THE CORROSION OF STEEL IN SALINE
SOLUTIONS OF HYDROGEN SULFIDE

By

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Submitted in Partial Fulfillment of the

Requirements for the S.B. Degree

from the

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Signature of Author ....

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

Signature of Thesis Supervisor ....

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

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,

Signature redacted

Sanford J. Neuhaus

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

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SUMMARY

It was originally proposed to study the cathodic pro-
tection 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 electro-
lytes. 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 <u>hydrogen sulfide stimulates</u> 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 <u>cathode</u> reaction, in
considering the aerated iron plate as the <u>cathode</u>. 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 anodic control.

The hydrogen sulfide by depressing both 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 pro-
tection 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 poten-
tial 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 _current_
furnished from a source external to the specimen in question
until the cathode areas attain a potential equal to the
potential of the anode areas at zero current density. (Point

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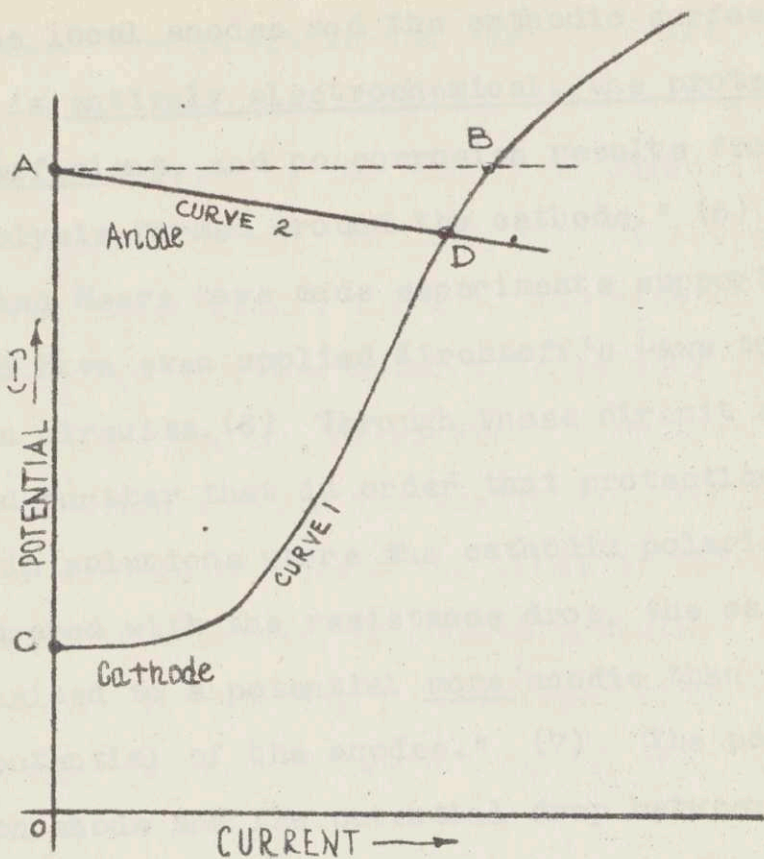
FIG. I.
POLARIZATION CURVES
(From Brown and Mears with some
omissions - footnote 5)

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 <u>entirely electrochemical, the protection is 100</u>
<u>per cent. efficient</u>, 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 <u>more</u> 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. <u>Differential Aeration Cells</u>

It has been shown, principally through the work of U.R.
Evans, that oxygen concentration cells are of primary im-
portance 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 differen-
tial aeration cell is an ideal method of obtaining corro-
sion 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

CATHODE   PROTECTION ANODE   LOCAL ANODE

FIG. II B

ELECTRICAL CIRCUIT — CATHODIC PROTECTION WORK
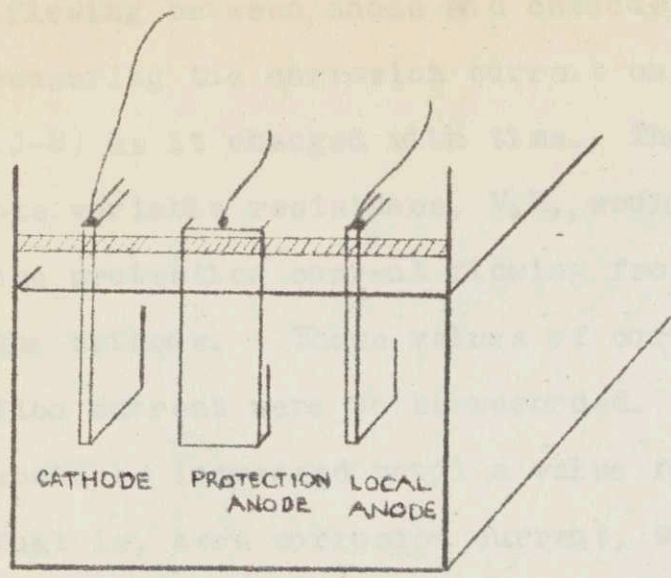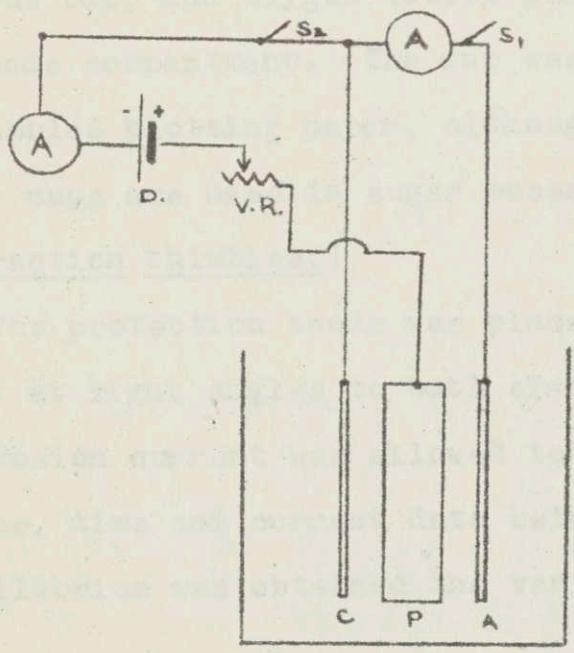
LEGEND

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

(flowing between anode and cathode) come to equilibrium and
measuring the corrosion current on an ammeter with S_1 (Fig.
closed
II-B) as it changed with time. Then S_2 would be closed and
the variable resistance, V.R., would be varied thus changing
the protection current flowing from the protection anode to
the cathode. These values of corrosion current and protec-
tion 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 compart-
ment 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.
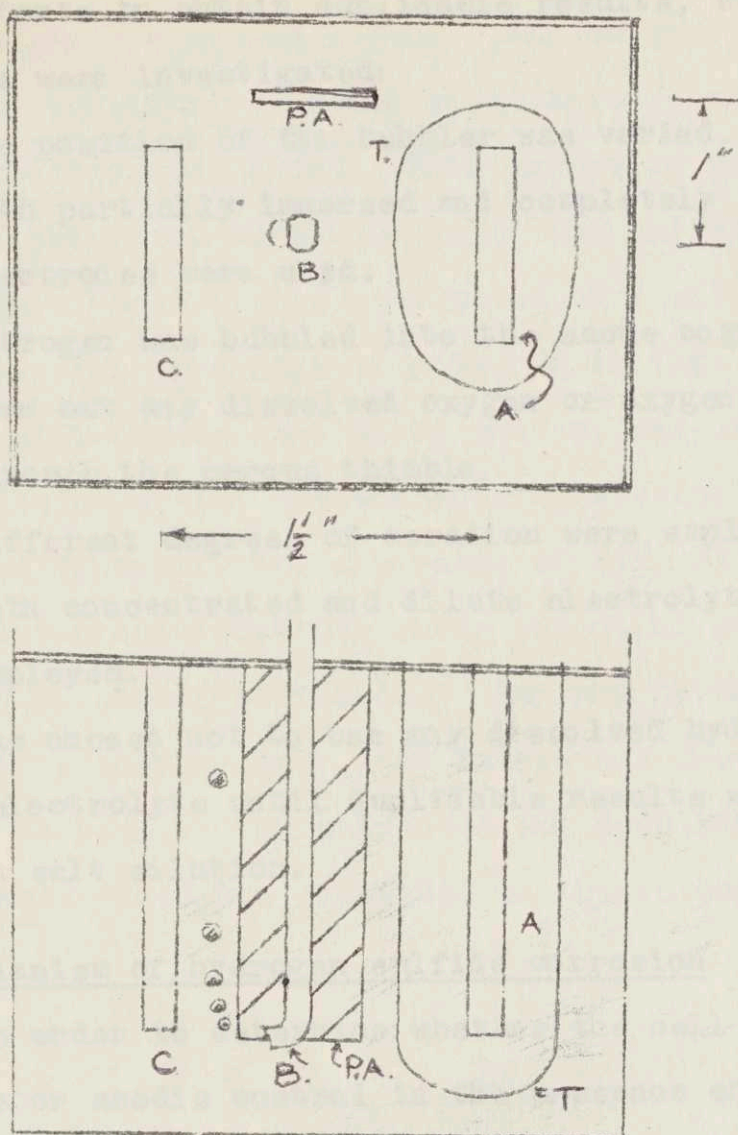
DIFFERENTIAL AERATION CELL

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 ^{F}ig. 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 ^{F}ig. XI shows the potentiometer connected for anode potential measurements (although S_2 should be closed). ^{F}or 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.

F I G. XI

ELECTRICAL CIRCUIT FOR POTENTIAL MEASUREMENTS

~ LEGEND ~

A - MILLIAMMETER
C - CATHODE
L.A. - ANODE
H - CALOMEL (SAT.) HALF-CELL
S₁ S₂ - SWITCHES
S.B. - SAT KCl-AGAR
         SALT BRIDGE
P. - POTENTIOMETER
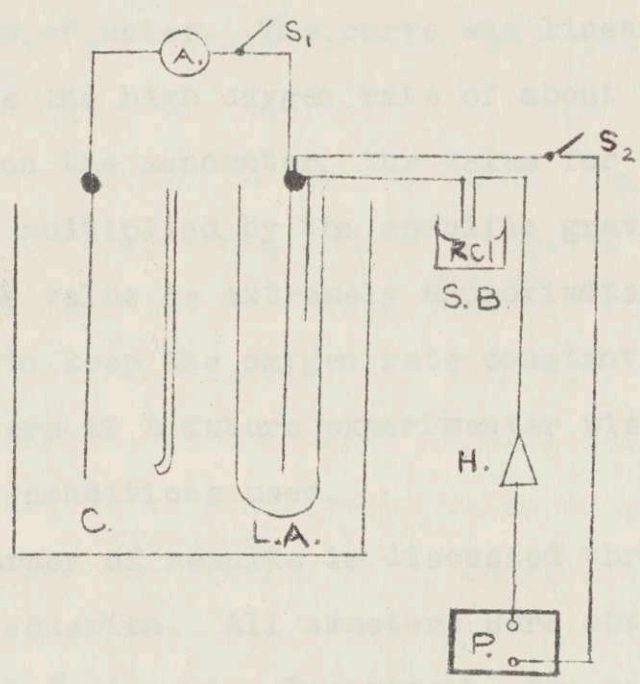
RESULTS AND DISCUSSION OF RESULTS

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. <u>Cathodic Protection Investigations</u>

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 im-
mersed, 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 un-

controllable. 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
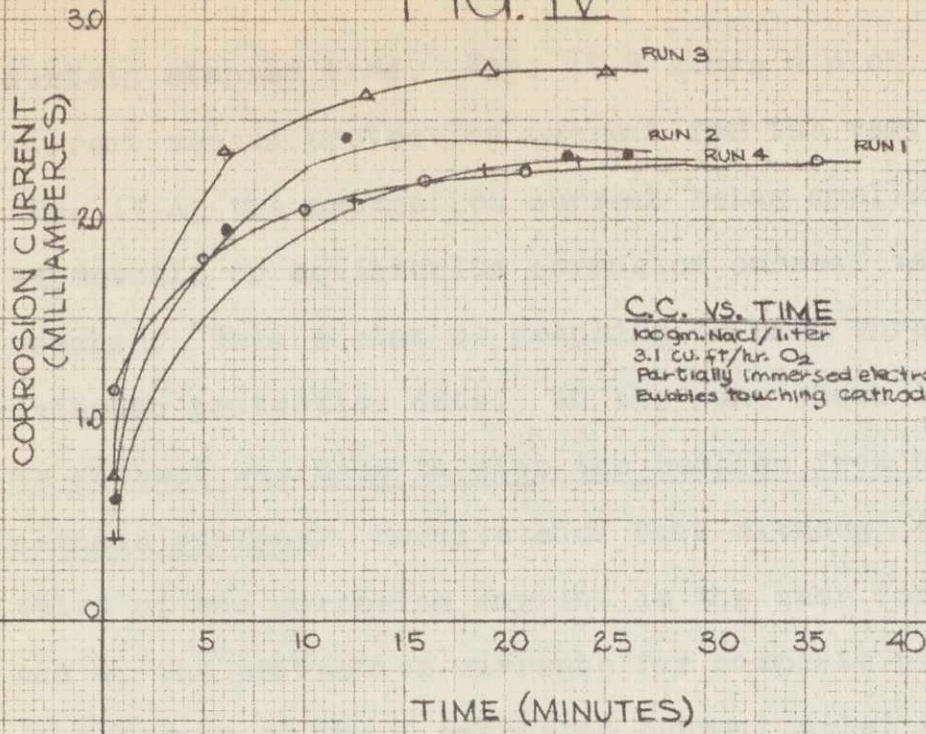
FIG. IV

C.C. VS. TIME
100 gm. NaCl/liter
3.1 cu. ft/hr. O₂
Partially immersed electrodes
Bubbles touching cathode
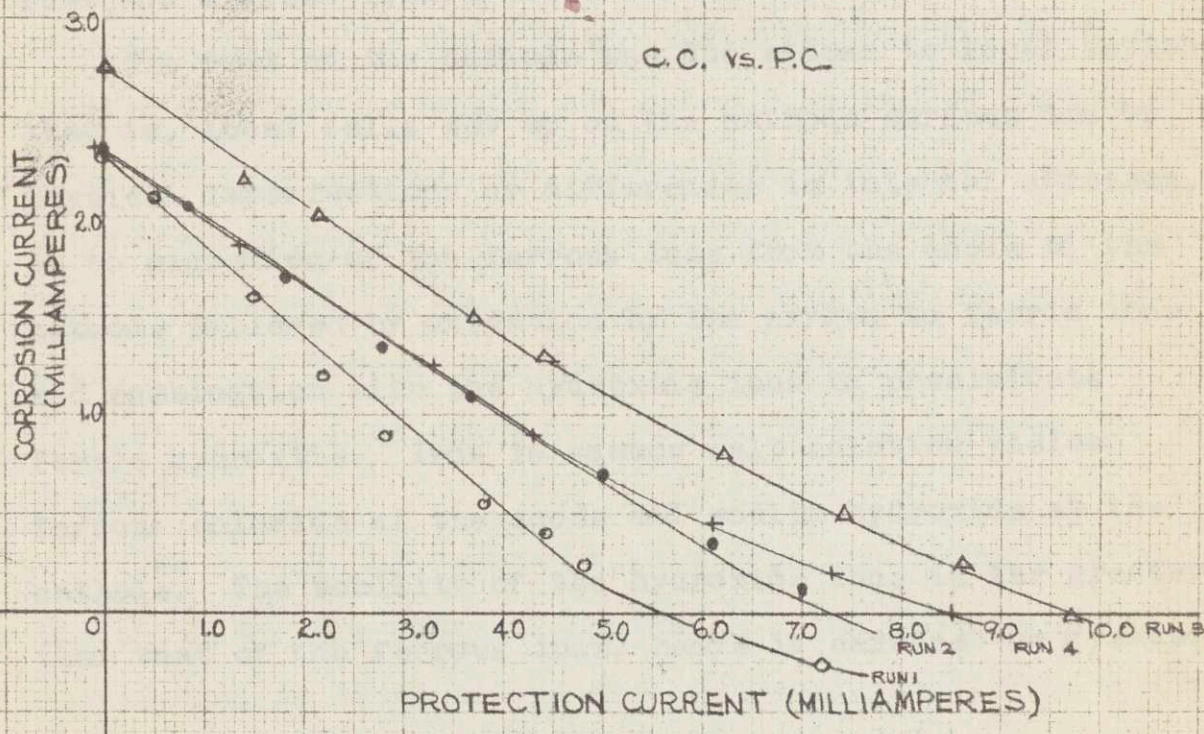
C.C. VS. P.C.

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.

FIG. VI.

C.C. VS. TIME
Conditions same
as Fig III, except
bubbler behind
cathode.

CORROSION CURRENT
(MILLIAMPERES)

RUN 3

RUN 1

RUN 2

TIME (MINUTES)

C.C. VS. P.C.

CORROSION CURRENT
(MILLIAMPERES)

RUN 2
RUN 1
RUN 3

PROTECTION CURRENT
(MILLIAMPERES)
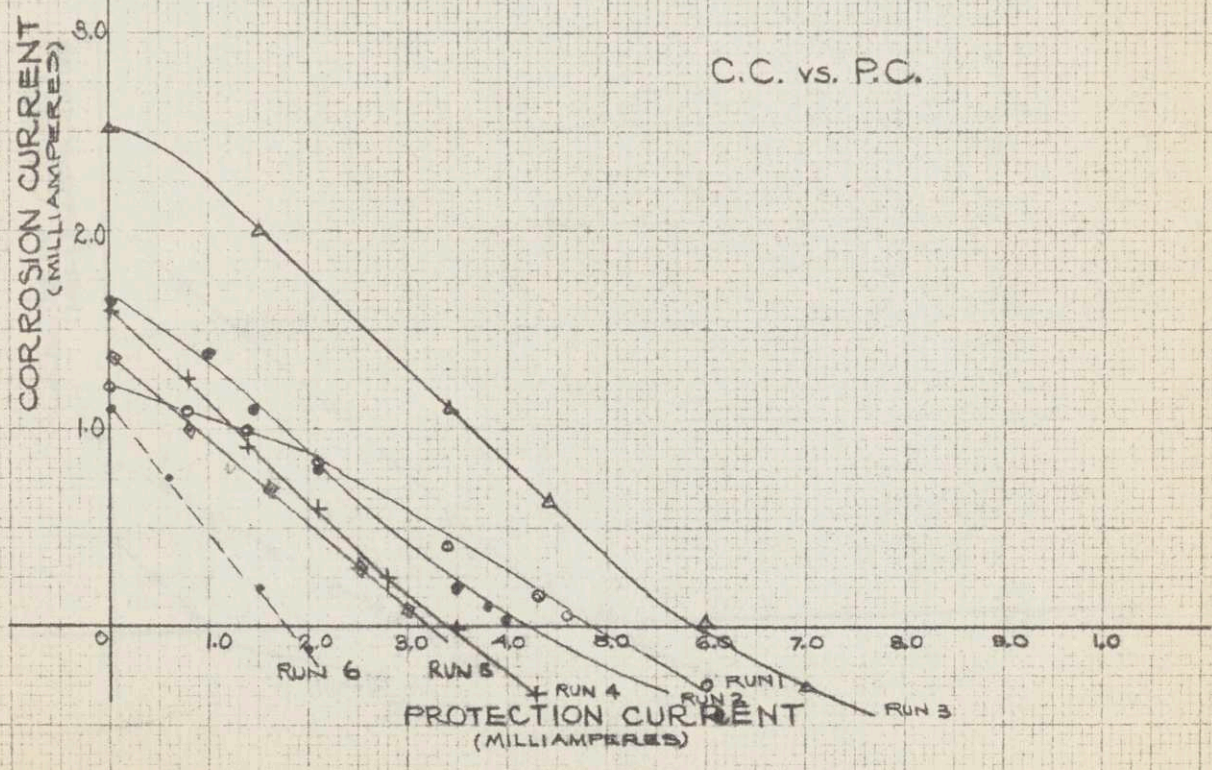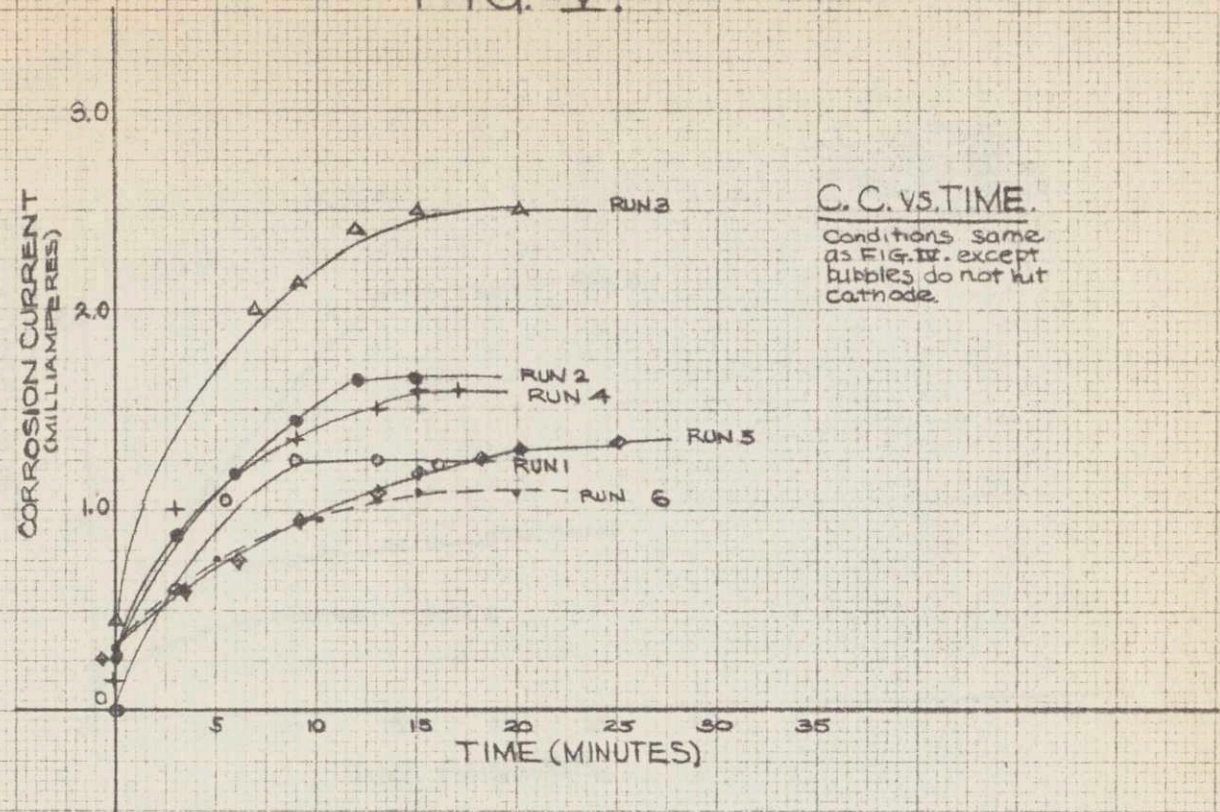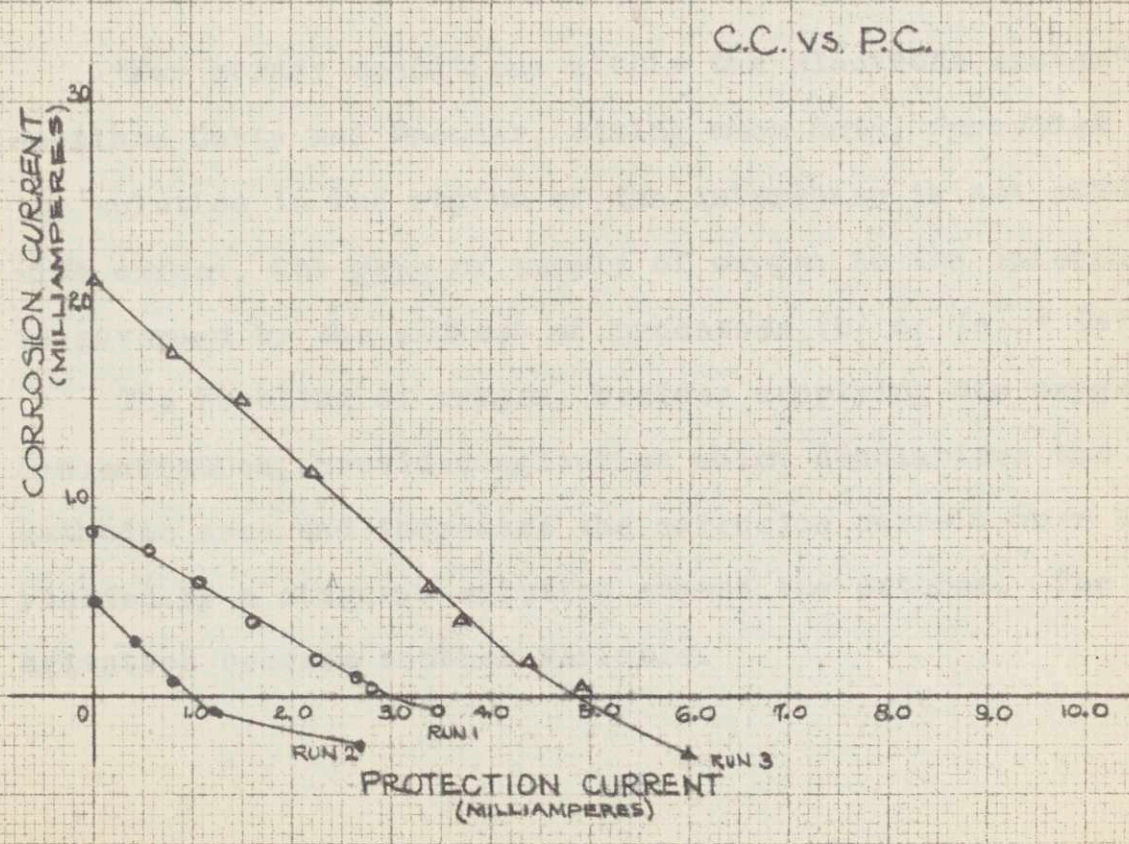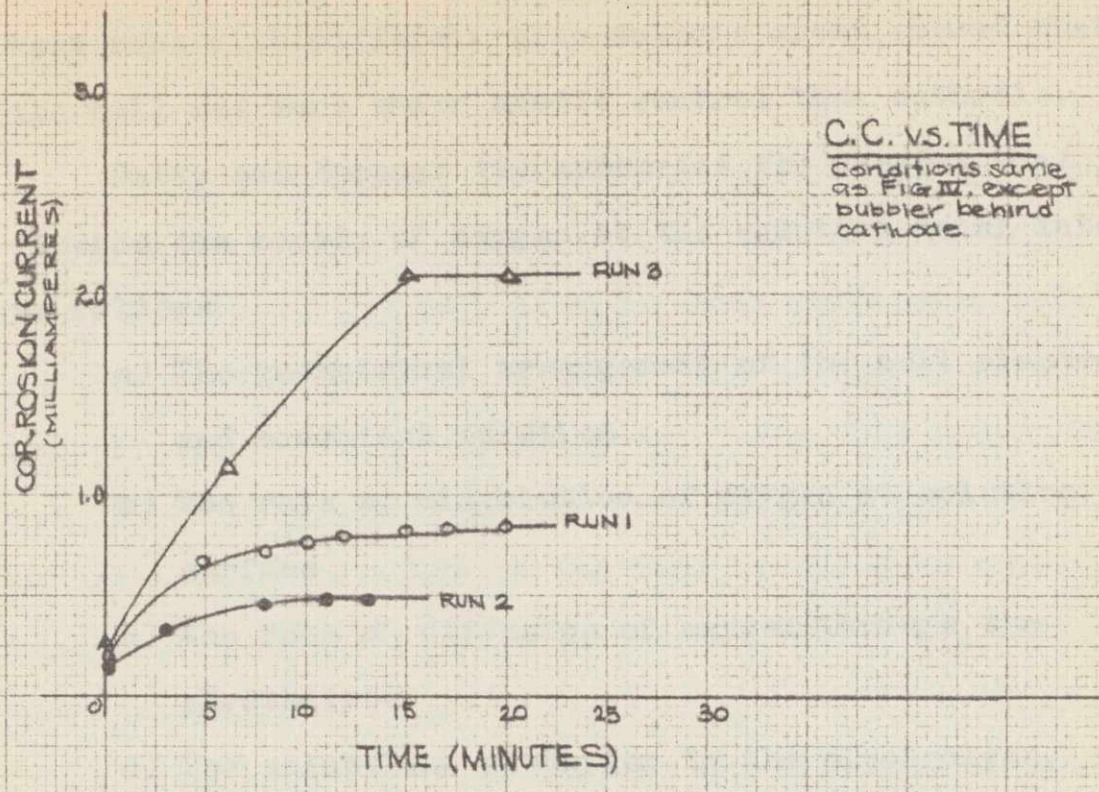
test runs with different size cathode areas showed that
the cell was more under anodic control than cathodic.

Gatty and Spooner (9) summarize the factors that in-
fluence 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.

RUN 2
RUN 3
RUN 1
RUN 4

CORROSION CURRENT (MILLIAMPERES)

TIME (MINUTES)

C.C. VS. P.C.

CORROSION CURRENT (MILLIAMPERES)

RUN 4   RUN 3   RUN 1   RUN 2

PROTECTION CURRENT
(MILLIAMPERES)
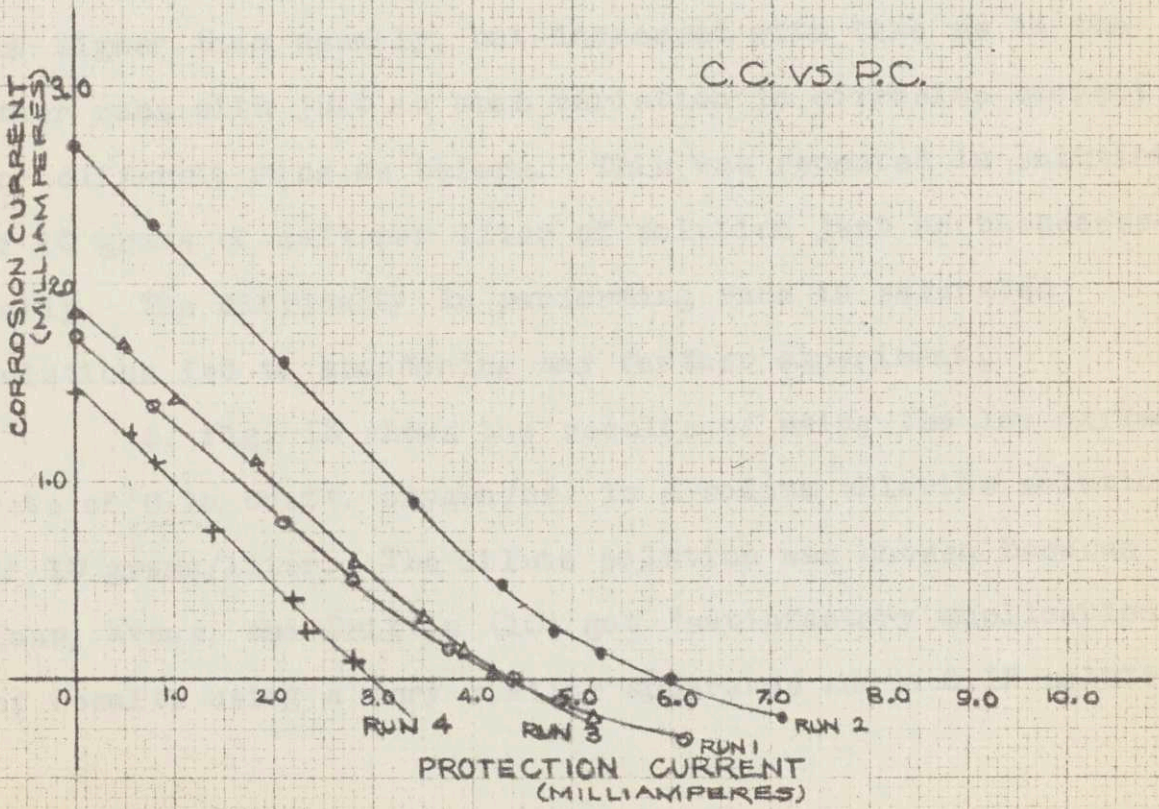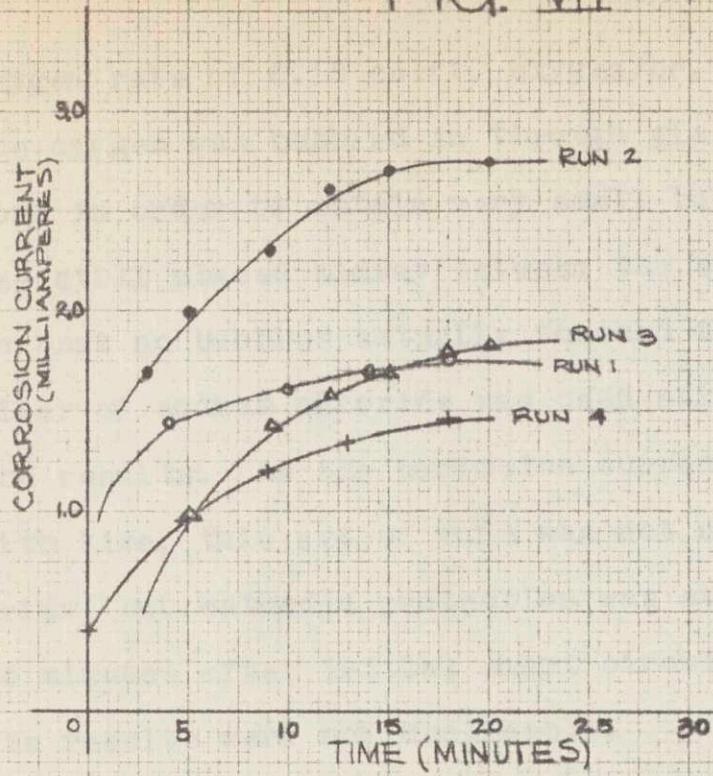
oxygen rate of 0.15 cu.ft. oxygen/hr. was substituted and
the oxygen was bubbled in through glass tubing with capillary
bore in order to obtain very small bubbles. The bubbler
was still placed midway between the electrodes and arranged
so that no bubbles actually touched the cathode. 100 grams/
liter 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 equili-
brium, 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 be-
come 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 unsuccess-
fully. 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)

RUN 2
RUN 1 RUN 4
RUN 3

TIME (MINUTES)

C.C. VS. P.C.

CORROSION CURRENT (MILLIAMPERES)

RUN 3   RUN 4   RUN 1   RUN 2

PROTECTION CURRENT
(MILLIAMPERES)

SJN

FIG. IX.

C.C. VS TIME
10 grams NaCl/liter
0.15 cu. ft. O₂/hr.

C.C. VS. P.C.
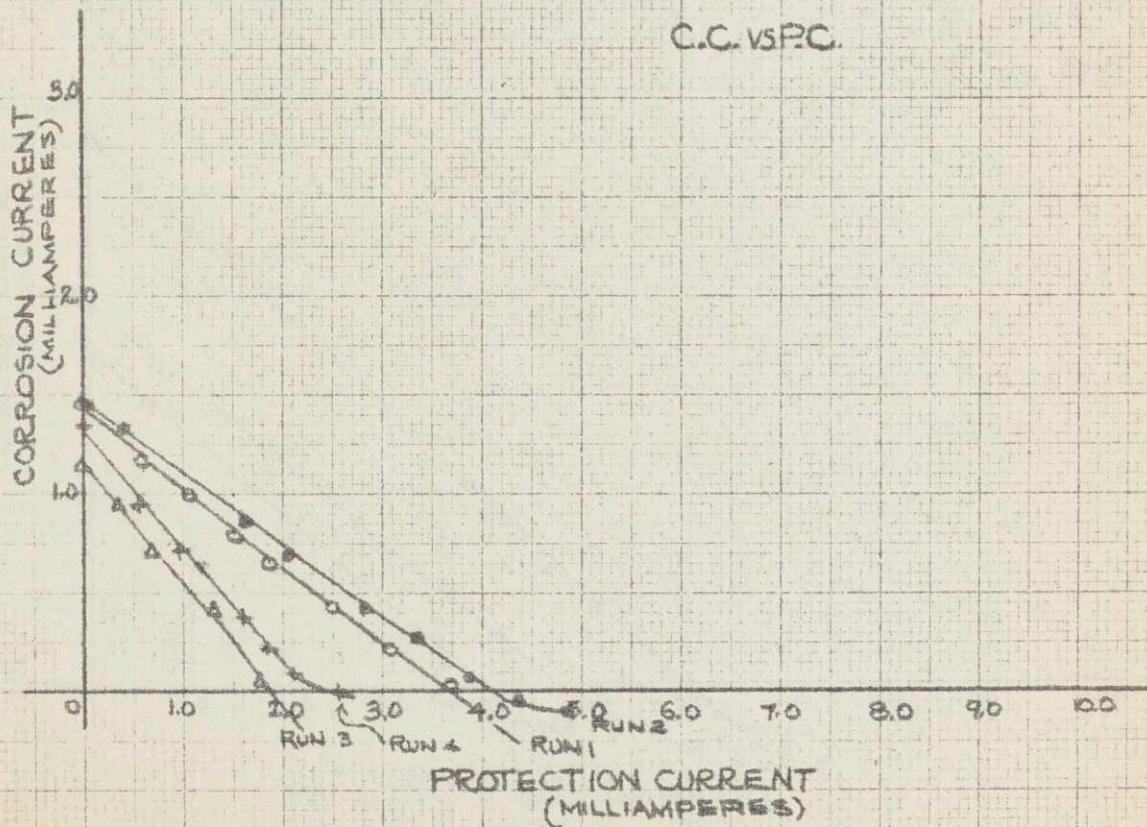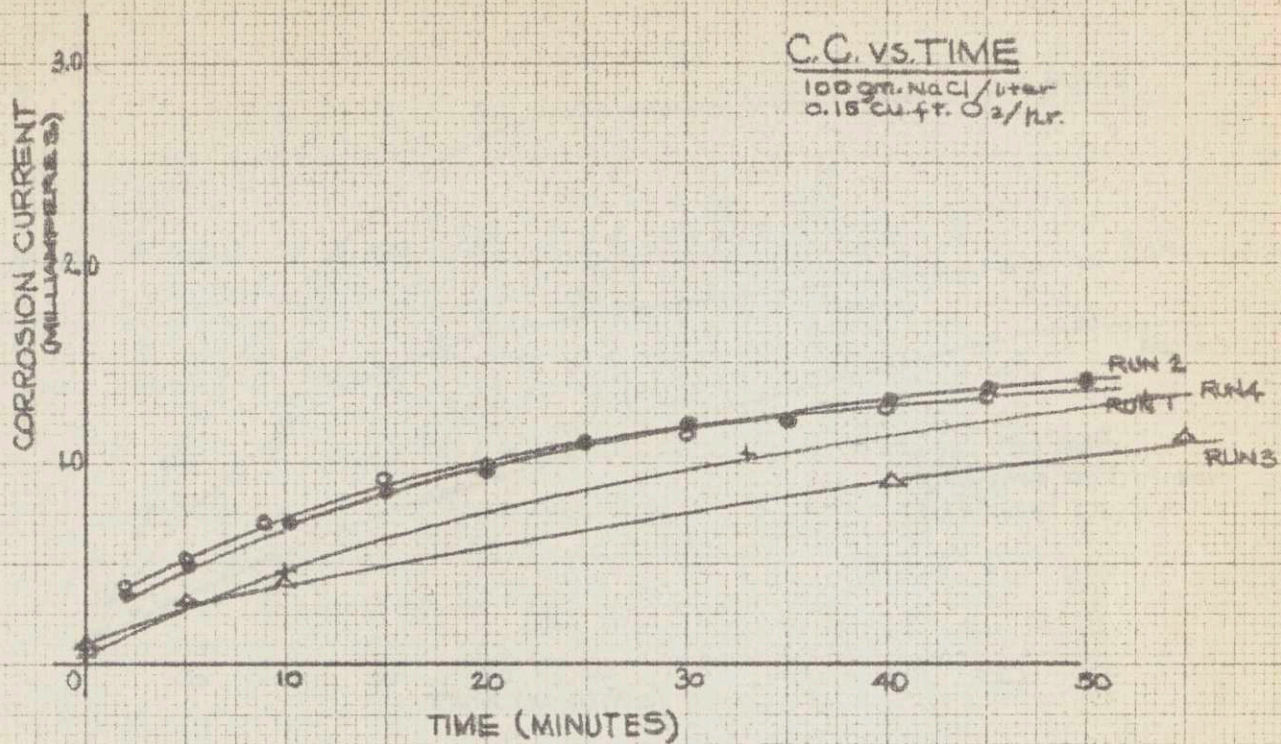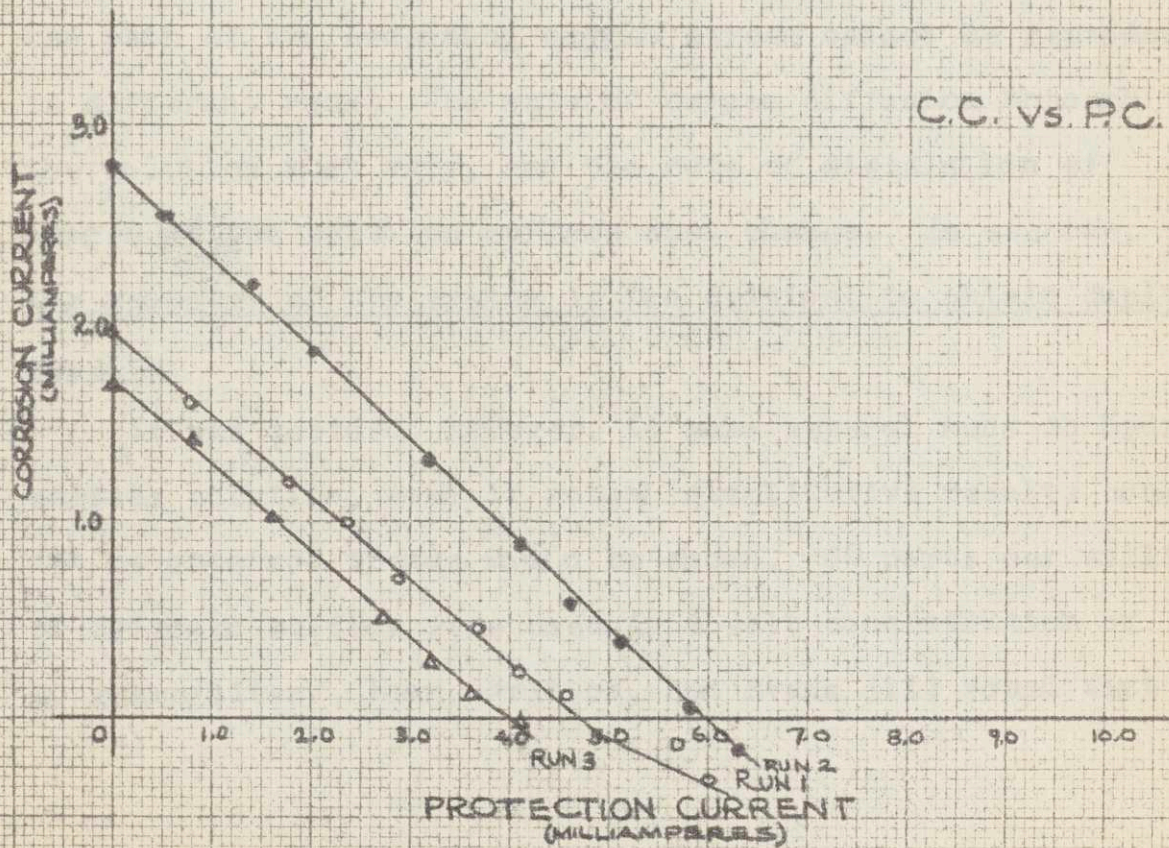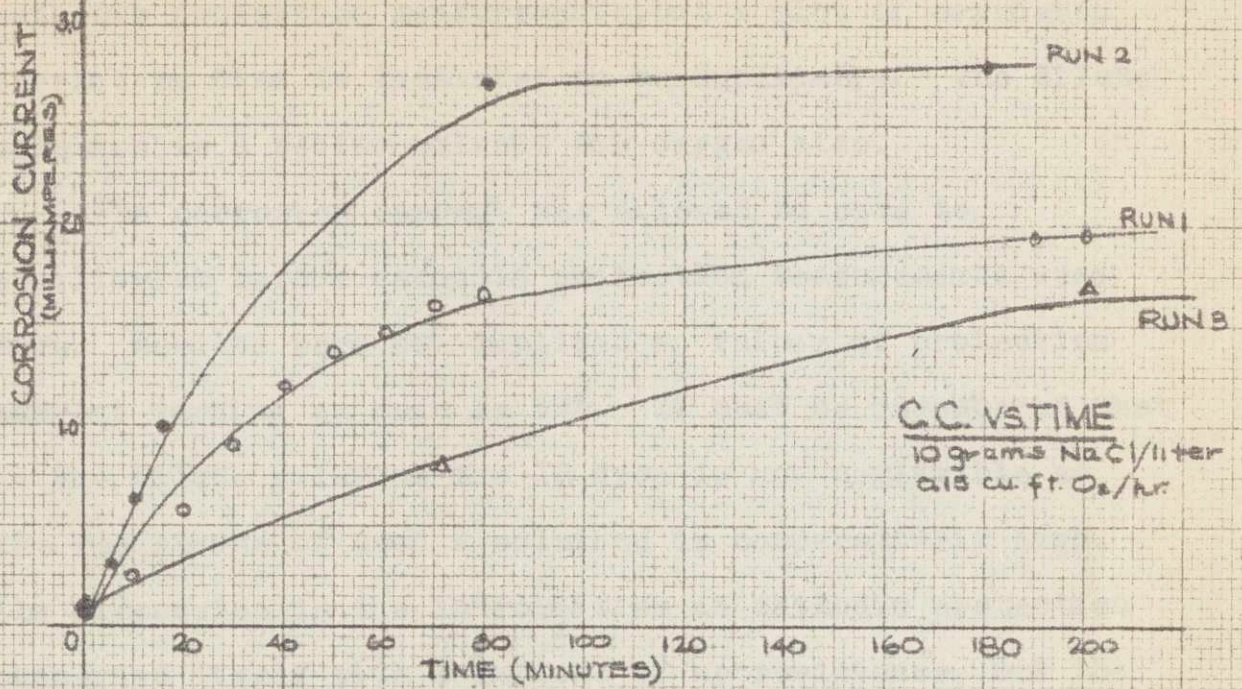
of potassium chloride. They, of course, did not do any

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 <u>that the order of magnitude of corrosion currents is the same as runs without hydrogen sulfide.</u> 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. <u>Mechanism of hydrogen sulfide corrosion</u>

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

C.C. VS. TIME
10 grams NaCl/liter
0.15 cu. ft O₂/hr.
-- 50 p.p.m. H₂S --
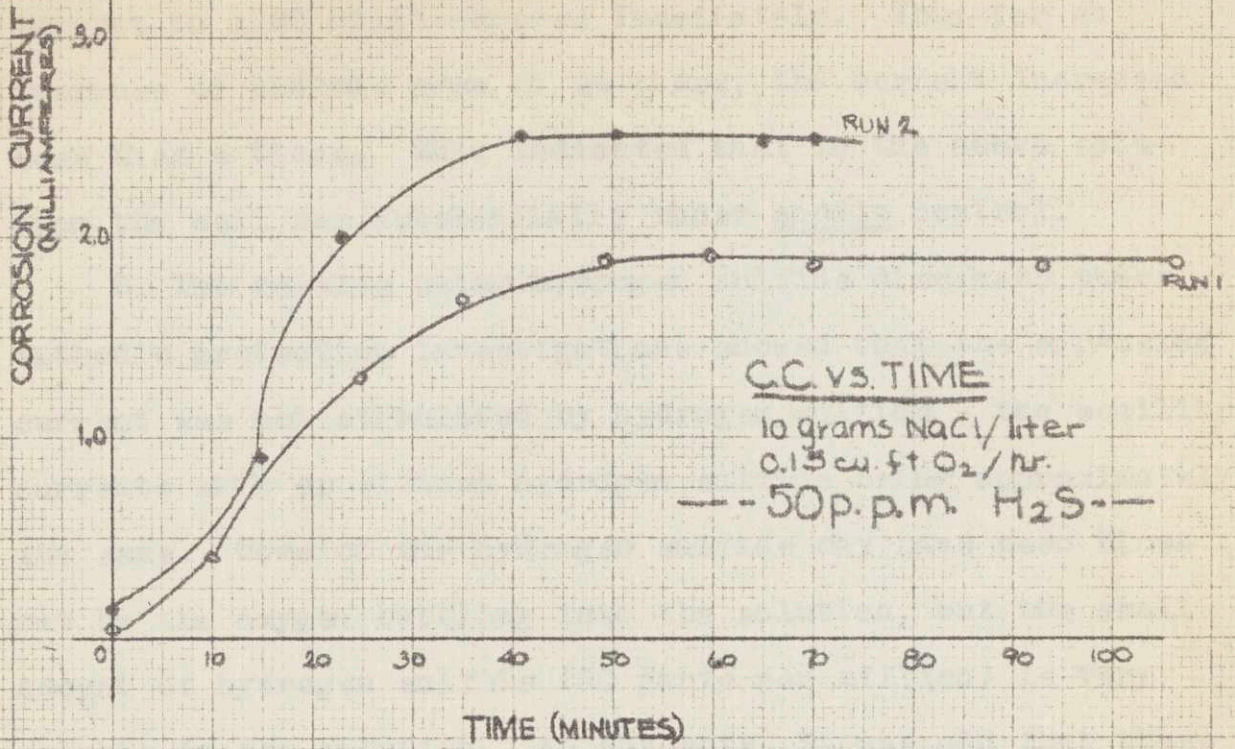
C.C. VS. P.C.
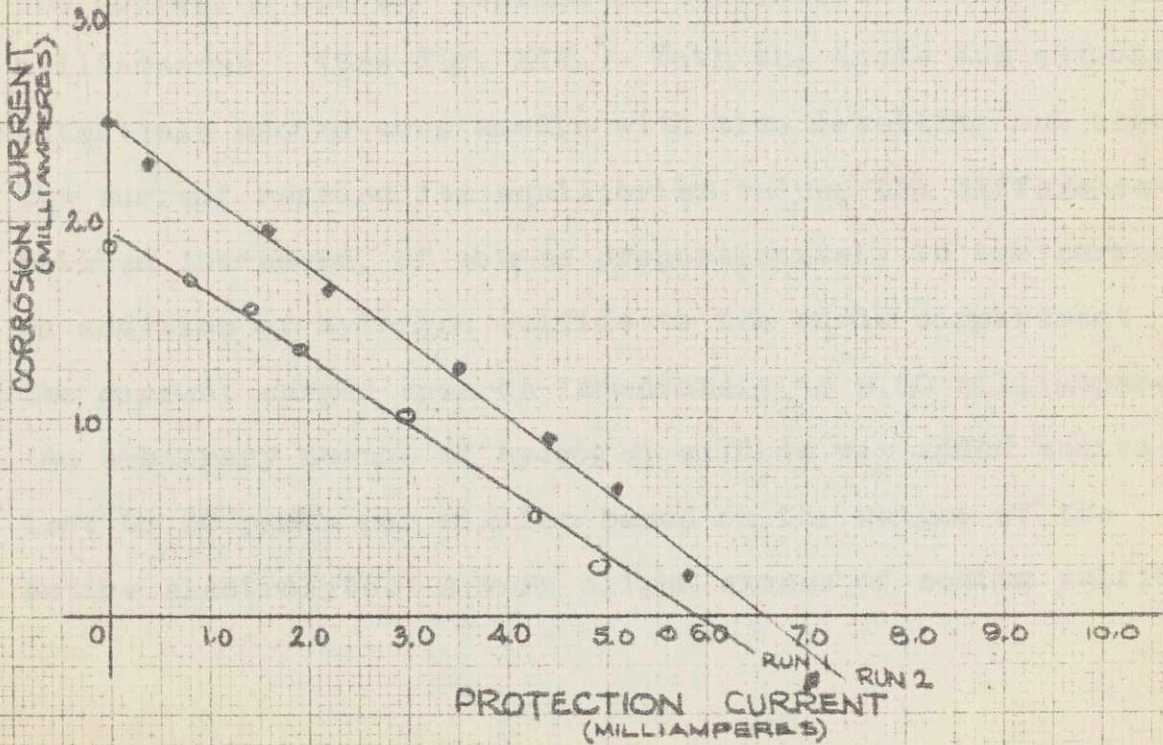
current to 1.90 milli-amperes immediately. Thus for an increase of cathode area of 24 times, the current increased less than 4 times. This indicated that in the above solution the cell was substantially under <u>anodic</u> control.

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 H₂S ADDED TO ANODE COMPARTMENT
AFTER " " " "
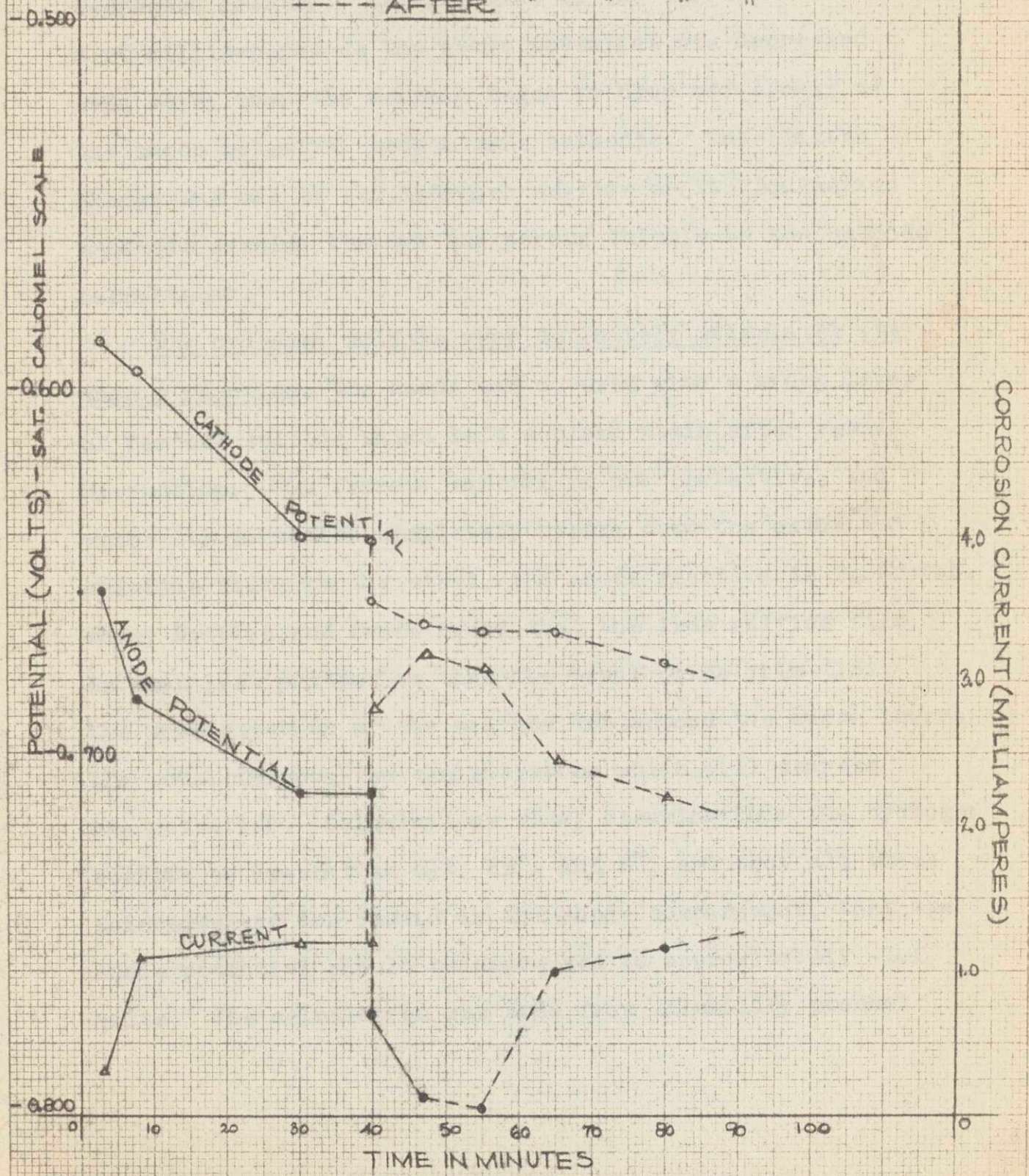
over the 2:1 mol ratio quantity of hydrochloric acid was
used to avoid the effects of "free" acid.) The cathode
potential was depressed slightly and the anode potential
depressed greatly. As time went on the current rose to
3.20 milliamperes as the anode potential was depressed
even more; then the current 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 computa-
tions 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 <u>pure anode</u> -- 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 <u>cathode</u> 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 compart-
ment, 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 con-
tained 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 VS. CORROSION CURRENT
TIME

——— BEFORE H₂S ADDED TO CATHODE COMPARTMENT
- - - - AFTER " " " " "

CATHODE POTENTIAL

CURRENT

ANODE POTENTIAL

POTENTIAL (VOLTS) - SAT. CALOM. EL. SCALE

CORROSION CURRENT (MILLIAMPERES)

TIME IN MINUTES

sjn

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
<u>negatively.</u> 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 act-
ing 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 <u>is</u>, 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:

$$H^+ \quad \longrightarrow \quad H_{atom} \quad \longrightarrow \quad 1/2 \; H_2 \; molecule$$

$$1/2 \; H_2 + 1/4 \; O_2 = 1/2 \; H_2O$$
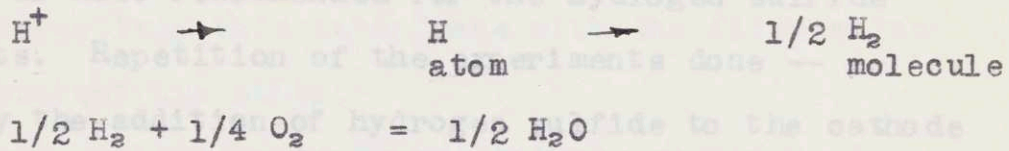
The precipitation of some sulfide either from local
action or direct attack might shield the dissolved oxygen

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 <u>protective at
the cathode.</u>

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 ob-
tained 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.

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.

A P P E N D I X

Volume of porous thimble = 174 cc.

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

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

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

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

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

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

Equation 3

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

I. COMPUTATIONS

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

$$Na_2S + 2HCl = 2NaCl + H_2S$$
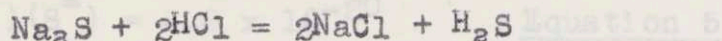
Assumptions: That no hydrogen sulfide or ions produced therefrom leave porous thimble (which is logical as we are considering instant after addition).

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

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

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

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

$$H_2S = H^+ + HS^-, \quad HS^- = S^= + H^+$$
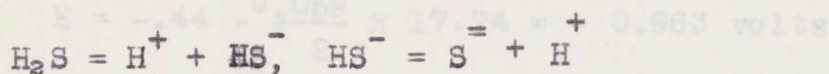
$\therefore K_1 = \dfrac{(H^+)(HS^-)}{(H_2S)} = 0.91 \times 10^{-7}$ Equation 1

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

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

Equation 3

$\dfrac{30 \text{ cc} \times 0.1N}{1000 \times 174} = 0.0172$ 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 <u>Electrochemistry.</u>

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

$E = E_0 - \dfrac{0.059}{2} \log Q$

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

$E = -.44 - \dfrac{0.059}{2} \times 17.74 = -0.963$ 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 <u>pure</u> anode.

FIG.XIV

II. CALIBRATION CURVE
of
OXYGEN MANOMETER

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

Y-axis: $\left(\text{CU. FT. } O_2/\text{HR.}\right) \times 10$

DIFFERENCE IN ARMS (SQUARES OF 1·T GRAPH PAPER ∴ IN $\frac{\text{INCHES}}{2}$)
— WATER —

sjn

54.
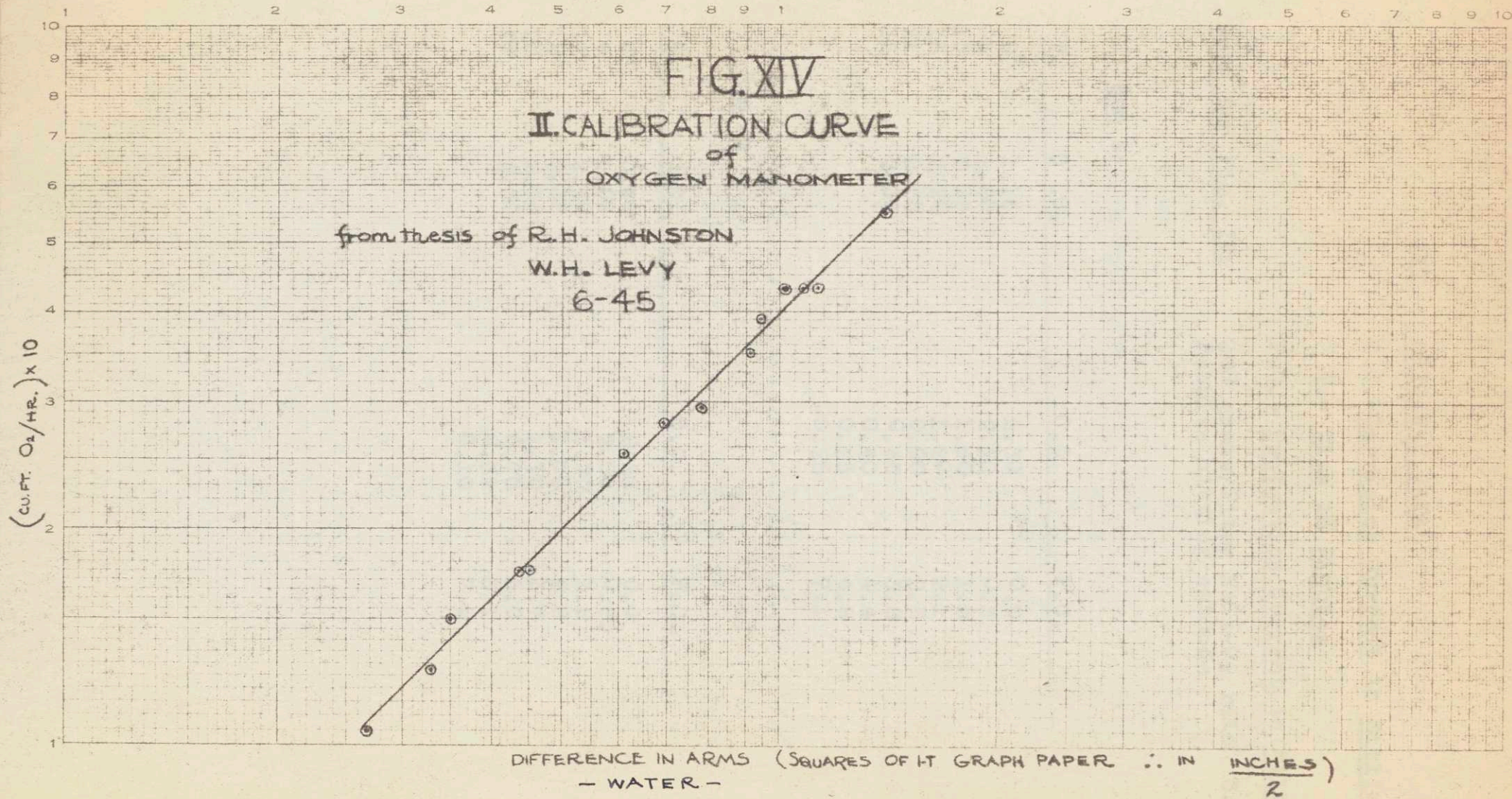
III.   ORIGINAL DATA

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

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

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: or Fig. VI: 100 grams NaCl/liter – O_2 Rate: 3.1 cu.ft./hr. – Bubbler behind cathode.

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 <u>behind</u> 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

Data for Fig. VIII: 100 grams NaCl/liter - O₂ rate: 0.16 $\frac{cu.ft.}{hr.}$

- Bubbler midway - Electrodes
completely immersed, etc.

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.	
0	0.05	10 grams NaCl/liter
		O_2 rate: 0.15 cu.ft./hr.
10	0.19	50 p.p.m. H_2S
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.

T.	C.C.	CATHODE POTENTIAL	ANODE POTENTIAL
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.

T.	C.C.	CATHODE POTENTIAL	ANODE POTENTIAL
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

IV BIBLIOGRAPHY AND FOOTNOTES

Britton, S.C., Hoar, T.P., and Evans, U.R.
"THE EFFECT OF HYDROGEN SULFIDE ON THE CORROSION OF

OTHER data are available in RESEARCH NOTEBOOK.

Steel Institute (England), 193?, 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.

Hatty and Spooner
"ELECTRODE POTENTIAL BEHAVIOR OF CORRODING METALS
IN AQUEOUS SOLUTIONS"
Great Britain-1936.

Hill, W.H., "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.

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.