with scaled, smooth, and cast iron skin surfaces, with various voltages and current strengths. From all results about 66 per cent of the iron anodes, with electrolysis corrosion efficiency under 100 per cent, gave an average of 81 per cent efficiency. The remaining 33 per cent of anodes at 100 per cent efficiency and over, gave an average of 110 per cent. Lead anodes gave an efficiency of from 80 to 150 per cent. From these results no law connecting any of the variable factors with a definite electrolysis efficiency is noted.

Electrical or galvanic phenomena found in connection with auto-electrolysis were studied. Two identical electrodes of copper (platinum could have also been used) were made, and covered with pads of cotton cloth or filter paper. These terminals were connected to a suitable electrometer. Wetting the pads with dilute acid and placing them on an iron surface, an electromotive force was produced. The resulting current was caused by the iron ions passing into solution at a faster rate in one electrolyte than in the other. The effect is also observed after using soil under the terminals instead of pure acid electrolyte. The energy generated is dependent on various factors, the voltage is due primarily to the solution tension of the metal. Its amount is determined exactly as in primary cells, by the algebraic sums of the contact potentials at the

positive and negative terminals. Studies of these potentials and the resulting current strengths have been made. A Weston 15 volt voltmeter is a suitable instrument to use for measurement of voltage with electrodes as described about one inch in diameter. This instrument does not indicate the true voltage, on account of the limited current flow, but by using a potentiometer, it could be found. A special inclined capillary Lippman electrometer was constructed for this work and found excellent. It takes no current and indicates potential up to 0.8 volt accurately. A Weston milliammeter may be used to measure the current. In making such electrical surveys on bright pure iron, usually the electrode put down first is found to be electropositive. The current flow would be from the iron under it. Using ordinary moist clay as electrolyte and two similar copper terminals, placing one clay first on pure bright iron, and in a few seconds the other in another place on the same piece of iron, closing the circuit with the copper terminals through the Lippman electrometer, voltage up to 0.1 was indicated. The copper terminals may be reversed, also reversing the electrometer, to determine if there is any voltage due to dissimilarity between them - there should be none. Care should be used to avoid contact between terminals and iron.

With this method, using moist soils as electrolytes, potentials were measured between points on many kinds and conditions of irons found in commercial use. On clean ordinary

surfaces, would be found 0 to 0.1 volt, clean iron to mill scale 0.3 to 0.5, clean iron to copper 0.8 to 1.0, clean iron to carbon 0.8 to 1.0, clean iron to red rust 0.3 volt. The clean iron would be electropositive in all cases, current would leave it and cause corrosion.

The destructive effects of auto-electrolysis depend upon the electronegative material to a considerable degree. If it is copper, with a flaw exposing iron, under auto electrolytic conditions a hole will be drilled in the iron in a surprisingly short time. A superficial corrosion will expose the graphite carbon in cast iron, a point is made electronegative and the iron ions are removed through the porous electrolyte-saturated soft material, characteristic of corroded cast iron. Mill scale, if thick and unbroken, is a good protection to iron, but if broken, becomes a source of danger, it is electronegative. There is a saving feature that explains why black iron pipes last as well as they do. As action proceeds, the mill scale is slowly reduced to metallic iron by the H. ions that may be uncombined for the moment and the area of corrosion is spread. In soils where the electrolytic conditions are not favorable, as in clean sand, action may be suspended indefinitely, only a small amount of rust forming.

Localized corrosive action on iron, commonly called pitting, is destructive for iron pipes, as a leak is caused in comparatively short time. Pitting may be caused by action

AUTO-ELECTROLYSIS TABLE V.

Iron lost from corrosive action of natural soils. Column A, grams per year lost from plates; column B, grams lost per year per square inch of corroded area. Area of plates 4.8 to 5.5 square inches. Plates underlined treated 1.07 years, all others (except 4" pipe) .23 years.

| | CAST IRON | | MILD STEEL | | | | 99.94% Ingot | | | |
|---------------------------|----------------|-----------------|---|-------------|-------------|-------------|----------------|------|------|------|
| | <u>As Cast</u> | <u>Polished</u> | With Mill Scale | | Polished | | Sheet Polished | | | |
| | A. | B. | A. | B. | A. | B. | A. | B. | | |
| Soils | | | | | | | | | | |
| Clay | | | 1.36 | 0.90 | 0.83 | 0.41 | .992 | 0.34 | 0.47 | 0.12 |
| 21.5% water | 2.02 | 1.18 | <u>1.17</u> | <u>0.51</u> | | | | | | |
| Black Peat | | | 3.44 | 2.65 | 2.22 | 2.47 | 2.82 | 1.76 | 2.82 | 1.47 |
| 39.4% Water | 2.75 | 1.05 | <u>1.70</u> | <u>0.57</u> | | | | | | |
| Mixed | | | 2.41 | 1.60 | 1.29 | .807 | 1.69 | 0.70 | 1.17 | 0.47 |
| 27.8% Water | 1.48 | 1.18 | <u>0.84</u> | <u>0.45</u> | <u>1.06</u> | <u>0.59</u> | | | | |
| Loam | 1.51 | 0.66 | | | <u>0.97</u> | <u>0.52</u> | | | | |
| Clay and Black Peat | 171. | 5.18 | 4" cast iron pipe, 41.5" long, treated .85 year. | | | | | | | |

AUTO-ELECTROLYSIS TABLE

To determine corrosion rates in soils, using the original and extracted soils and the water solution made as near as possible of the same soluble salt concentration as salts had in original soils. Armco iron analysis 1, plates 0.55 x 3.0 inches, treated 552 hours.

| | <u>Original soil</u> | <u>Extracted soil</u> | <u>Solution</u> |
|-----------------|--------------------------|---------------------------|-----------------|
| Clay A, % water | 17.4 | 22.0 | |
| Grams iron lost | .0147 | .0090 | .029 |
| Clay B, % water | 26.4 | 33.6 | |
| | .0207 | .0545 | .0245 |
| Peat C, % water | 82.5 | 84.0 | |
| | .0238 | .0169 | .0247 |
| Peat D, % water | 45.8 | 59.0 | |
| | .1208 | .0488 | .0340 |

TABLE VII.

A comparison of auto-electrolysis in different soils, using Armco iron analysis 1, 1.3 x 2.5 inch polished plates. Grams iron lost after treating 528 hours in fiber cells. Water content approximately the natural percentage.

| | |
|--------------------------------------|-------|
| Clay A..... | .0198 |
| Dark gray clay, Pierre, So. Dak..... | .0613 |
| Yellow clay, Indiana..... | .0915 |
| Light white clay, Havana, Cuba..... | .0295 |
| Yellow clay, Havana, Cuba..... | .3249 |
| Blue clay, Minneapolis..... | .0597 |
| Peat D..... | .1230 |

A comparison of auto-electrolysis on sheet irons and steels as specified, treated in fiber cells, clay A, 528 hours. Grams iron lost from 1.3 x 2.5 inch plates.

| | |
|-------------------------------------|-------|
| Armco iron 1, heavy scale..... | .0054 |
| " draw filed..... | .0650 |
| " polished..... | .0534 |
| Sheet steel 3, irregular scale..... | .0808 |
| " draw filed..... | .0702 |
| " polished..... | .1967 |

around an electronegative particle in contact with the iron. The + Fe ions leave the iron surface, setting up the current flow. The action will continue because the reaction products, Fe, H, and O ions are removed from the system as such. In time, the Fe becomes $\text{Fe}_2\text{O}_3 \times \text{H}_2\text{O}$, insoluble, but porous, and conducting. O helps to form it. H ions are removed as H_2O formed from the OH ions of electrolysis. If free H_2 were formed (rapid action) the current would be reduced or stopped by insulation due to the gas film on the electronegative area. With the slower action current flow is practically continuous, whence the corrosion rate is continuous. This is borne out both by general observations and experiments. Table V. shows corrosion rates approximately the same for different times specified.

Also, cells were set up with steel in different soils and electrolytes, so arranged as to collect all evolved gases. Cleaned mild steel, analysis 4, 1.12 x 4.25 inches, treated 600 hours. Grams loss from steel in pure water was 0.023, cinders 0.1687, peat D 0.208, peat C 0.050, clay A 0.0473. No gas came from these cells. In $\frac{N}{10}$ H_2SO_4 steel loss was 0.700 grams in 120 hours, evolving 314 c.c. of gas. After this (solution not renewed) iron loss was 0.0155 grams in 480 hours with no gas. Whence corrosion in the soil cells was purely electrolytic, with perfect depolarization, allowing a continuous corrosion rate.

Pitting will occur in polished, pure irons (analysis 1) in a clean well mixed clay, due to the same causes with no apparent electronegative areas to direct or localize the reaction. This may be due to either or both the following causes, slight differences, in the iron itself, or concentration cells set up in the clay. Using the Lippman electrometer with electrodes of similar metal, preferably small platinum wires, surveys over a piece of moist clay showed potentials of 0.01 to 0.02 volt between different points. Attempts were made in this way to locate the low potential points on a smooth clay surface. Then a polished pure iron plate was placed on it. Allowing action to continue a few days, the iron was examined to see if the corroded areas had any definite relation to these low points. Fair correspondence was obtained on one specimen, but others did not give definite results. These potentials are very difficult to locate, but it is probable they aid in starting local actions on the iron surface, producing red rust in small amount. This is electronegative and action then becomes definite and pitting proceeds.

A different type of corrosion cell was used to duplicate conditions of underground structures for further experiments on auto-electrolysis measurements. Three-inch bituminized fiber conduit was cut in sections about three inches long and filled with soil, in which was placed the iron plate. Sheet rubber disks placed in the ends made them air and moisture

tight, and paraffined wooden disks over these completed the cell. With this arrangement, the specimen could be subjected to pressure. Sets were made up to determine the effects of different pressures and temperatures encountered in practice. These results are found in Table VIII.

Lead, having a very low solution tension, is not so susceptible to auto-electrolysis as is iron. External conditions will produce corrosion, however, in a somewhat different manner. If two soils are in contact with a metal, one of which contains a substance subject to a change of valence⁽¹⁰⁾ we may expect an electrical current flow. This current will enter the metal as part of its circuit, and leave it again, in the near proximity of the bi-electric soil, causing corrosion of the cathode areas⁽¹¹⁾.

Lead is also liable to corrosion from other conditions. Pipes leaving moist cement floors often corrode near the floor line. Cable covers lying in cement ducts and lead pipes in mortar walls are also destroyed. If water from condensation or other sources is allowed to collect or run down or around a lead structure under conditions when soluble salts are present, there will be formed a concentration cell⁽¹²⁾. The electromotive force set up is caused by different velocities of different ions, which would be found in any surroundings

(10) Jones, Elements of Phys. Chem., p. 476

(11) Scofield and Stenger, Corrosion of Metals in Natural Soils, Elect.Ry.Jour., 1914, p. 1092.

(12) Bigelow, Theoretical and Physical Chemistry, p.478.

AUTO-ELECTROLYSIS TABLE VIII.

Corrosion rates, grams lost from plates in 480 hours. Pure ingot iron, analysis 1, No. 16 gage, 1.3 x 2.5 inch polished. The first horizontal row for each soil was at a temperature of 20 to 22 Cent., the second, 14 to 15, the third 8 to 10. Covers practical external conditions of buried water pipes.

| Pressures, Lbs. per sq.in. | <u>0</u> | <u>2.8</u> | <u>5.7</u> | <u>8.6</u> | <u>10</u> |
|-------------------------------|----------|------------|------------|------------|-----------|
| Soil A. | .0075 | .0090 | .0317 | .0102 | .0297 |
| Water 16% | .0534 | .0063 | .0127 | .0489 | .0243 |
| | .0118 | .0608 | .0045 | . | .0109 |
| Soil Clay B. | .0307 | .0317 | .0354 | .0352 | .0262 |
| Water 25% | .0622 | .0574 | .0459 | .0205 | .0867 |
| | .0540 | .0632 | .0499 | .0463 | .0317 |
| Soil clay | .0128 | .0482 | .0681 | .0201 | .0205 |
| Water 16% | .0432 | .0445 | .0267 | .0370 | .0367 |
| | .0130 | .0623 | .0139 | .0148 | .0354 |
| Soil Peat D. | .2310 | .2678 | .2965 | .2598 | .2411 |
| Water 53% | .1875 | .2933 | .2418 | .2585 | .2354 |
| | .1710 | .2115 | .0990 | .2068 | .2352 |

Comparing ingot iron 1 and copper bearing steel 7,
0 pressure, 20°-22° Cent.:

| <u>Soils</u> | <u>Iron</u> | <u>Cu. Steel</u> |
|--------------|-------------|------------------|
| A | .0075 | (.0987) |
| | | (.1564) |
| B | .0307 | |
| Clay | .0128 | .0464 |
| Peat D | .1710 | .2673 |

of a pipe in cement or soil. The more dilute solution would be the fresh moisture supply, the more concentrated solution would be near the metal surface in the surrounding medium. Common specific instances of this type of corrosive action are seen at the bases of trolley poles at the ground line. It occurs also if the pole is set in cement. This is a plausible explanation of the corrosion of the lead cable covers at Havana, previously mentioned. The bottom side of the cover lay in detritus, electrolytically more concentrated. The dilute solution would be from condensation and the intermittently flowing water in the conduit, in contact with the upper surface of the lead.

ANALYSES OF SOILS.

400 grams of soil were extracted for several weeks, using about 10 l. of water for each sample. The solutions were evaporated and analyzed. Figures given are grams per 1000 grams of soil.

| | <u>A</u> <u>Clay</u> | <u>B</u> <u>Clay</u> | <u>C</u> <u>Peat</u> | <u>D</u> <u>Peat</u> |
|--|-------------------------|-------------------------|-------------------------|---------------------------|
| Al ₂ O ₃ | | | | .3480 |
| SiO ₂ | .0146 | .1550 | .0061 | .1181 |
| CaO | .4580 | .1515 | .1012 | .8240 |
| MgO | .2740 | tr. | tr. | .1074 |
| SO ₃ | 1.4364 | .2600 | .1035 | 5.1130 |
| Ignited) Solids) | 2.5000 | .850 | .3620 | 8.620 |
| Total) Solids) | 2.838 | 1.175 | .6280 | 13.2480 |
| CaSO ₄ ppt. on boiling solution | | | | <u>18.2400</u> 31.4880 |

Clay A, from street east end Selby Tunnel, St. Paul, 6 ft. depth.

Clay B, from Snelling Av. & Lake St., Minneapolis, 4 ft. depth.

Peat C, from swamp north of Lake Harriet, 4 ft. depth.

Peat D, from Summit & Wabasha, St. Paul, 6 ft. depth.
Also found at location of Clay A.

Resistance of clay A, per cubic centimeter, 23.75 per cent water, at 3.6 Cent., 860 ohms; 15 Cent., 620 ohms; 25 Cent., 484 ohms; 26.1 Cent., 463 ohms.

With 20.56 per cent water, at 26.1 Cent., 527 ohms;
15.25 per cent water, 846 ohms.

Water content soil A, 17.4%; B, 26.4%, C, 82.5%, D, 45.8%.

ANALYSES OF IRONS

| No. | <u>1</u> | <u>3</u> | <u>4</u> | <u>5</u> | <u>6</u> | <u>7</u> |
|-----|----------|----------|----------|----------|----------|----------|
| | | | | 2.20 | 3.23 | |
| | | | | .73 | .41 | |
| C. | .02 | .200 | .060 | 2.93 | 3.64 | .153 |
| Si. | .003 | .003 | tr. | 3.070 | 1.62 | |
| S. | .005 | .041 | .019 | .051 | .133 | |
| Mn. | .011 | .432 | .365 | .283 | .324 | |
| P. | .000 | .010 | .027 | .500 | .458 | |
| Cu. | .000 | .170 | .000 | tr. | tr. | .233 |

1. Armco pure ingot iron No. 16 sheet.
3. No. 16 sheet.
4. No. 22 sheet.
5. From six inch cast iron pipe.
6. Cast iron, cast in 1/8 x 1 inch strips, broken two inches long, for test in soils.
7. No. 20 sheet, American Sheet & Tin Plate Co.

Conclusions

Electrolysis of underground structures may be caused by certain definite conditions, which may be determined by electrical measurements and a study of the environments.

The electrolytic theory is applicable to corrosion of underground iron and lead structures.

In comparing the corrosive resistance of different types of irons and steels, a careful study of the conditions under which the irons are to be used should be made, and tests conducted under these conditions. One or two tests are not sufficient, several should be carried out.

From experiments performed, and corrosion rates found, the probable life of an iron structure in given soils may be predetermined. The weight of 1/8 inch iron one square inch in area is 15.8 grams. Assuming corrosion forms a conical pit, the metal removed weighs 5.2 grams. From data of table V. the yearly rate of corrosion per square inch is 0.83 grams. $\frac{5.2}{.83}$ is 6.2 years, the approximate life of a mild steel black iron pipe with 1/8 inch wall, in clay A.

A factor showing the tendency of an iron to pit would be the corrosion rate per square inch of corroded area. The cast iron pipe noted in table V. was severely pitted.

The ordinary coatings, mill scale, poor grades of galvanizing, casting skin and tar dips on cast iron have little value as protection against auto-electrolysis, and in cases accelerate it. Tar dips lengthen the life of cast iron by delaying the action, but the coating will soon fail in spots.

The longer life of cast iron is due only to its greater wall thickness, Chart 6, page 17a.

Corrosion rates of iron are little affected by temperature changes within the range usually found about water pipes.

Corrosion rates are appreciably increased by pressures within the range of pressures met in practice due to depths of burial.

Admitting or excluding air from a test cell has no appreciable effect on corrosion rates.

POTENTIAL DROPS FROM CURRENT FLOW
 BETWEEN #16 CLEAN PURE IRON ELECTRODES
 $1\frac{1}{4} \times 2\frac{1}{2}$ INCHES - 8 INCHES APART IN CLAY A
 IN $6 \times 7 \times 10$ INCH BOX.
 MEASURED WITH LIPPMAN ELECTROMETER.

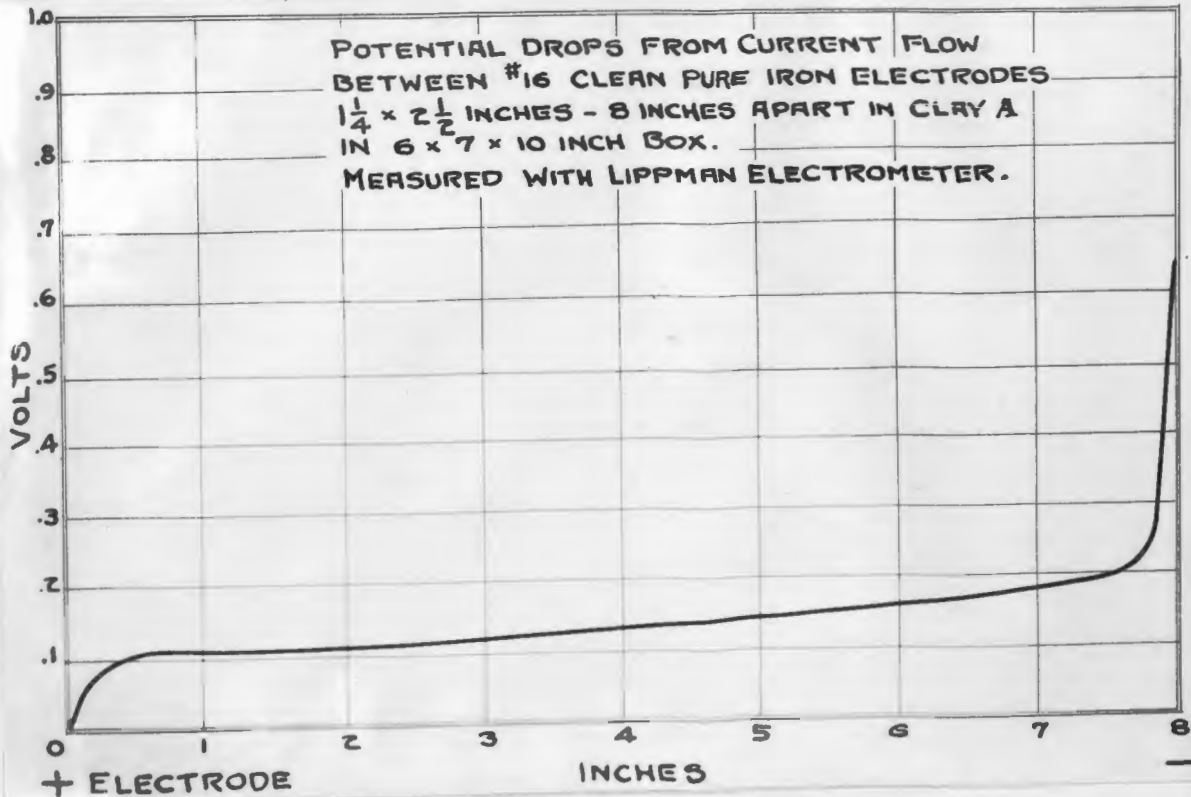
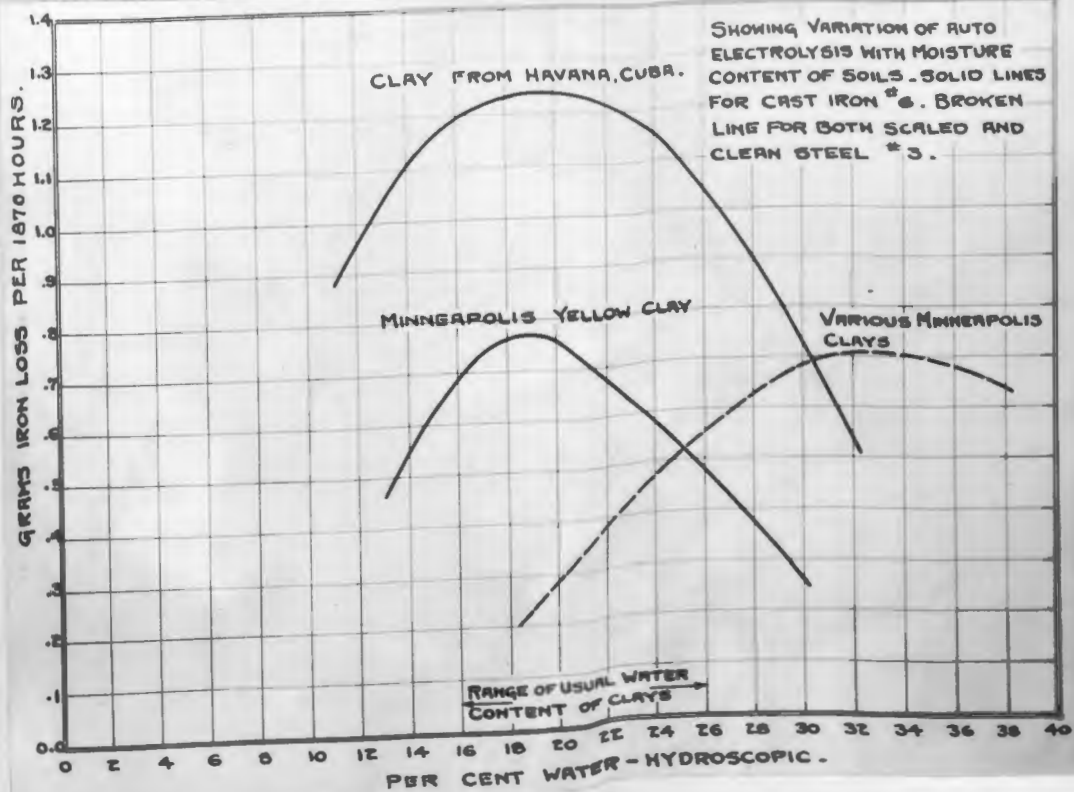


Chart 5



SHOWING VARIATION OF AUTO
 ELECTROLYSIS WITH MOISTURE
 CONTENT OF SOILS. SOLID LINES
 FOR CAST IRON #6. BROKEN
 LINE FOR BOTH SCALED AND
 CLEAN STEEL #3.

Chart 6

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