LIBRARY
COPY

THE CORROSION OF STEEL IN SALINE SOLUTIONS OF HYDROGEN SULFIDE

By

SANFORD J. NEUHAUS

Submitted in Partial Fulfillment of the

Requirements for the S.B. Degree

from the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

1945

Signature of Author . .....

Department of Chemical Engineering, June, 1945 .....

Signature of Thesis Supervisor .....

517 Beacon Street
Boston, Massachusetts
June 10, 1945

Professor George W. Swett
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge, Massachusetts

Dear Sir:

This thesis entitled The Corrosion of Steel in Saline Solutions of Hydrogen Sulfide is submitted in accordance with the requirements for the S.B. degree.

Respectfully yours,

Sanford J. Neuhaus

- A C K N O W L E D G M E N T S -

The author wishes to express his gratitude to Dr. D.B. Broughton, his thesis supervisor for the advice and aid given during this investigation.

Professors W.K. Lewis and E.A. Hauser, and Mrs. J.M. Findlay provided much help, and the author is very thankful.

The author also appreciates the aid rendered by Professor G. Dietrichson of the Chemistry Department and by the Electrical Engineering Department in their loaning of equipment.

R.H. Johnston and W.H. Levy, fellow students, loaned the author a manometer and oxygen rate calibration for which the author is grateful.

TABLE OF CONTENTS

	Page
Summary	1.
Introduction	4.
General Procedure	11.
Results and Discussion of Results	
Accuracy of Measurements	18.
Cathodic Protection Investigations	19.
Mechanism of Hydrogen Sulfide Corrosion	34.
Conclusions	43.
Recommendations	45.

APPENDIX

Computations	47.
Calibration Curve	49.
Original Data	50.
Bibliography and Footnotes	65.

SUMMARY

It was originally proposed to study the cathodic protection of steel in saline solutions of hydrogen sulfide. Cathodic protection, as used here, means substantially the impression of an external potential, producing a current counteracting the corrosion current flowing from the anode portion of the steel to the cathode portion. The cathode is thereby polarized to the anode potential, no corrosion current can flow, and no metal dissolution can occur. This holds only if the corrosion is solely electrochemical.

In order to simulate actual corroding conditions a differential aeration cell was set up using as a cathode a specimen of iron waxed on back and edges and as an anode a totally waxed specimen with a small scratch exposing the metal surface. Sodium chloride solutions were the electrolytes. This cell was a failure.

A differential aeration cell was constructed by arranging electrodes in two compartments of a cell, being separated by placing the anode in a porous paper cup. The electrodes were externally connected through a milliammeter, and oxygen was bubbled into the cathode compartment. The corrosion current was allowed to come to equilibrium and then various external protective currents were applied until

the corrosion current became zero. Results were not duplicable with or without hydrogen sulfide; the position of the bubbler, the degree of aeration, the concentration of the electrolyte, and other variables were investigated in order to obtain reproducible results. Inability to duplicate results was due primarily to some local action on the cathode surface and inability to duplicate the oxygen diffusion rate to the cathode. The latter in turn was due to failure to keep constant one or several of the following factors:

a) The geometrical arrangement of the cell

b) The rate of dissolution of oxygen at the solution surface

c) Agitation

To study the mechanism of hydrogen sulfide corrosion, hydrogen sulfide was added to each of the compartments during different runs, and potential and current measurements taken.

Results showed that hydrogen sulfide stimulates the anode reaction. The hydrogen sulfide removes some of the ferrous ions concentrated around the anode as insoluble ferrous sulfide, thereby driving the anode reaction to the right. At the anode the controlling factor is the ferrous ion concentration.

Hydrogen sulfide retards the cathode reaction, in considering the aerated iron plate as the cathode. In reality

it is not a pure cathode and physical imperfections act as local anodes on the specimen. As a result, a concentration of ferrous ion is present around the cathode, and the addition of hydrogen sulfide precipitates out ferrous sulfide (and ferric sulfide due to oxidation by the oxygen). This accelerates whatever anode reaction is occurring on the cathode, and makes the overall cathodic potential more anodic. In fact it was found that twenty minutes after addition of the sulfide to the cathode compartment, the cell even reversed itself. The reversal was not immediate due to conditions at the metal-solution interface. Time was required for the sulfide ions to migrate thru this surface film and for dynamic equilibrium to be established between the reaction rates for sulfide ion and ferrous ion production.

Another contributing factor at the cathode is the loss of oxygen by reduction by the sulfide, oxygen that is not replaced quickly enough. The supply and diffusion of oxygen is of paramount importance at the cathode surface.

The cell, containing 50 parts per million hydrogen sulfide in 10 grams of sodium chloride per liter is substantially under <u>anodic</u> control.

The hydrogen sulfide by depressing <u>both</u> the anode and cathode potential did not accelerate the overall corrosion current. This is contrary to the general view held that hydrogen sulfide does accelerate electrochemical corrosion.

It is to be remembered, however, that the cathode of these experiments was not a pure cathode and that the corrosion current read on the milliammeter short-circuiting the electrodes was not a true measure of the corrosion current as local action was present on the electrodes.

INTRODUCTION

I. Hydrogen Sulfide Corrosion

Hydrogen sulfide causes serious corrosion in illuminating gas mains when oxygen and water are present. In pipelines carrying sewage and polluted water, hydrogen sulfide corrosion is encountered. Oil-well apparatus is frequently attacked by saline solutions of hydrogen sulfide. The corrosion of oil-cracking equipment by hydrogen sulfide takes place at high temperatures (900°F), but here the mechanism is strictly direct combination of the sulfide with the iron and is not electrochemical (1).

Hydrogen sulfide makes the water it is dissolved in acidic and causes rapid corrosion even in the absence of oxygen(2). Speller claims that in the presence of oxygen sulfuric acid may be formed as a reaction product, and when little oxygen is present, elementary sulfur and the iron sulfides are formed. Watson (3) found that in illuminating gas mains the effect of hydrogen sulfide is decreased when the water vapor and oxygen in the gas are reduced.

Britton, Hoar, and Evans (4) found that hydrogen sulfide in small quantities (less than five parts per million) accelerated the total attack on steel when added to potassium chloride solutions. Here the intensity of attack was diminished,

because the area attacked was extended. The acceleration of corrosion was shown to be due to the stimulation of the anodic reaction, owing to the precipitation of iron salts as non-protective iron sulfide and consequent interference with the usual protection mechanism.

II. Cathodic Protection

It was originally intended to study the cathodic protection of steel in saline solutions of hydrogen sulfide. Failure to find a differential aeration cell that would yield duplicable results led to the study of the mechanism of hydrogen sulfide corrosion and the choice of the present title. Interesting data were obtained, however, on the cathodic protection of steel.

The use of galvanized iron has had wide-spread application. The zinc coating is anodic to the iron and, as current flow takes place from the anode to cathode in solution, theoretically no dissolution of the iron can occur. Similarly an external potential can be applied, opposing the corrosion current. Brown and Mears present the theory of cathodic protection excellently.

"The electrochemical theory of corrosion, in its broadest sense, postulates that heterogeneities of the metal surface, the corroding medium, or both, cause differences in potential to exist on different areas of the metal surface, with the result that current flows between these areas. The less

electro-negative areas (cathodes) of the most common metals polarize in chloride solutions in the manner shown in Fig. I, Curve 1. The more electro-negative points (anodes) of most metals do not polarize in chloride solutions to as great an extent. This point is illustrated in Fig. I, Curve 2. The current which causes corrosion, neglecting the small IR drop thru the liquid and metal is given by the intersection of the two curves (Point D). Because of the polarization caused by the current flow from the anode areas thru the solution to the cathode areas, the potential of all points then is equal."

"However, this nearly equipotential surface is obtained by a current flowing from local anodes on the specimen. Naturally, such a current flow causes anodic dissolution or corrosion. If the potential required can be furnished from a source other than the anodes on the specimen itself, it should be possible to polarize the cathode areas until they attain the potential of the intersection D. Even under these conditions, since at zero current density, the potential of (unpolarized) anodic points on the specimen would still be anodic to point D, some current would flow from these areas through the solution to the cathode areas ..... If the cathode areas are polarized further by <u>current furnished from a source external to the specimen in question</u> until the cathode areas attain a potential equal to the potential of the anode areas at zero current density. (Point

FIG. I

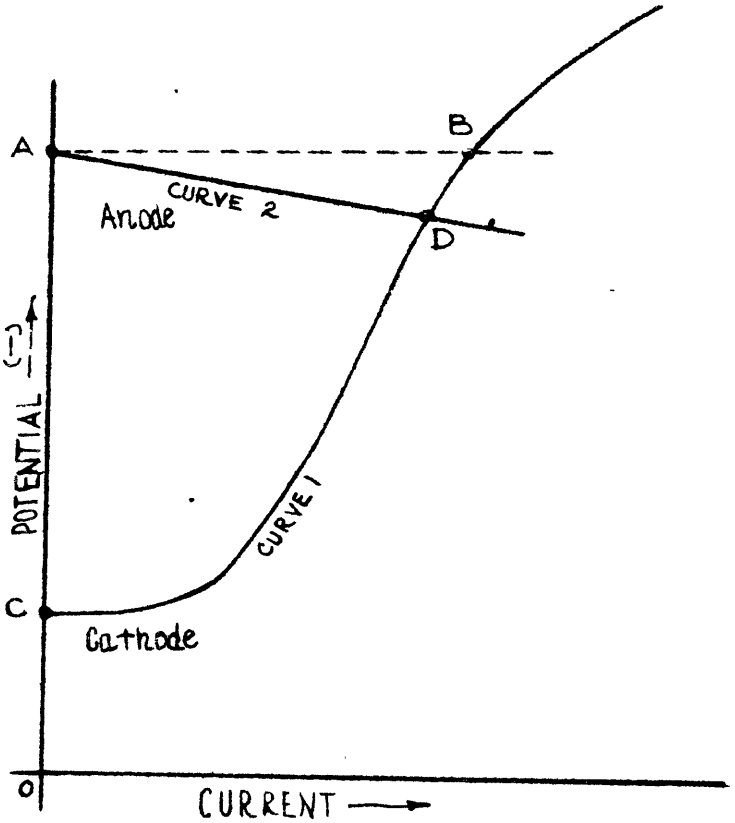


FIG. I.

POLARIZATION CURVES
(From Brown and Mears with some omissions - footnote 5)

B - the open circuit anode potential), then the entire surface is made equipotential without the local anodic points on the specimen furnishing any current. Thus no currents can flow between the local anodes and the cathodic surface, if the corrosion is entirely electrochemical, the protection is 100 per cent. efficient, and no corrosion results from the products of electrolysis formed around the cathode." (5)

Brown and Mears have made experiments supporting their theory and have even applied Kirchhoff's Laws to cathodic protection circuits.(6) Through these circuit analyses, they have found further that in order that protection may be complete in solutions where the cathodic polarization is small compared with the resistance drop, the cathode must be depolarized to a potential more anodic than the open-circuit potential of the anodes." (7) The position of the protection anode and the potential drop between the cathode and protection anode also affects the current required for complete protection.

III. Differential Aeration Cells

It has been shown, principally through the work of U.R. Evans, that oxygen concentration cells are of primary importance in the electrochemical corrosion of metals. Areas that are shielded from oxygen become anodic to areas which are in contact with solutions richer in oxygen. If a small

hole or scratch, through which oxygen cannot diffuse rapidly, exits on a metal surface, it will become anodic to the aerated area around the imperfection. Current will flow between the unaerated and aerated areas, and anodic dissolution of the metal follows. "Since the rate of attack is determined by the supply of oxygen to the whole surface outside the pit, and since it is all concentrated on the small area within the pit, the rate at which the corrosion bores into the metal will be very great." (8) Changes in aeration can bring about a reversal of polarity - a membrane which diverts the oxygen from the cathode can cause the cathode to become the anode of the cell. This accounts for the uniform corrosion sometimes encountered as contrasted to "pitting". Agitation plays an important part in that it distributes the oxygen over the metal surface.

It would seem then that the use of a simulated differential aeration cell is an ideal method of obtaining corrosion data; it has been used by many investigators.

The usual method has been to separate identical pieces of metal in solution (usually waxed on the backs and edges) by a piece of parchment or the like and bubble air or oxygen into one compartment. The aerated compartment becomes the cathode and the stagnant one the anode.

Mention has been made in the literature of using a method in which one electrode is waxed on the back and edges leaving one face bare, while the other electrode is completely coated with wax and a thin scratch or scratches made on one face. The air dissolved on the electrolyte or any aeration causes this cell to act identically like the cavity discussed above, the scratch becoming anodic to the bare plate.

IV. Purpose of Research

As mentioned above original intentions were to investigate the cathodic protection of steel in saline hydrogen sulfide solutions. Failure to find a suitable differential aeration cell led to the study of the mechanism of hydrogen sulfide corrosion. For this reason the various parts of the thesis are divided into two distinct sections.

Intentions were originally to study the cathodic protection of steel in various concentrations of hydrogen sulfide dissolved in a rather concentrated sodium chloride electrolyte. Another phase would have been to use a constant hydrogen sulfide concentration in a variable concentration of sodium chloride. Still another phase would have been to vary the degree of aeration while keeping both the hydrogen sulfide and salt concentrations constant.

GENERAL PROCEDURE

All specimens were hot-rolled mild steel analyzing:

Carbon -	0.20%
Manganese -	0.7-1.0%
Phosphorus -	0.045% maximum
Sulfur -	0.055% maximum

The specimens were ground down on grinding belts and finished to No. 00 emery. They were cleaned with benzene before waxing to remove any glue or adhering emery particles. Through all the investigations the specimen electrodes were placed 1 1/2" apart, parallel to each other.

I. Cathodic Protection Investigations

A. In order to investigate cathodic protection the scratch method referred to in the introduction was used. One specimen was waxed completely on faces and edges and scratched, while the other was waxed on the back face and edges, leaving one face bare. The protection anode was made of platinum foil and was placed at right angles to the iron electrodes as shown in Fig. II-A. The electrical circuit was as shown in Fig. II-B. It was decided to attempt to duplicate results in a rather concentrated solution of sodium chloride before any hydrogen sulfide was used. It was intended to have the corrosion current

FIG. II

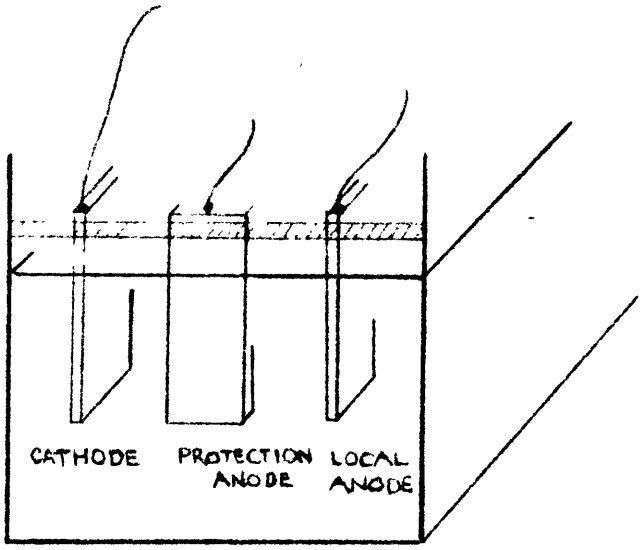
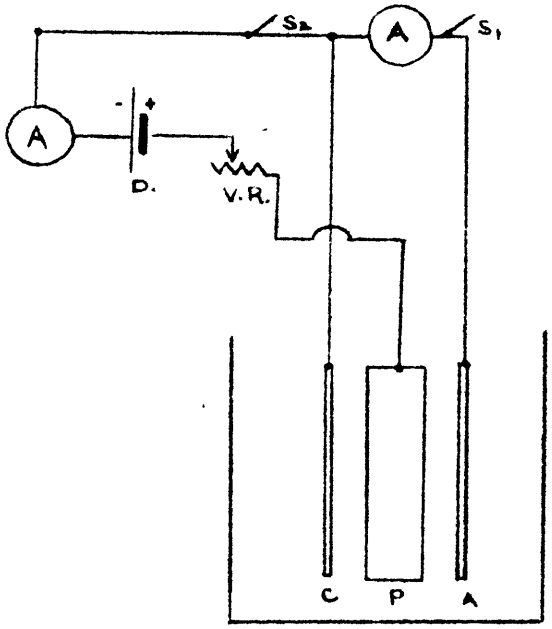


FIG. II A

CORROSION CELL



LEGEND

A - Ammeter
S - Switch
D - Dry cell
V.R: Variable Resistance
C - Cathode
P - Protection Anode
A - Local Anode

FIG. IIB

ELECTRICAL CIRCUIT – CATHODIC PROTECTION WORK

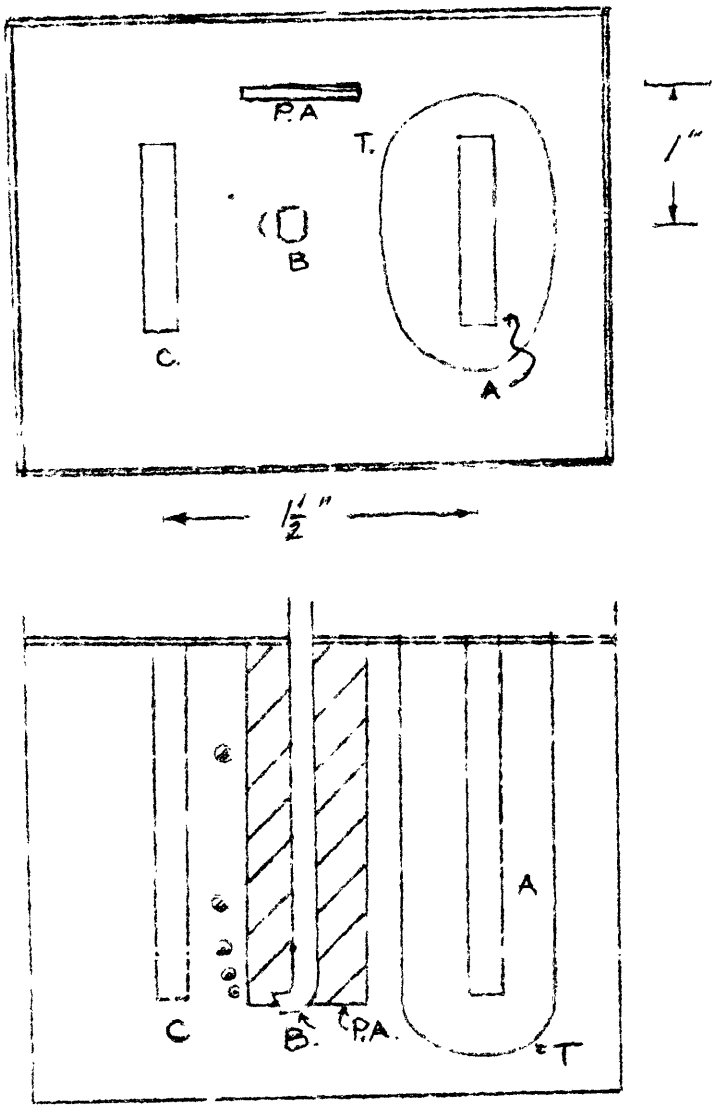
(flowing between anode and cathode) come to equilibrium and measuring the corrosion current on an ammeter with S_1 closed (Fig. II-B) as it changed with time. Then S_2 would be closed and the variable resistance, $V_a R_a$, would be varied thus changing the protection current flowing from the protection anode to the cathode. These values of corrosion current and protection current were to be recorded. The protection current would be increased until a value for complete protection, that is, zero corrosion current, was obtained.

The degree of aeration in the cell was varied.

B. The failure of the "scratch" method led to the adoption of the usual experimental differential aeration cell (Fig. III). Both the local anode and cathode were waxed on rear face and edges, being placed in the cell with the bare faces facing each other. The local anode was placed in a porous cup, and oxygen (99.5% pure) was bubbled into the cathode compartment. The cup was made of paper and somewhat resembled blotting paper, although it had larger pores. (The cups are used in sugar research and are known as extraction thimbles.)

The protection anode was placed in the cathode compartment at right angles to both electrodes as in part A. The corrosion current was allowed to come to an equilibrium value, time and current data being recorded. After equilibrium was obtained the variable resistance (Fig.II-B)

FIG. III.



DIFFERENTIAL AERATION CELL

Legend

A ANODE
B BUBBLER
C CATHODE
P.A. PROTECTION ANODE
T. POROUS THIMBLE

was changed to obtain protection current data as described in part A. above. The protection current was increased until a value for complete protection was obtained.

In efforts to obtain duplicable results, several cell variables were investigated:

1. The position of the bubbler was varied.
2. Both partially immersed and completely immersed iron electrodes were used.
3. Nitrogen was bubbled into the anode compartment to blow out any dissolved oxygen or oxygen seeping in through the porous thimble.
4. Different degrees of aeration were employed.
5. Both concentrated and dilute electrolytes were employed.

It was chosen not to use any dissolved hydrogen sulfide in the electrolyte until duplicable results were obtained in plain salt solution.

II. Mechanism of hydrogen sulfide corrosion

A. In order to determine whether the cell was under cathodic or anodic control in the presence of 50 parts per million hydrogen sulfide, the usual totally immersed cathode was replaced by a smaller one. The anode was the usual totally immersed one. The same cell of Fig. III was used. After equilibrium was reached, a larger cathode area was switched in, replacing the small one, and the

abrupt change in current noted.

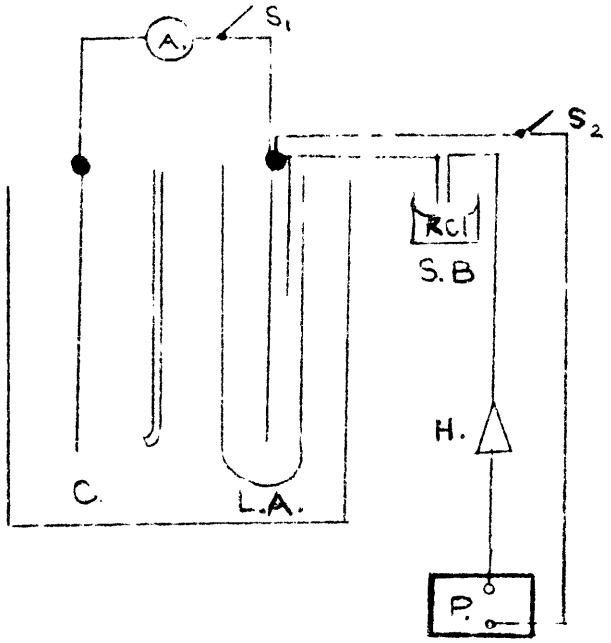
B. The effect of adding hydrogen sulfide to the anode compartment only and then to the cathode compartment only during separate runs was noted. The current was allowed to come to equilibrium (reach an asymptote), and then the hydrogen sulfide was added. Both corrosion current measurements and potential measurements of the individual electrodes were taken. These latter were based on a saturated calomel half-cell. The apparatus is pictured in Fig. XI. While current measurements were being made S_1 was closed and S_2 open; while potential measurements were being made S_2 was closed and S_1 open. The apparatus of Fig. XI shows the potentiometer connected for anode potential measurements (although S_2 should be closed). For the cathode potential measurements another agar salt bridge was used leading from the cathode to the saturated KCl solution, and the potentiometer lead was connected to the cathode.

FIG. XI

ELECTRICAL CIRCUIT FOR POTENTIAL MEASUREMENTS

~ LEGEND ~

A - MILLIAMMETER
C - CATHODE
L.A. - ANODE
H - CALOMEL (SAT.) HALF-CELL
S_1, S_2 - SWITCHES
S.B. - SAT KCl-AGAR SALT BRIDGE
P. - POTENTIOMETER



RESULTS AND DISCUSSION OF RESULTS

Accuracy of Measurements

The milli-ammeters used throughout the reseach were reported calibrated to about 3% of scale.

The potential readings were made only to three places, whereas the potentiometer was good to four.

The oxygen rates were computed from the calibration curve obtained for the manometer by Johnston and Levy. (See Appendix). The manometer was calibrated up to about 7.5 inches of water. The curve was linear, so in order to compute the high oxygen rate of about 3 inches of mercury pressure on the manometer, the value for the 3 inches of water was multiplied by the specific gravity of mercury, 13.6. The value is extremely approximate, but as the aim was only to keep the oxygen rate constant, the actual value only matters if a future experimenter wishes to use the identical conditions used.

Accuracy of results is discussed throughout the body of the discussion. All ammeters were obtained from the Electrical Engineering Department, the potentiometer from the Department of Physical Chemistry. C.P. sodium chloride and U.S.P. sodium sulfide were used. The oxygen was 99.5% pure.

I. Cathodic Protection Investigations

A. The iron specimens were each 5" x 1" x 1/16", and the scratches were vertical, 1" x 1/16" x 1/32"; the scratches were put in by a milling machine to afford better duplication. The protection anode was 5" x 1" x 1/16". Both the cathode and protection anode were partially immersed, 3" being below the interface. The entire scratches on the local anode was submerged. An electrolyte of 100 gm./liter of sodium chloride was used.

The cell contained only the oxygen from the dissolved air. At the start when the cell was first short-circuited with the ammeter the current was of the order of magnitude of 5 micro-amperes; the current would begin to drop slowly, and then the cell would suddenly reverse itself. It would sometimes reverse itself several times during a period of several minutes. On some runs current would flow from the scratch to the plate as expected and drop slowly, settling out at an equilibrium value of around 2 or 3 microamperes. On similar runs, under seemingly identical conditions current would flow from the plate to the scratch. Increasing the number of anode scratches increased the current only very slightly.

The solution was then aerated by blowing air into the solution in order to increase the oxygen concentration around the cathodic plate; the area of the cathodic plate

was doubled also to increase the current flow. When first short-circuited with the ammeter, the current rose rapidly to about 25 microamperes and then slowly fell until it reached a constant value around 15 microamperes. This type cell too had reversed polarity on different runs.

It appeared on analysis that the scratch was too large and gave rise to local action in the cavity itself. Thinner scratches were made by cutting with a knife blade through the wax, but as before the polarity was reversed on similar runs. No matter which the direction of current flow when air was bubbled very close to the cathode the current rose and when bubbled past the anode the current dropped. This was as it should be if the current was flowing from scratch to plate. The oxygen concentration gradient was increased when air was bubbled past the cathode and decreased when past the anode (oxygen diffusing into the cavity). However, the phenomenon is unexplainable when the current is flowing from plate to scratch.

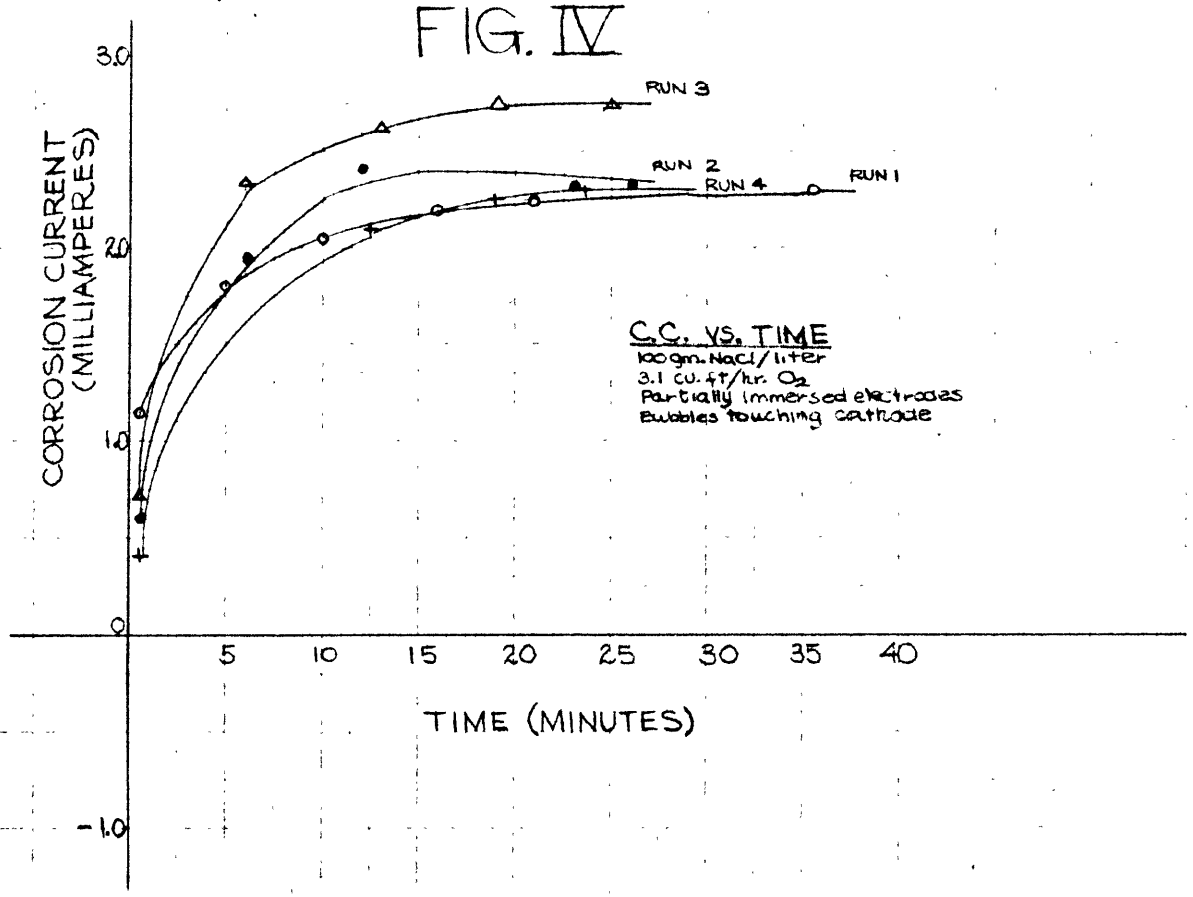
Similar results occurred in saturated solutions. It was impossible to study cathodic protection in such a cell. The aeration was the governing factor and was uncontrollable. The currents were extremely small (0-25 micro-amps.), and the potential difference across the cell was perhaps too small to maintain constant. The scratches were vertical - a small oxygen concentration gradient might

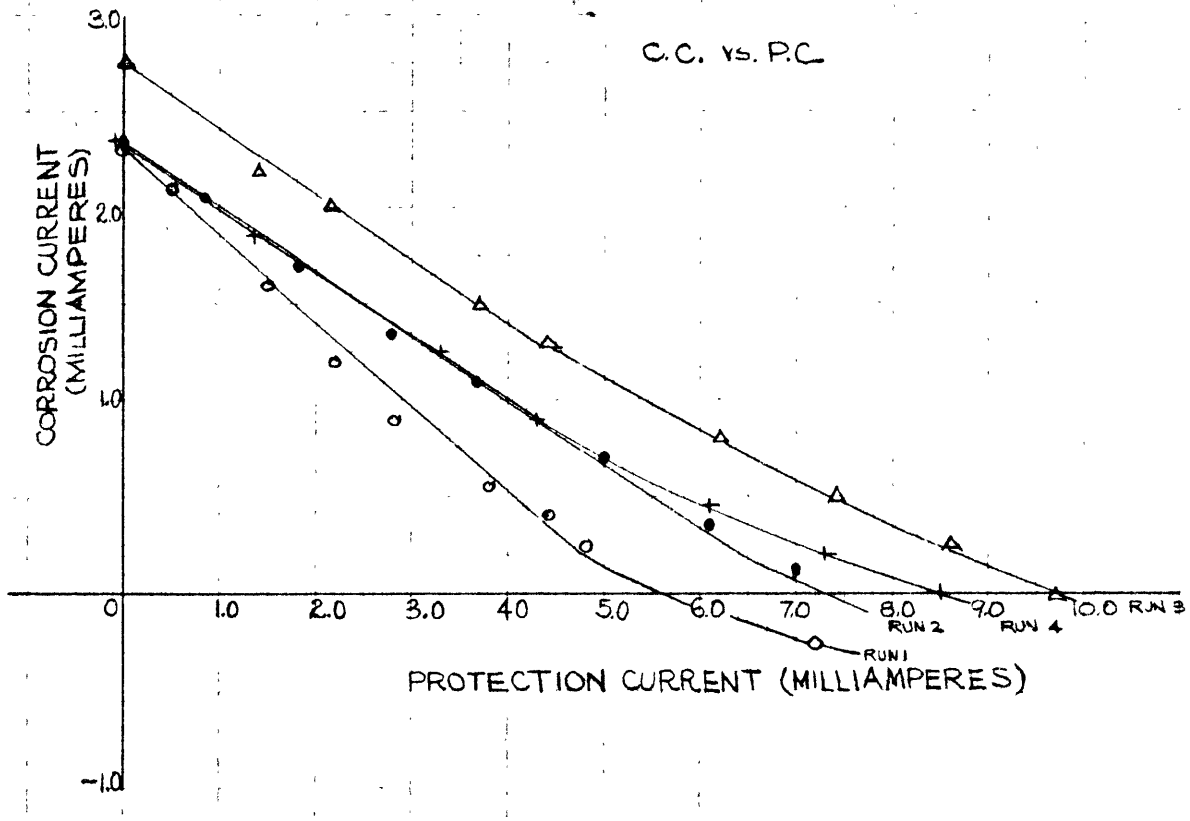
have existed due to the difference of concentration at different depths of the solution. Several runs with horizontal scratches yielded similar results, however.

B. The "scratch" method was abandoned and replaced by the differential aeration cell described in the General Procedure. The paper thimble was in the shape of a long cylinder 43 x 120 mm. The specimens measured as in Part A, 5" x 1" x 1/16".

1. A series of runs were made with the bubbler between the electrodes, with a sodium chloride concentration of 100 gm/l. (negligible resistance), with partially immersed electrodes (3" being below the surface), and with an oxygen rate of approximately 3.1 cu.ft. oxygen/hr. (see discussion of accuracy of measurements). This high oxygen rate provided much agitation, it being hoped that this would diffuse the gas uniformly throughout the solution so that no concentration gradient existed on the cathode between points at different depths in the electrolyte. The diffusion of oxygen through the porous thimble had to be considered, but this seemed negligible and was not possible to control anyway. Distilled water was used throughout and negligible dissolved air was present in the anode compartment, the thimble being sealed off with paraffin. Figure IV shows the results with the bubbler midway between the electrodes. The Fig. IV-A shows a plot of corrosion current versus time for a series of runs under identical conditions; it can be seen how the current reaches an asymptote after a

FIG. IV


CORROSION CURRENT (MILLIAMPERES)
3.0
2.0
1.0
0
-1.0
RUN 3
RUN 2
RUN 4
RUN 1
C.C. VS. TIME
100 gm. NaCl/liter
3.1 cu. ft/hr. O2
Partially immersed electrodes
Bubbles touching cathode
5
10
15
20
25
30
35
40
TIME (MINUTES)


C.C. vs. P.C.
CORROSION CURRENT (MILLIAMPERES)
3.0
2.0
1.0
0
-1.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
RUN 3
RUN 2
RUN 4
RUN 1
PROTECTION CURRENT (MILLIAMPERES)

certain elapsed time. Fig. IV-B shows a plot of corrosion current versus protection current for the various runs in Fig. IV-A, the protection current being applied after the asymptotic or equilibrium corrosion current value had been reached. This system of graphing is used throughout on the cathodic protection data. In the runs shown in Fig. IV no attempt was made to stop the bubbles from hitting the cathode surface. Results show that although the equilibrium value of the corrosion current is the same for Runs 1, 2, and 4, the protection currents for complete protection (intercepts on the 0 corrosion current axis) vary greatly from 5.6 milliamperes to 9.7 milliamperes for seemingly identical conditions, a difference of 55%. At the end of these runs small areas of the cathode were covered with rust, and a green film covered the anode.

The rust on the cathode was due either to local action, that is, local cells set up on the cathode surface due to physical imperfections or differences in internal stresses, or to migration of the ferrous ions from the anode to the cathode followed by oxidation by the oxygen to ferric ions and combination with the hydroxide ions to precipitate ferric hydroxide. Iron in common salt solution yields ferrous chloride at the anode and sodium hydroxide at the cathode. The mobility of the hydroxide ions is far greater than that of the ferrous ions, hence it carries the greater

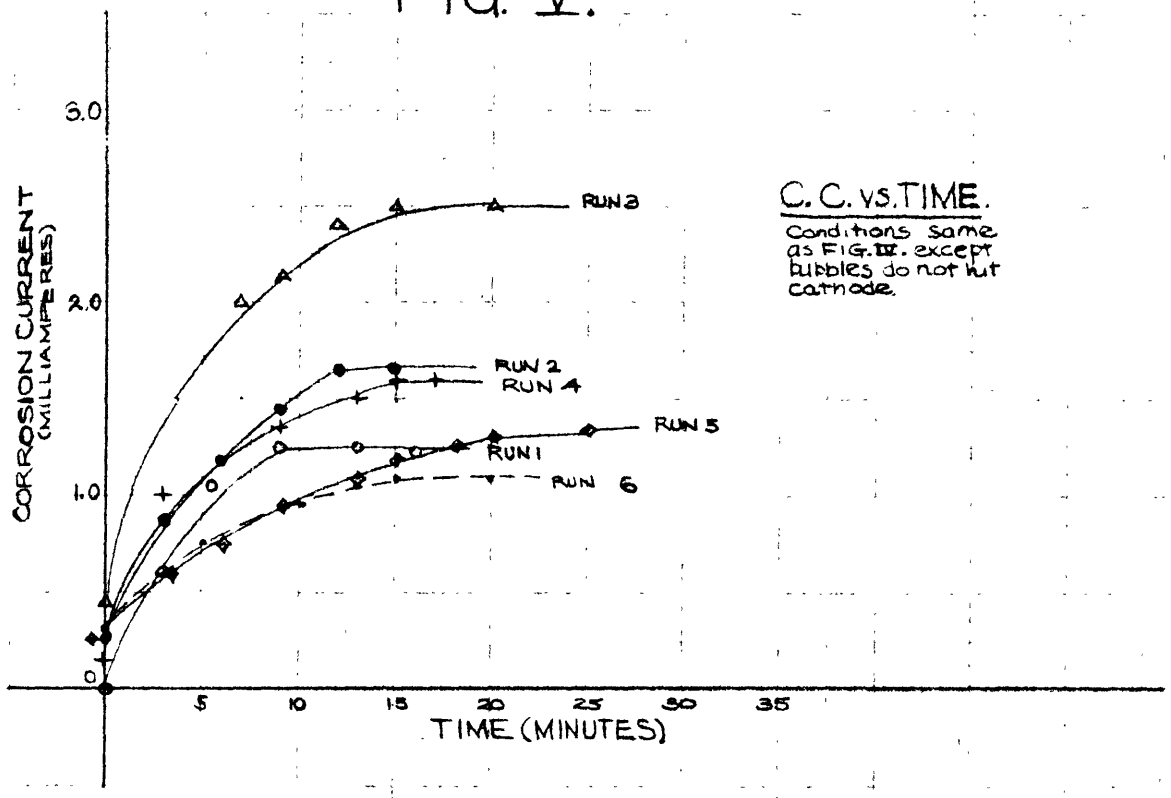
portion of the current and does most of the migrating. It is doubtful, then, that the ferrous ion migrates far, and it is to be concluded that the rust on the cathode is due to local action. The green film on the anode was the ferrous chloride.

A set of runs was made with conditions the same as above with the exception that the oxygen bubbles did not touch the cathode. The bubbler was still midway between the electrodes. Results were no better than before as can be seen from Fig. V, extreme runs varying by over 200%. Fig. VI shows three runs with the bubbler placed behind the cathode with the obviously poor duplication.

It was apparent from the first set of runs that the position of the bubbler was critical. Moving it slightly--pushing the ascending oxygen stream closer or further away from the cathode -- changed the corrosion current markedly. Placing the bubbler behind the cathode served to remove the glass rod from between the electrodes, which might have interfered differently with ionic flow on different runs. Rust was present on the cathode to a small extent and the green film of ferrous chloride on the anode. It was decided to continue using the bubbler midway between the electrodes.

The rate of diffusion of oxygen to the cathode seemed, at this time, the controlling factor. The changes of cathode surface due to local action were extremely small, and a few

FIG. V.


C. C. VS. TIME.
Conditions same as FIG. III. except bubbles do not hit cathode
CORROSION CURRENT (MILLIAMPERES)
3.0
2.0
1.0
0
RUN 3
RUN 2
RUN 4
RUN 5
RUN 1
RUN 6
5
10
15
20
25
30
35
TIME (MINUTES)

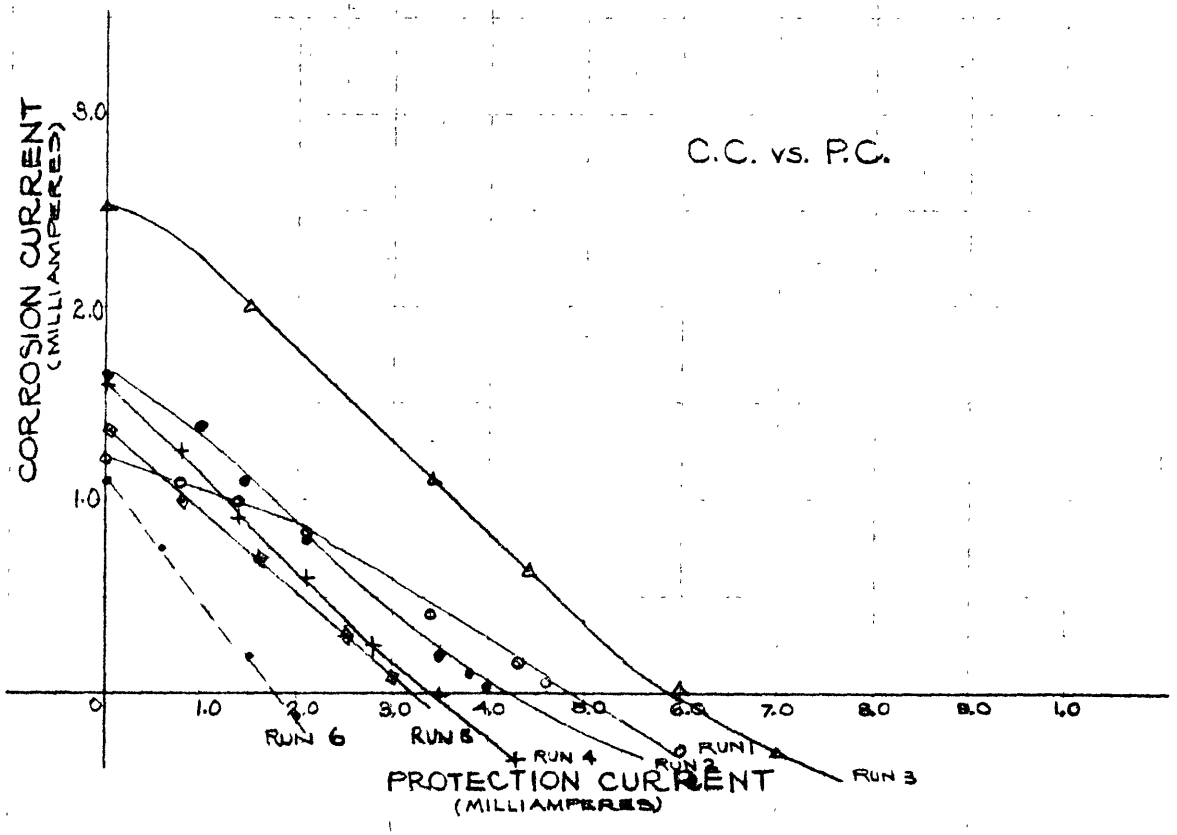
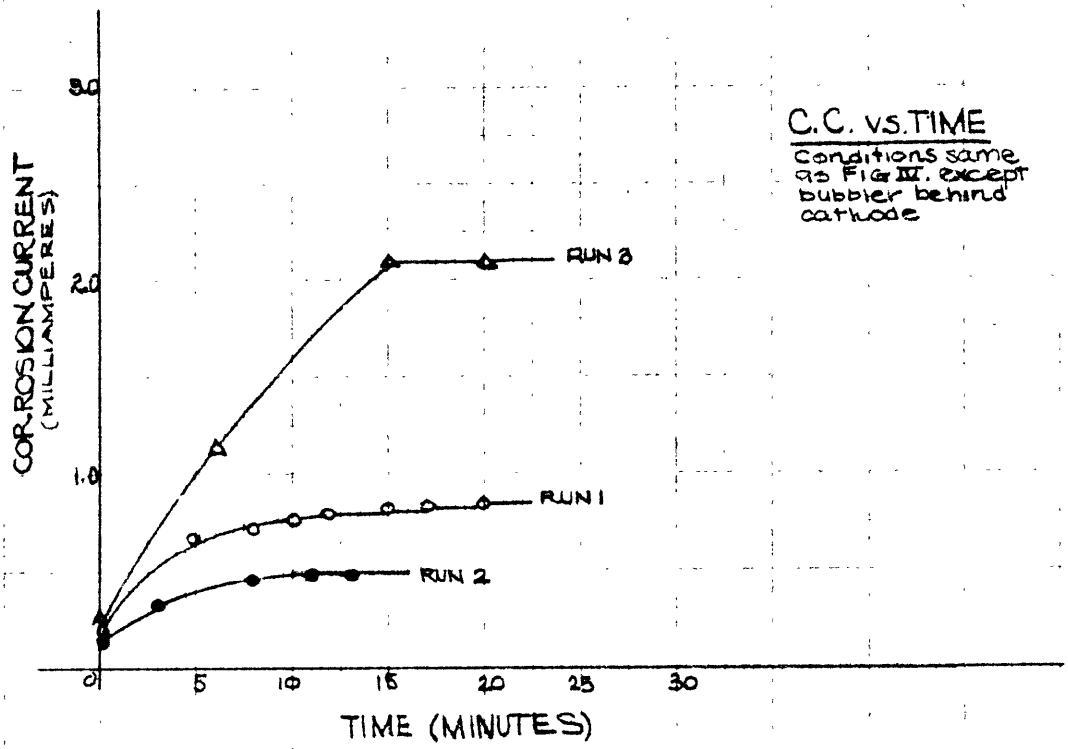
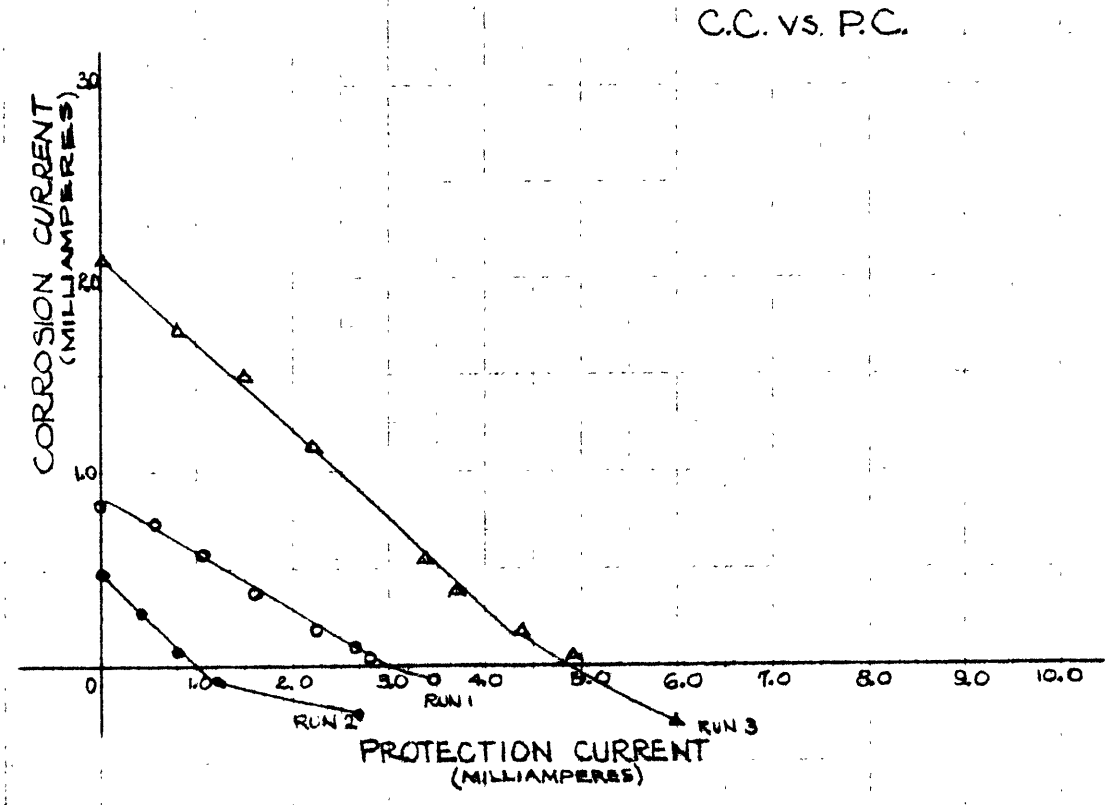

C. C. vs. P. C.
CORROSION CURRENT (MILLIAMPERES)
3.0
2.0
1.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
1.0
RUN 6
RUN 5
RUN 4
RUN 2
RUN 1
RUN 3
PROTECTION CURRENT (MILLIAMPERES)

FIG. VI.


C.C. vs. TIME
Conditions same as Fig III. except bubbler behind cathode
CORROSION CURRENT (MILLIAMPERES)
3.0
2.0
1.0
RUN 3
RUN 1
RUN 2
0
5
10
15
20
25
30
TIME (MINUTES)


C.C. vs. P.C.
CORROSION CURRENT (MILLIAMPERES)
30
20
10
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
RUN 1
RUN 2
RUN 3
PROTECTION CURRENT (MILLIAMPERES)

test runs with different size cathode areas showed that the cell was more under anodic control than cathodic.

Gatty and Spooner (9) summarize the factors that influence the supply of oxygen at the solution-metal interphase as follows:

a) The geometrical arrangement of the cell electrodes and contained solution
b) The rate of dissolution of oxygen at solution surface
c) The rate of diffusion of oxygen through the electrolyte
d) The solubility of oxygen in the electrolyte, i.e. as dependent upon nature of solute
e) The partial pressure of oxygen above the solution
f) Stirring

"For steady conditions within the electrode system", continue Gatty and Spooner, citing much data, "provided the solution in the region of the interphase is not saturated with oxygen, the rate of supply of oxygen to the interphase is governed by the slowest of processes (b) or (c)." (9)

The bubbling of oxygen, besides supplying the oxygen concentration, provided agitation which depolarizes the cathodic area and increases the corrosion current over that yielded by a stagnant solution around the cathode. The agitation becomes another variable.

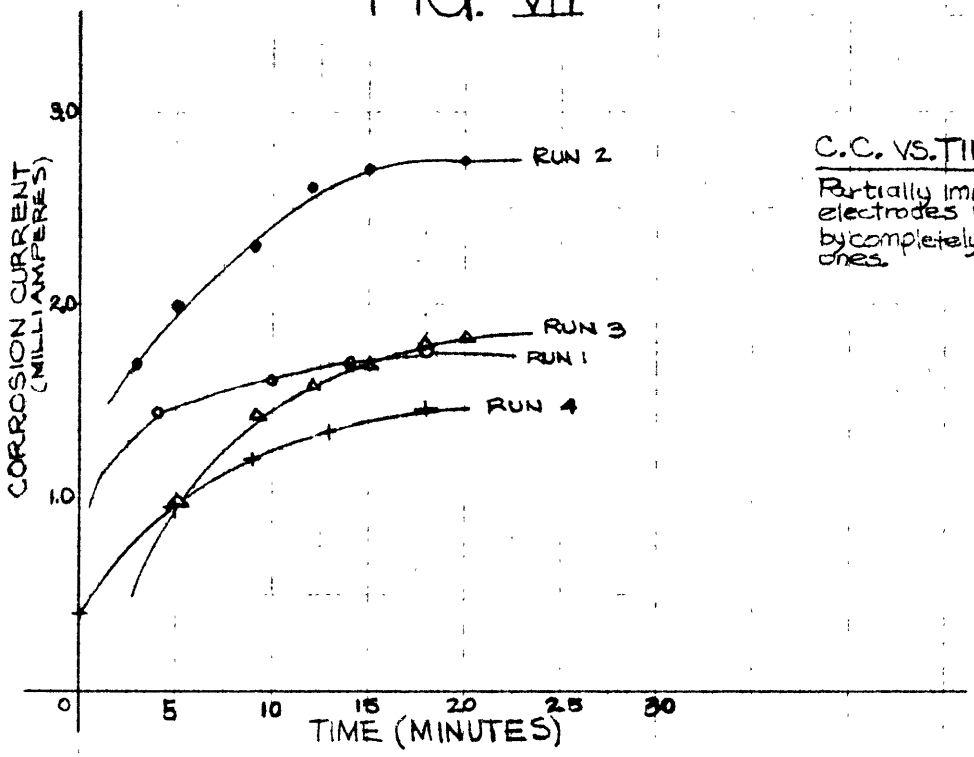
It is seen how many variables are encountered and must be kept constant.

2. In order to avoid the complications (if any important ones exist) present at the air-metal-solution interphase totally immersed electrodes were substituted for the partially immersed ones. The electrode areas were each 3" x 1", completely submerged. Fig. VII shows the results which again show very poor duplication. In spite of this, it was decided to use totally immersed specimens through the remaining experiments to avoid the possible complications.

3. In order to counteract the diffusion of oxygen into the anode compartment, however slight it might be, nitrogen was bubbled thru the compartment at a constant rate, to blow out with it all the oxygen. This method did not produce duplicable results -- the same concentration, 100 grams sodium chloride/liter being used, a bubbler midway between electrodes, same oxygen rate, etc. The agitation provided by the nitrogen offered added resistance to current flow and cut down the current to several hundred micro-amperes at equilibrium.

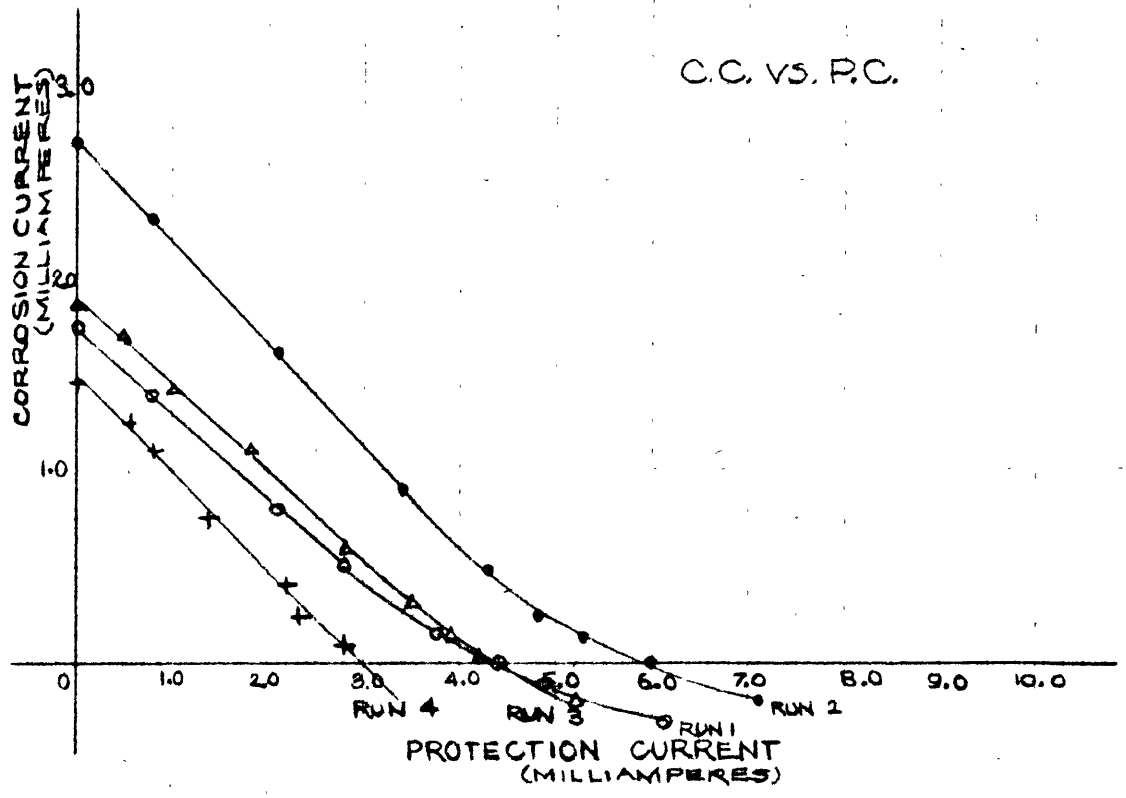
4. It was decided to vary the degree of aeration; 3.1 cu.ft. oxygen/hr. was quite high and the vigorous bubbling through the solution might manifest itself by making it very difficult to duplicate the agitation. An

FIG. VII



C.C. VS. TIME

Partially immersed electrodes replaced by completely immersed ones.

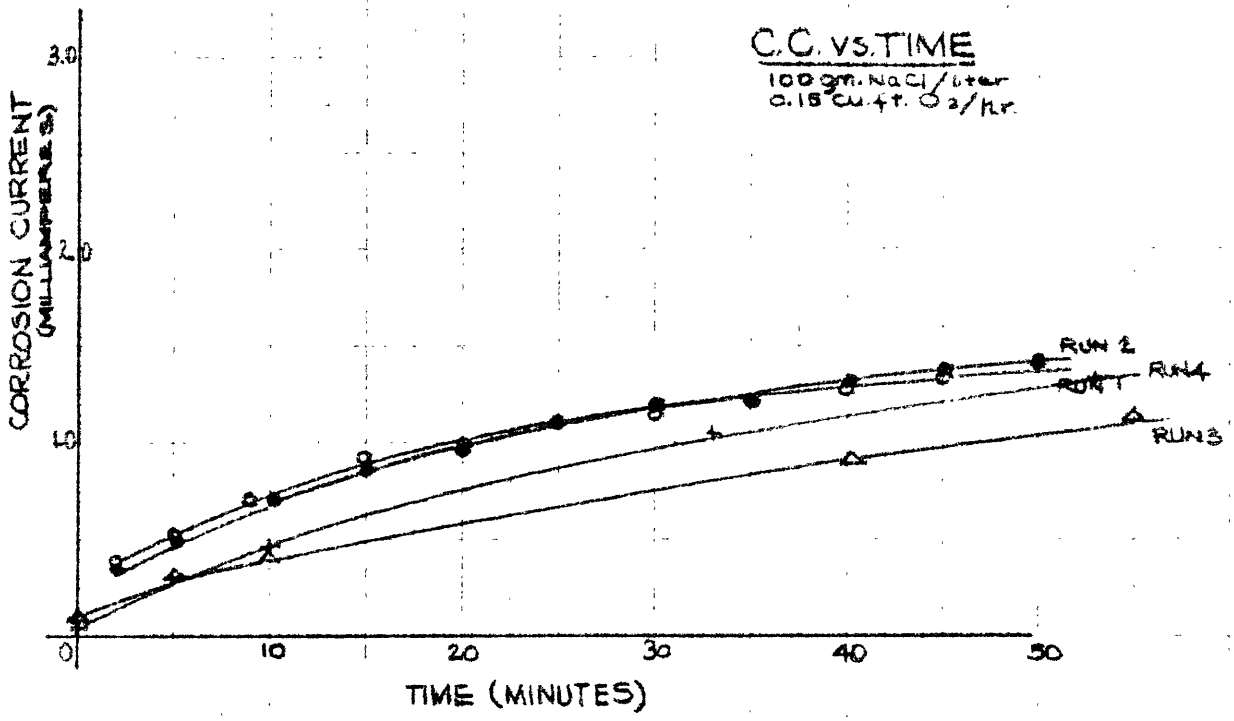


oxygen rate of 0.15 cu.ft. oxygen/hr. was substituted and the oxygen was bubbled in through glass tubing with capillary bore in order to obtain very small bubbles. The bubbler was still placed midway between the electrodes and arranged so that no bubbles actually touched the cathode. 100 grams/liter of sodium chloride was used still. Fig. VIII shows the results. As the corrosion current increases slowly with time, this set of runs was not allowed to reach equilibrium, but cathodic protection was started between 50 and 55 minutes after initial short circuiting of the electrodes. The results were not duplicable.

Allowing a solution of 100 grams/liter of salt to become saturated with oxygen and then placing the electrodes and apparatus in this solution (with unoxygenated solution in the anode compartment) was tried. The current started out higher than usually, but increased with time as in the other runs with just as much variation in corrosion current for different runs as before. This was repeated in solutions of 10 grams of salt per liter of solution just as unsuccessfully. The difficulty in performing runs in saturated solutions led to abandoning any further experiment.

5. Fig. IX shows the results of using the low oxygen rate of 0.15 cu.ft. oxygen/hr. in a sodium chloride solution of 10 grams/liter. The dilute solution was chosen because Hoar, Evans, and Britton (10) got "satisfactory duplication of results using a very similar apparatus and a 0.1N solution

FIG. VIII.


C.C. VS. TIME
100 gm. NaCl / liter
0.15 cu. ft. O2 / hr.
CORROSION CURRENT (MILLIAMPERES)
3.0
2.0
1.5
0
10
20
30
40
50
TIME (MINUTES)
RUN 2
RUN 4
RUN 1
RUN 3

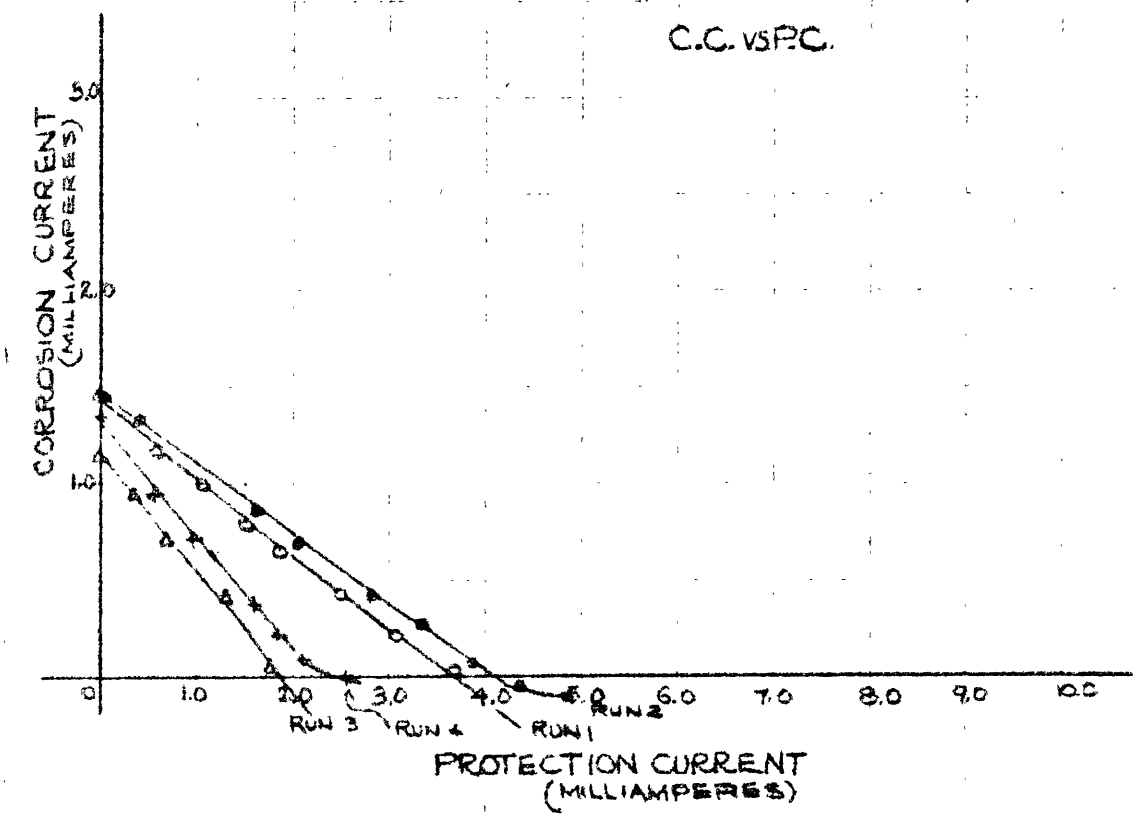
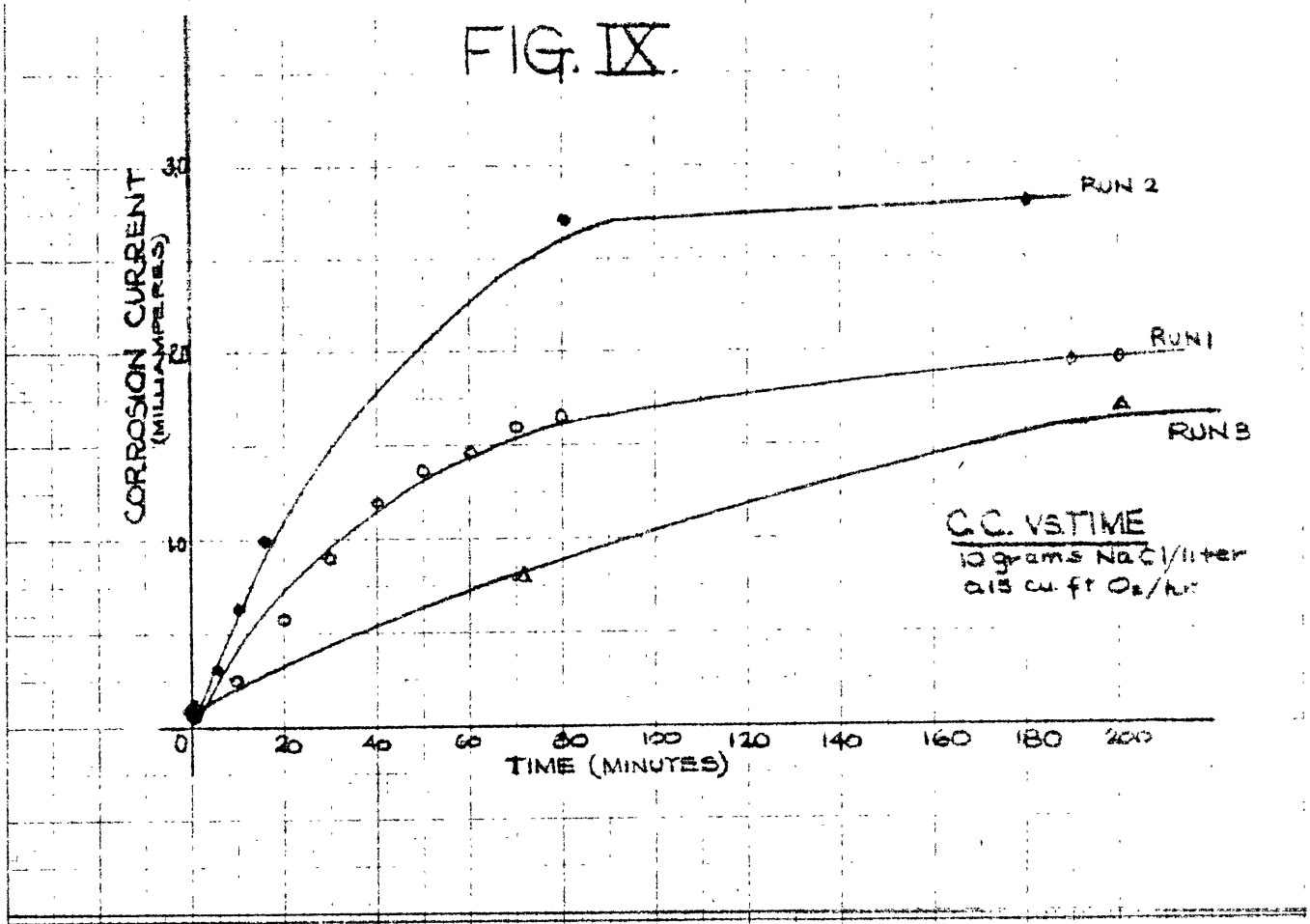
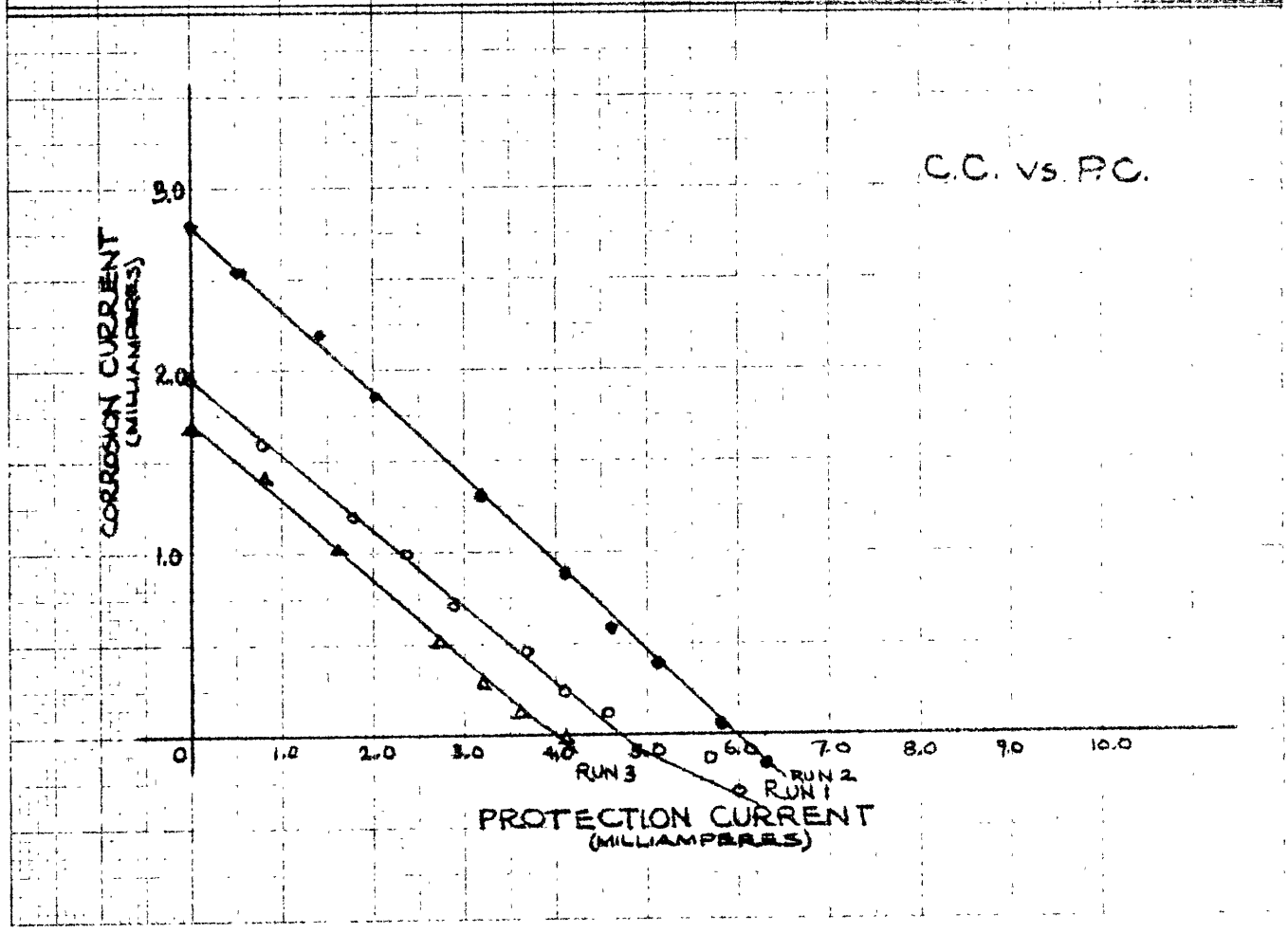

C.C. VS P.C.
CORROSION CURRENT (MILLIAMPERES)
3.0
2.0
1.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
RUN 3
RUN 4
RUN 1
RUN 2
PROTECTION CURRENT (MILLIAMPERES)

FIG. IX.


CORROSION CURRENT (MILLIAMPERES)
30
20
10
0
20
40
60
80
100
120
140
160
180
200
TIME (MINUTES)
RUN 2
RUN 1
RUN 3
C.C. VS. TIME
10 grams NaCl/liter
.015 cu. ft O2/hr


C.C. vs. P.C.
CORROSION CURRENT (MILLIAMPERES)
3.0
2.0
1.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
RUN 3
RUN 2
RUN 1
PROTECTION CURRENT (MILLIAMPERES)

of potassium chloride. They, of course, did not do any cathodic protection measurements, but a plot of corrosion current vs time is indicated to be duplicable. The dilute solution is a better solvent for oxygen also.

The corrosion current was allowed to come to equilibrium before cathodic protection measurements were made. Results were not duplicable, values of protection current varying as much as 50%. It must be remembered that in the dilute solution the IR drop is not negligible as the resistance of such a solution is comparatively high. The discussion in the introduction on cathodic protection concerned itself with solutions of no resistance, but the application to solutions of high resistance follows easily.

6. It was apparent from all the above results that conditions were not duplicable in the cell setup. Evidently the path of the ascending oxygen stream cannot be reproduced in different runs. The rate of oxygen diffusion through the solution must vary, and the rate of dissolution of oxygen at the solution surface must change. In essence, the geometry of the system is too critical to obtain duplicable results.

It was decided, however, to make several runs in hydrogen sulfide solution; even if actual quantitative results could not be obtained trends would be shown. 50 parts per million of hydrogen sulfide were used in a salt concentration of 10 grams/liter. Hoar, Britton, and Evans (11) found that

stimulation by hydrogen sulfide in 0.1N potassium chloride begins at about 5 parts per million and reaches an asymptote at about 10 parts per million.

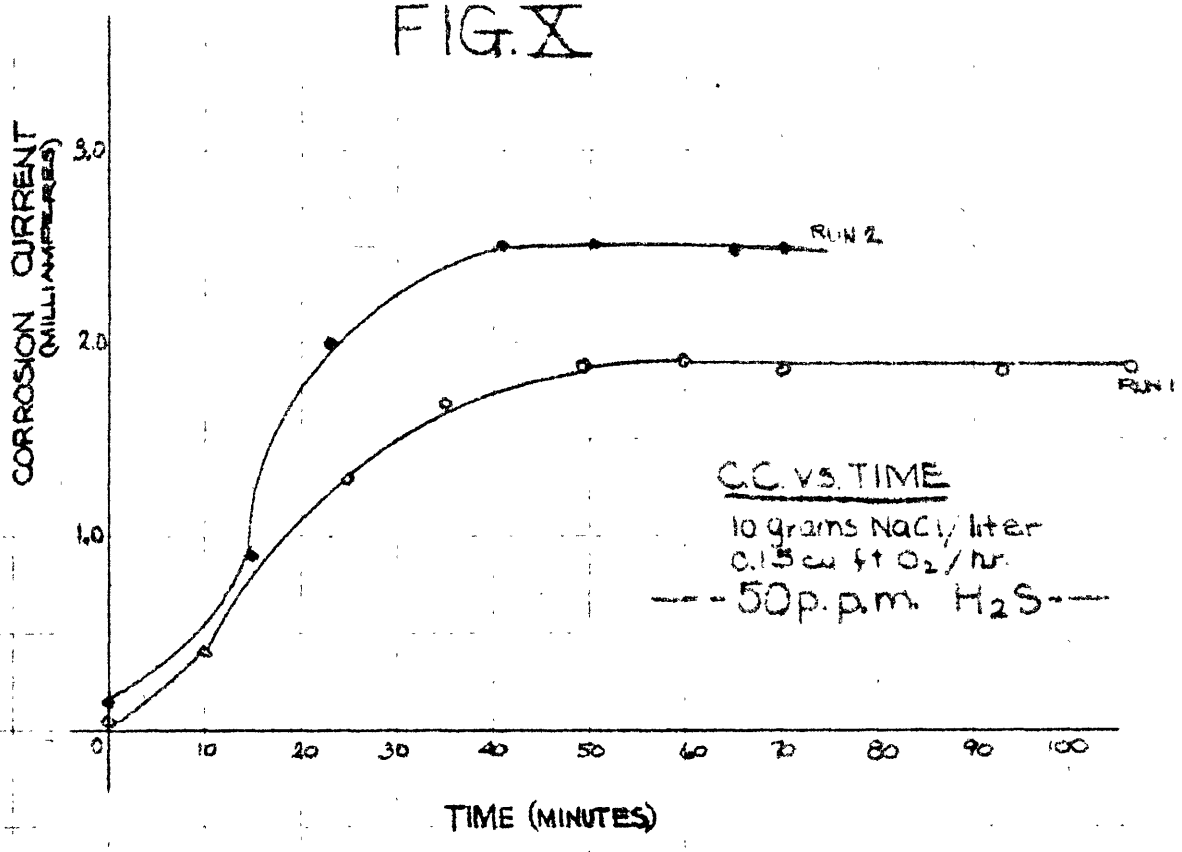
Results show no duplication (Fig. X) and also the astounding fact that the order of magnitude of corrosion currents is the same as runs without hydrogen sulfide. Hoar, Britton, and Evans (11) found in a similar run with a similar aeration cell that dissolved sulfide increases the corrosion current about five times. The hydrogen sulfide was added in the mol ratio of two parts of hydrochloric acid to one part of sodium sulfide. This result led to the study of the mechanism of hydrogen sulfide corrosion.

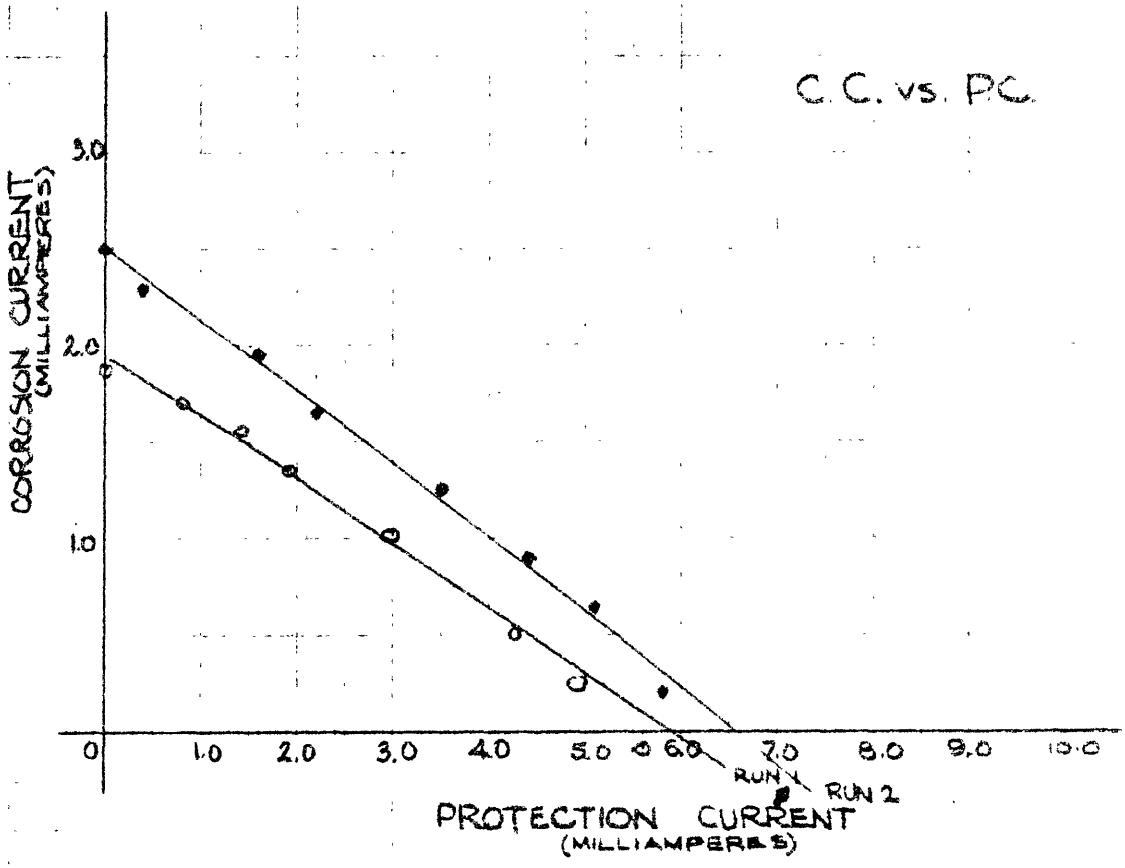
At the end of the run the electrodes were both black with ferrous and ferric sulfide precipitates. The fact that the cathode was black led one to believe that there was a great amount of local action. Using 1" x 1/4" electrodes (horizontal), in an effort to keep down local action by using smaller areas, did not yield any better results.

II. Mechanism of hydrogen sulfide corrosion

A. Using a 1" x 1/4" cathode area and a 1" x 3" anode area in a solution of 50 parts per million hydrogen sulfide (10 grams/liter sodium chloride), the equilibrium current was 0.53 milliamperes. Suddenly switching in a cathode area of 4" x 1-1/2" to replace the small area increased the

FIG. X


CORROSION CURRENT (MILLIAMPERES)
3.0
2.0
1.0
0
10
20
30
40
50
60
70
80
90
100
TIME (MINUTES)
RUN 2
RUN 1
C.C. vs. TIME
10 grams NaCl / liter
0.15 cu ft O_2 / hr.
--- 50 p.p.m. H_2S ---


C. C. vs. P.C.
CORROSION CURRENT (MILLIAMPERES)
3.0
2.0
1.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
RUN 1
RUN 2
PROTECTION CURRENT (MILLIAMPERES)

current to 1.90 milli-amperes immediately. Thus for an increase of cathode area of 24 times, the current increased less than 4 times. This indicated that in the above solution the cell was substantially under anodic control.

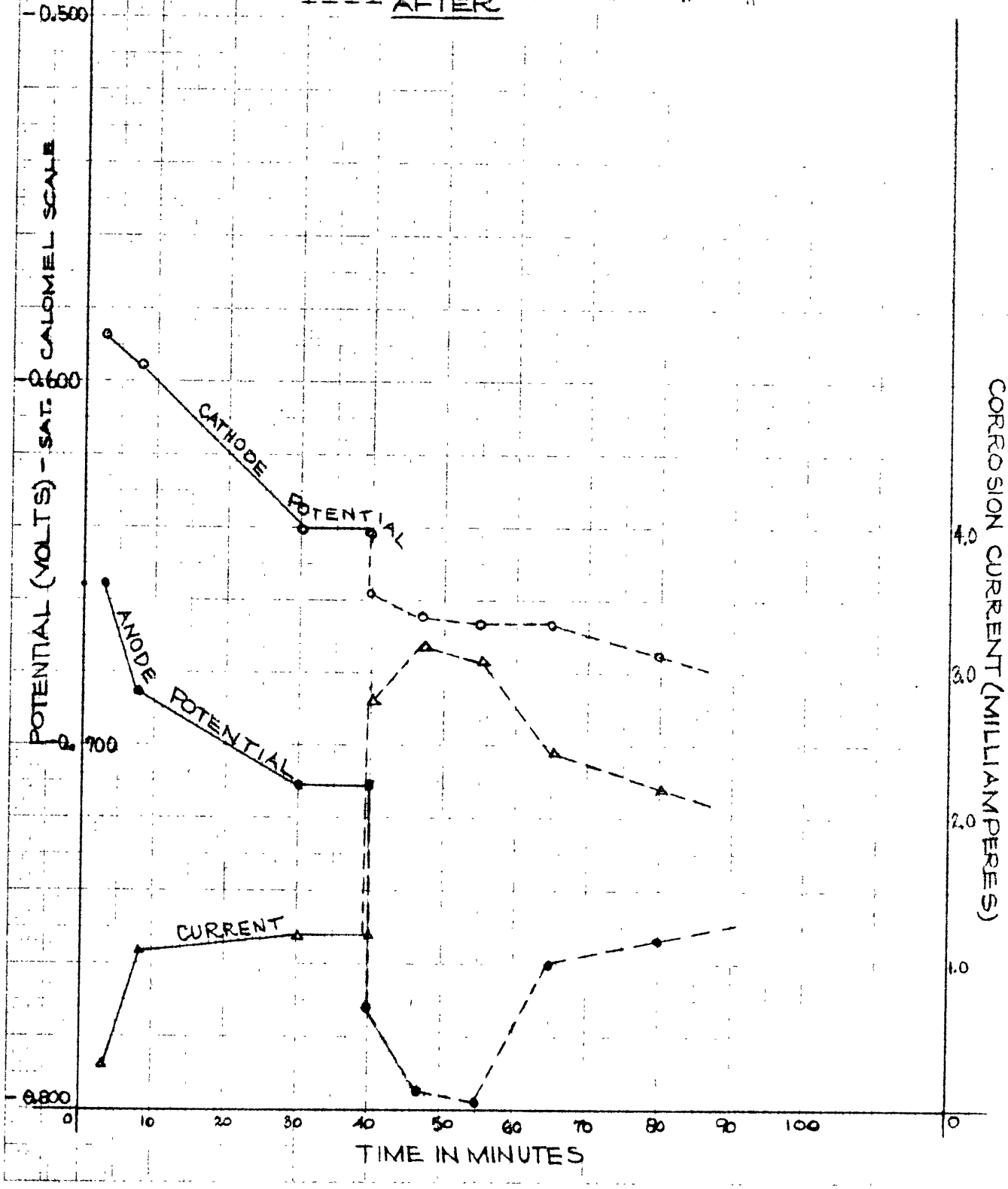
B. The results using hydrogen sulfide discussed under cathodic protection investigations showed that the corrosion current was not stimulated by hydrogen sulfide - the equilibrium currents with or without hydrogen sulfide being approximately the same. Some of the hydrogen sulfide may have been blown out by the oxygen bubbling into the solution, but the small amount of hydrogen sulfide (50 parts per million) is very soluble in the solution. At any rate, it was odd that there was no acceleration of the corrosion current.

Using an electrolyte of 10 grams/liter, 1" x 3" totally immersed electrodes, and an oxygen rate of 0.15 cu.ft/hr., the corrosion current reached an equilibrium value of 1.20 milliamperes. (See Fig. XII.) Both the anode and cathode potentials become more anodic with time levelling out when the current reached its equilibrium value; the difference between increased, of course proportionately to the current. On addition of hydrogen sulfide to the anode compartment the current surged upwards immediately to 2.80 milliamperes. (An arbitrary amount of hydrogen sulfide was added equivalent to 50 parts per million based on the weight of the entire electrolyte. A very slight excess of sodium sulfide

FIG. XII

ELECTRODE POTENTIALS (SAT. CALOMEL SCALE)
AND CORROSION CURRENT
VS
TIME

——— BEFORE H_2S ADDED TO ANODE COMPARTMENT
- - - - AFTER " " " "



over the 2:1 mol ratio quantity of hydrochloric acid was used to avoid the effects of "free" acid.) The cathode potential was depressed slightly and the anode potential depressed greatly. As time went on the current rose to 3.20 milliamperes as the anode potential was depressed even more; then the current began to drop off slowly as the anode potential became more cathodic. This latter change was due to the hydrogen sulfide or its ionization products seeping through the porous thimble to the cathode compartment.

The hydrogen sulfide very definitely stimulates the anodic reaction. The anode was covered with a black layer of ferrous sulfide which left a black stain after removal by rubbing. The ferrous sulfide is not protective, and since its formation completely breaks down the oxide and chloride films on the steel, the anode reaction is furthered. Hoar, Britton, and Evans found that the iron sulfide film is much less protective than the usual oxide film (13). The precipitation of the sulfide ion around the anode lowers the total ferrous ion concentration which will depress the potential. Calculations show, assuming that the hydrogen sulfide is present as H_2S, HS^-, and $S^=$, and that all these molecules and ion remain in the anode compartment, that the anode potential should be depressed to approximately -1.2 volts. The calculation was made from solubility product

and ionization constant data and is shown in the computations in the Appendix. The anode potential is depressed to approximately -0.8 volts, which appears to indicate that the anode is not acting like a pure anode -- that there is some local action present on it. The experimental work was repeated several times with only current measurement and twice with current and potential measurements.

With the identical setup, a run was made adding hydrogen sulfide to the cathode compartment. Before it was added, it was noted that the corrosion current reached an asymptote at 0.80 milliamperes, principally through the depression of the anode potential. See Fig. XIII. On the addition of the sulfide (same amount as before) to the cathode compartment, the current dropped immediately to 0.30 milliamperes. The cathode potential was very greatly depressed, while the anode potential only very slightly. As time increased both potentials were depressed, the cathode greater than the anode, so that at one point the cell even reversed itself. Fig. XIII should be consulted.

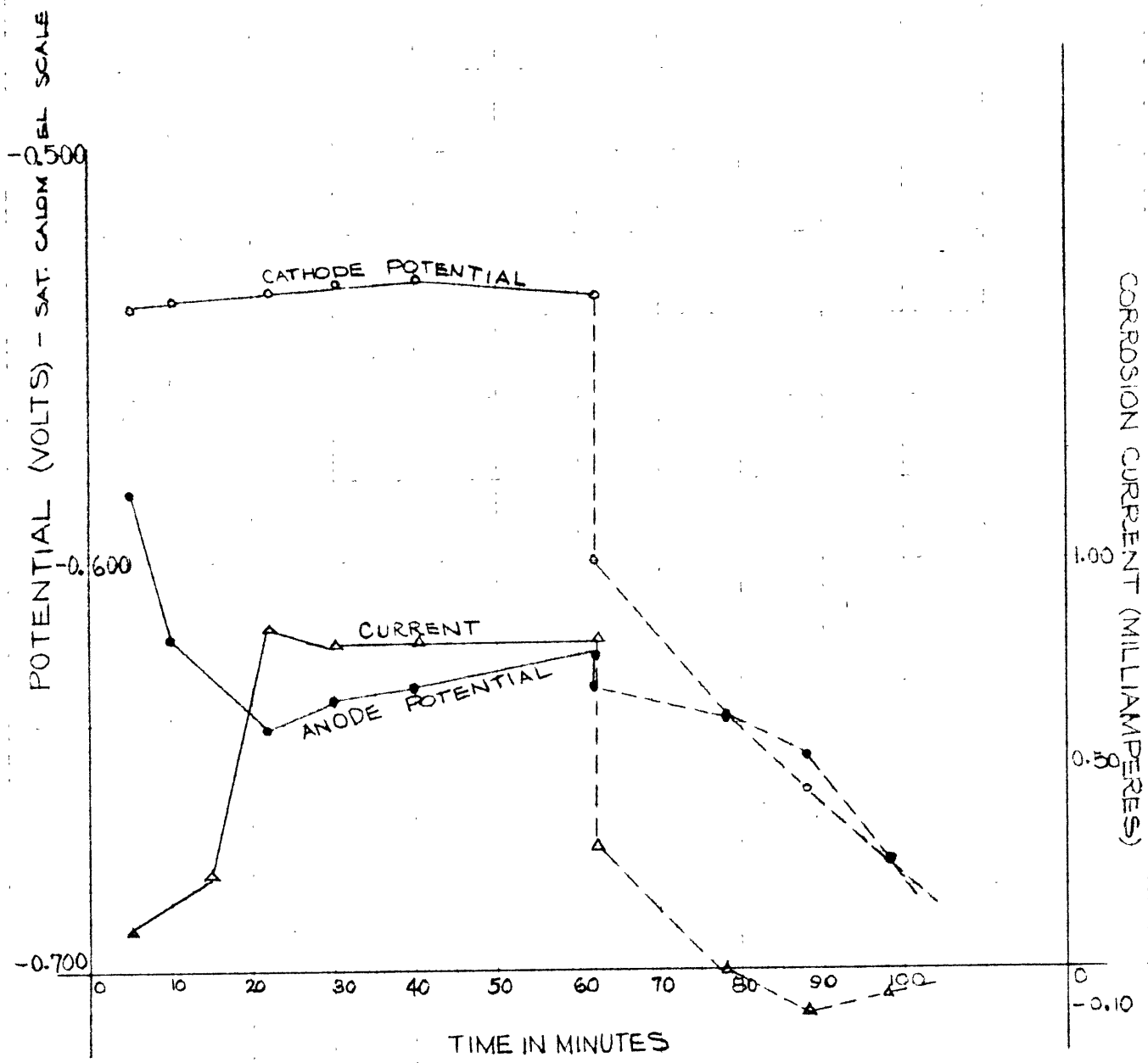
It was very difficult finding an explanation for the observations. It was felt that perhaps the solution contained colloidal sulfur that carried a positive charge -- this might be attracted to the cathode where it could form a protective film. The solution had the cloudiness of

FIG. XIII.

ELECTRODE POTENTIALS (SAT. CALOMEL SCALE) AND CORROSION CURRENT VS. TIME

——— BEFORE H_2S ADDED TO CATHODE COMPARTMENT

- - - - AFTER " " " " "



SJR

colloidal sulfur at the end of the run, as did the solutions at the end of all hydrogen sulfide runs. A black coating of the iron oxides covered all of the cathode. Microscopic observation of the solution by Dr. Hauser showed it to contain colloidal sulfur, but electrolysis of the solution between platinum electrodes showed it to be charged negatively. This showed that the sulfur was not attracted to the cathode. The presence of the black iron sulfides on the cathode surface indicated that the cathode was not acting as a pure cathode, and that local action was present. Perhaps a concentration of ferrous ion existed around the cathode and the sulfide removed some of it as precipitate; similarly the protective oxide film may have been replaced with a non-protective iron sulfide layer, thus stimulating the cathode anodically and making the cathode potential more anodic.

However, it is quite evident that the cathode is, in spite of the local action, primarily a cathode, and a reason must be found to account for the potential depression and the drop in current. The simplest explanation might be found by consideration of the cathodic reaction:

$$H^+ \rightarrow \underset{\text{atom}}{H} \rightarrow \underset{\text{molecule}}{1/2\ H_2}$$

$$1/2\ H_2 + 1/4\ O_2 = 1/2\ H_2O$$

The precipitation of some sulfide either from local action or direct attack might shield the dissolved oxygen

from the hydrogen and prevent the removal of the hydrogen as water. This would cause the accumulation of hydrogen and by the mass action law would retard the cathodic reaction. In essence the sulfide precipitate might be protective at the cathode.

It is seen that, as the hydrogen sulfide depresses the anode potential when added to the anode compartment and depresses the cathode potential when added to the cathode compartment, the difference in potentials when the hydrogen sulfide was added to the electrolyte (in both compartments) was approximately the same as when no hydrogen sulfide was added.

.....

The results of the cathodic protection work show that the method used was not a good one and must be modified if it is to be used at all. Modification would include using smaller specimens so that they can not only be ground with fine emergy, but polished on cloth polishing wheels with fine abrasives. This would cut down local action to as much a minimum as is possible to obtain. Also a method of aeration to yield duplicable results must be found.

The use of smaller specimens with subsequent careful polishing is also recommended for the hydrogen sulfide experiments. Repetition of the experiments done -- especially the addition of hydrogen sulfide to the cathode compartment -- is also suggested, as the results herein obtained indicate that hydrogen sulfide does not appreciably accelerate corrosion of steel in salt solutions.

CONCLUSIONS

The "scratch" method did not provide a suitable differential aeration cell to produce duplicable results for cathodic protection experiments.

The "porous membrane" type of differential aeration cell failed to provide duplicable results although the position of the bubbles, the degree of aeration, the concentration of the electrolyte, totally and partially immersed electrodes, and other variables were investigated. This was due primarily to some local action on the cathode surface, and inability to duplicate the oxygen diffusion rate to the cathode. The latter was in turn due to failure to keep constant one or several of the following factors:

a) The geometrical arrangement of the cell

b) The rate of dissolution of oxygen at the solution surface

c) Agitation

Hydrogen sulfide stimulates the anode reaction mainly through the precipitation of iron as the iron sulfides which are non-protective; this interferes with the films which normally protect the steel.

Hydrogen sulfide retards the cathode reaction. The reason for this is not actually known by the author. The

colloidal sulfur present in solution from the oxidation of hydrogen sulfide was negatively charged, and could not be attracted to the cathode to form a protective film. It is possible that some iron sulfide precipitated by local action at the cathode might act protectively at the cathode shielding the cathode from oxygen, resulting in oxygen starvation there.

The cell, containing 50 parts per million hydrogen sulfide in 10 grams NaCl/liter is substantially under anodic control.

The hydrogen sulfide by depressing both the anode and cathode potential did not accelerate the overall corrosion current. This is opposed to the general view held that hydrogen sulfide does accelerate electrochemical corrosion. It is possible that the method or apparatus is at fault.

RECOMMENDATIONS

The results of the cathodic protection work show that the method used was not successful, and must be modified if it is to be used at all. Modification would include using smaller specimens so that they can not only be ground with fine emery but polished on cloth polishing wheel with fine abrasives as well. This would keep local action down to as much a minimum as is possible to obtain. Also a method of aeration to yield duplicable results must be found.

The use of smaller specimens with subsequent careful polishing is also recommended for the hydrogen sulfide experiments. Repetition of the experiments done on the mechanism of hydrogen sulfide corrosion -- especially the addition of hydrogen sulfide to the cathode compartment -- is also suggested as the results herein obtained indicate that hydrogen sulfide does not appreciably accelerate the corrosion of steel in salt solutions.

A P P E N D I X

I. COMPUTATIONS

Calculation of anode potential immediately after addition of hydrogen sulfide to anode compartment.

$$Na_2S + 2HCl = 2NaCl + H_2S$$

Assumptions: That no hydrogen sulfide or ions produced therefrom leave porous thimble (which is logical as we are considering instant after addition).

That the anode acts as a pure anode and there are no local cells on anode.

Volume of porous thimble $= \frac{\pi(4.3)^2}{4} = 174$ cc.

0.400 grams $Na_2S \cdot 9H_2O$ added. $\therefore$ $\frac{0.400}{Na_2S \cdot 9H_2O \text{ sulfide added}} = 0.00167$ mols

$0.00167 \left(\frac{1000}{174}\right) = \underline{0.0096}$ mols $\underline{\text{sulfur}}$/liter added

$$H_2S = H^+ + HS^-, \quad HS^- = S^= + H^+$$

$$K_1 = \frac{(H^+)(HS^-)}{(H_2S)} = 0.91 \times 10^{-7} \quad \underline{\text{Equation 1}}$$

$$K_2 = \frac{(H^+)(S^=)}{(HS^-)} = 1.2 \times 10^{-15} \quad \underline{\text{Equation 2}}$$

Hydrogen balance $(HS^-) + 2(H_2S) + H^+ = 0.0172$ mols/liter

$\underline{\text{Equation 3}}$

$\frac{30 \text{ cc} \times 0.1N}{1000 \times 174} = 0.0172$ mols HCl added/liter

Sulfur balance: $(HS^-) + (H_2S) + (S^=) = .0096$

Equation 4

$K_3 = (Fe^{++})(S^=) = 3.8 \times 10^{-20}$ Equation 5

Ionation constant and solubility products from Creighton's Electrochemistry.

5 equations, 5 unknowns

Solving $(H_2S) = .0085$ mols/liter

$(HS^-) = .0004$ mols liter

$(S^=) = .0007$ mols liter

$(Fe^{++}) = 5.42 \times 10^{-17}$ mols/liter

$$E = E_o - \frac{0.059}{2} \log Q$$

where Q is product of the activities of the products divided by the product of the activities of the reactants.

$$E = -.44 - \frac{0.059}{2} \times 17.74 = -0.963 \text{ volts}$$

Creighton gives -0.280 for the saturated calomel half-cell.

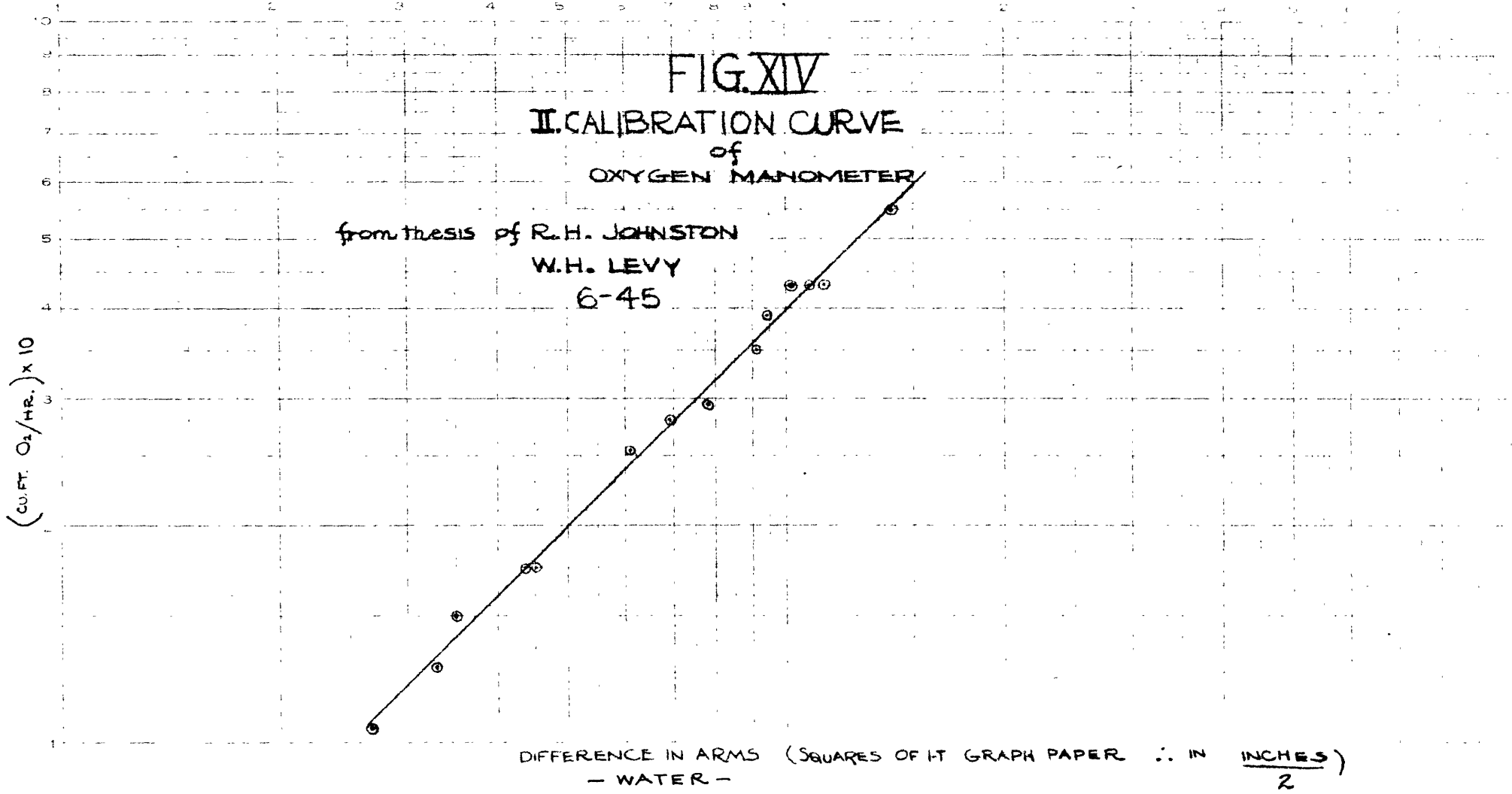
∴ E based on saturated calomel cell = -.963 - .280=-1.243

Comparing this to -0.800 from Fig. XII shows anode is not acting as pure anode.

FIG. XIV

II. CALIBRATION CURVE of OXYGEN MANOMETER

from thesis of R. H. JOHNSTON
W. H. LEVY
6-45



sjn

III. ORIGINAL DATA

C.C.=Corrosion Current in Milliamperes

T.= Time in Minutes

P.C.= Protection Current in Milliamperes

Data for Fig. IV: 100 grams/liter NaCl-O_2 rate: 3.1 cu.ft/hr.-Bubbles hitting cathode.

Run 1:

T.	C .C.	C.C.	P.C.
0^+	1.15	2.30	0.0
5	1.80	2.10	0.5
10	2.05	1.60	1.5
16	2.20	1.20	2.1
21	2.25	0.90	2.8
36	2.30	0.55	3.8
		0.40	4.4
		0.25	4.8
		-0.25	7.1

Run 2:

T.	C.C.	C.C.	P.C.
0^+	0.60	2.30	0.0
6	1.95	2.05	0.85
12	2.40	1.70	1.8
18	2.35	1.35	2.8
23	2.30	1.10	3.7
26	2.30	0.70	5.0
		0.35	6.1
		0.10	7.0

Run 3:

T.	C.C.		C.C.	P.C.
0^+	0.7		2.75	0
6	2.35		2.2	1.40
13	2.62		2.0	2.15
19	2.75		1.5	3.70
	2.75	Constant	1.3	4.40
			0.8	6.20
			0.5	7.40
			0.25	8.60
			0.0	9.70

Run 4:

T.	C.C.		C.C.	P.C.
0^+	0.40		2.3	0
13	2.10		1.85	1.35
19	2.25		1.25	3.3
	2.3	Constant	0.9	4.3
			0.45	6.1
			0.2	7.3
			0.0	8.5

Data for Fig. V: 100 grams/liter NaCl - O_2 rate 3.1 cu.ft./hr.- Bubbles do not touch cathode.

Run 1:

T.	C.C.	C.C.	P.C.
0	0	1.22	0
3	0.60	1.1	0.80
6	1.05	1.0	1.40
9	1.25	0.83	2.10
13	1.25	0.40	3.40
17	1.22	0.15	4.30
		0.06	4.60
		-0.30	6.00

Run 2:

T.	C.C.	C.C.	P.C.
0	0.25	1.65	0
3	0.88	1.38	1.0
6	1.18	1.1	1.45
9	1.44	0.8	2.10
12	1.65	0.2	3.50
15	1.65	0.1	3.80
		0.03	4.00
		-0.42	6.10

Run 3:

T.	C.C.	C.C.	P.C.
0	0.45	2.5	0.0
7	2.0	2.0	1.5
9	2.15	1.1	3.4
12	2.40	0.65	4.4
15	2.50	0.0	6.0
20	2.50	-0.3	7.0

Run 4:

T.	C.C.	C.C.	P.C.
0	0.15	0.0	1.6
3	1.00	0.8	1.25
9	1.35	1.4	0.90
13	1.50	2.1	0.60
15	1.60	2.8	0.25
17	1.60	3.5	0.0
		4.3	-0.35

Run 5:

T.	C.C.	C.C.	P.C.
0	0.25	1.35	0.0
3	0.60	1.0	0.8
6	0.75	0.7	1.6
9	0.95	0.3	2.5
13	1.10	0.1	3.0
15	1.20		
18	1.25		
20	1.30		
25	1.35		

Run 6:

T.	C.C.	C.C.	P.C.
0	0.30	1.1	0
5	0.75	0.75	0.6
10	0.95	0.20	1.5
13	1.05	-0.10	2.0
15	1.10		
20	1.10		

Data for Fig. VI: 100 grams NaCl/liter - O_2 Rate: 3.1 cu.ft./hr. - Bubbler behind cathode.

Run 1:

T.	C.C.	C.C.	P.C.
0	0.20	0.83	0.0
5	0.67	0.74	0.55
8	0.74	0.58	1.05
10	0.77	0.39	1.60
12	0.80	0.19	2.25
15	0.82	0.11	2.65
17	0.84	0.03	2.90
20	0.84	-0.07	3.45

Run 2:

T.	C.C.	C.C.	P.C.
0	0.15	0.49	0.0
3	0.34	0.28	0.4
8	0.46	0.08	0.8
11	0.48	0.04	0.9
13	0.49	-0.08	1.2
		-0.24	2.7

Run 3:

T.	C.C.	C.C.	P.C.
0	0.25	2.1	0.0
6	1.14	1.75	0.8
15	2.10	1.5	1.5
20	2.10	1.15	2.1
		0.55	3.4
		0.40	3.7
		0.18	4.4
		0.05	4.9
		- 0.30	6.0

Data for Figure VII - 100 grams NaCl/liter - O_2 rate: 3.1 cu.ft./hr. - Bubbler midway between electrodes.- Totally immersed electrodes.

Run 1:

T.	C.C.	C.C.	P.C.
4	1.4	1.75	0.0
10	1.6	1.55	0.5
		1.40	0.8
14	1.7	1.10	1.4
		0.80	2.1
18	1.75	0.50	2.8
		0.25	3.4
		0.15	3.75
		0.00	4.4
		-0.10	4.9
		-0.30	6.1

Run 2:

T.	C.C.	C.C.	P.C.
3	1.7	2.7	0
5	2.0	2.3	0.80
9	2.3	1.60	2.10
12	2.6	0.90	3.40
15	2.7	0.50	4.30
20	2.75	0.25	4.80
		0.15	5.30
		0.00	6.00
		-0.20	7.10

Run 3:

T.	C.C.	C.C.	P.C.
5	1.0	1.85	0.0
9	1.45	1.70	0.5
12	1.60	1.40	1.0
15	1.70	1.10	1.8
18	1.80	0.60	2.8
20	1.85	0.50	3.0
		0.30	3.5
		0.17	3.9
		0.03	4.2
		-0.20	5.2

Run 4:

T.	C.C.	C.C.	P.C.
0	0.40	1.45	0.0
5	0.95	1.25	0.55
9	1.20	1.10	0.80
13	1.35	0.75	1.40
18	1.45	0.40	2.10
		0.25	2.30
		0.10	2.80

Data for Fig. VIII: 100 grams NaCl/liter - O_2 rate: 0.15 $\frac{cu.ft.}{hr.}$

- Bubbler midway - Electrodes completely immersed, etc.

Run 1:

T.	C.C.	C.C.	P.C.
2	0.40	1.45	0.0
5	0.54	1.40	0.15
9	0.73	1.31	0.32
15	0.93	1.19	0.60
20	1.00	1.00	1.05
26	1.11	0.80	1.52
30	1.15	0.66	1.85
35	1.23	0.57	2.10
40	1.29	0.44	2.50
45	1.36	0.21	3.05
50	1.41	0.14	3.37
		0.03	3.65

Run 2:

T.	C.C.	C.C.	P.C.
2	0.37	1.45	0.0
5	0.50	1.32	0.4
10	0.71	1.20	0.65
15	0.86	1.02	1.20
20	0.98	0.85	1.58
25	1.10	0.70	2.05
30	1.18	0.56	2.37
35	1.23	0.44	2.85
40	1.30	0.34	3.15
45	1.35	0.30	3.35
50	1.40	0.07	3.90
55	1.45	0.02	4.10
		-0.02	4.38
		-0.10	4.85

Run 3:

T.	C.C.	C.C.	P.C.
0	0.10	1.15	0.0
5	0.32	0.95	0.35
10	0.42	0.71	0.65
40	0.92	0.42	1.15
55	1.15	0.06	1.71

Run 4:

T.	C.C.		C.C.	P.C.
0	0.06		1.33	0.0
10	0.45		1.20	0.22
33	1.05		0.96	0.55
53	1.33	Constant	0.72	0.95
			0.38	1.60
			0.22	1.85
			0.11	2.10
			0.00	2.55

Data for Fig. IX: 10 grams NaCl/liter - O2 rate : 0.15 cu.ft./hr. Bubbler midway - Totally immersed electrodes, etc.

Run 1:

T.	C.C.	C.C.	P.C.
0.	0.06	1.92	0.0
10	0.25	1.85	0.3
20	0.59	1.65	0.8
30	0.90	1.19	1.8
40	1.20	0.98	2.4
50	1.37	0.72	2.9
61	1.46	0.46	3.7
70	1.60	0.25	4.1
80	1.65	0.15	4.55
190	1.95	-0.12	5.70
200	1.95	-0.30	6.00

Run 2:

T.	C.C.	C.C.	P.C.
0	0.06	2.80	0.0
5	0.31	2.55	0.5
10	0.64	2.20	1.4
15	1.00	1.85	2.0
80	2.70	1.30	3.2
180	2.80 Constant	0.88	4.1
		0.60	4.6
		0.40	5.1
		0.05	5.8
		-0.15	6.3

Run 3:

T.	C.C.	C.C.	P.C.
0	0.08	1.70	0.0
71	0.80	1.63	0.3
200	1.70	1.55	0.5
		1.42	0.8
		1.20	1.1
		1.02	1.6
		0.85	1.9
		0.50	2.7
		0.30	3.2
		0.15	3.6
		0.00	4.1

Data for Fig. X: 10 grams NaCl/liter - O_2 rate: 0.15 $\frac{\text{cu.ft.}}{\text{hr.}}$ -
50 PARTS PER MILLION H_2S ADDED-
Bubbler midway, etc.

Run 1:

T.	C.C.	C.C.	P.C.
0	0.05	1.85	0
10	0.40	1.70	0.8
25	1.30	1.55	1.4
35	1.68	1.35	1.9
49	1.85	1.00	3.0
60	1.85	0.50	4.3
71	1.78	0.25	4.9
80	1.85	- .10	5.6
93	1.85		
107	1.85		

Run 2:

T.	C.C.	C.C.	P.C.
0	0.15	2.50	0.0
15	0.90	2.30	0.4
23	2.00	1.95	1.6
41	2.50	1.65	2.2
50	2.50	1.25	3.5
65	2.45	0.90	4.4
70	2.48	0.65	5.1
		0.20	5.8
		-0.40	7.0

Data for run to determine whether cell is under anodic or cathodic control in hydrogen sulfide solution (50 parts per million).

T.	CC.	10 grams NaCl/liter O_2 rate: 0.15 cu.ft./hr. 50 p.p.m. H_2S
0	0.05	
10	0.19	
20	0.25	
60	0.53	
70	0.53	
80	0.53	

3" x 1" anode used. At end of 80 min. a 4" x 1-1/2" cathode switched in replacing a 1" x 1/4" cathode used up to 80 minutes. Current to 1.9 milliamperes immediately.

Data for FIG. XIII

T.	C.C.	CATHODE POTENTIAL	ANODE POTENTIAL
5	0.10	0.538	0.583
10	0.24	0.536	0.619
22	0.84	0.534	0.641
30	0.80	0.532	0.634
40	0.80	0.531	0.631
62	0.80	0.535	0.623
	0.30	0.600	0.631
H_2S ADDED TO CATHODE COMP.			
78	0.00	0.638	0.638
88	-0.10	0.656	0.648
98	-0.05	0.673	0.674

Data for FIG. XII

T.	C.C.	CATHODE POTENTIAL	ANODE POTENTIAL
3	0.30	0.587	0.657
8	1.10	0.595	0.685
30	1.20	0.641	0.711
40	1.20	0.642	0.711
H_2S ADDED TO ANODE COMP.			
47	3.20	0.664	0.795
55	3.10	0.666	0.798
65	2.45	0.666	0.760
80	2.20	0.675	0.754

OTHER data are available in RESEARCH NOTEBOOK.

IV BIBLIOGRAPHY AND FOOTNOTES

Britton, S.C., Hoar, T.P., and Evans, U.R.
"THE EFFECT OF HYDROGEN SULFIDE ON THE CORROSION OF IRON BY SALT SOLUTIONS" The Journal of the Iron and Steel Institute (England), 1932, No. II, pp. 365-373.

Brown, R.H., and Mears, R.B.
"A THEORY OF CATHODIC PROTECTION"
Transactions of the Electrochemical Society,
Vol. 74-1938, pp. 519-532.

Brown, R.H., and Mears, R.B.
"CATHODIC PROTECTION"
Transactions of the Electrochemical Society,
Vol. 81 - 1942, pp. 455-479.

Evans, U.R., Bannister, L.C., and Britton, S.C.
"THE VELOCITY OF CORROSION FROM THE ELECTROCHEMICAL STANDPOINT"
Proceedings of the Royal Society of London, Series A,
Vol. 131, 1931.

Gatty and Spooner
"ELECTRODE POTENTIAL BEHAVIOR OF CORRODING METALS IN AQUEOUS SOLUTIONS"
Great Britain-1938.

Hill, W.R., "LABORATORY TESTS OF CATHODIC PROTECTION OF STEEL IN VARIOUS CORROSIVE SOLUTIONS"
Petroleum Engineer, Sept. 1941, pp. 51-57.

Speller, F.N.
"CORROSION - CAUSES AND PREVENTION"
McGraw-Hill (N.Y. 1935), pp. 1-52, 171-172, 515-522.

FOOTNOTES

1. Speller, pp. 34,171.
2. Ibid., P. 171.
3. Watson, W.V., INTERNAL CORROSION AND DEPOSITS IN GAS MAINS, Gas Age - Record 54, pp. 557-560, 1924. - Cited in Speller, p. 172.
4. Britton, Hoar, and Evans.
5. Brown and Mears, THEORY OF CATHODIC PROTECTION.
6. Brown and Mears, CATHODIC PROTECTION, pp. 457-460.
7. Ibid, P. 455.
8. Article by Evans, cited in Speller, P. 44.
9. Gatty and Spooner, P.272.
10. Britton, Hoar, and Evans.
11. Ibid.
12. Ibid.
13. Ibid.