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1984

SPONTANEOUS HEATING OF COAL
and
ELECTROCHEMICAL MEASUREMENTS OF CORROSION RATES

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Bijhan A. Naderi
May 1984

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SPONTANEOUS HEATING OF COAL
and
ELECTROCHEMICAL MEASUREMENTS OF CORROSION RATES

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I would also like to thank Dr. Holy again for his guidance and sincerity during my graduate study.

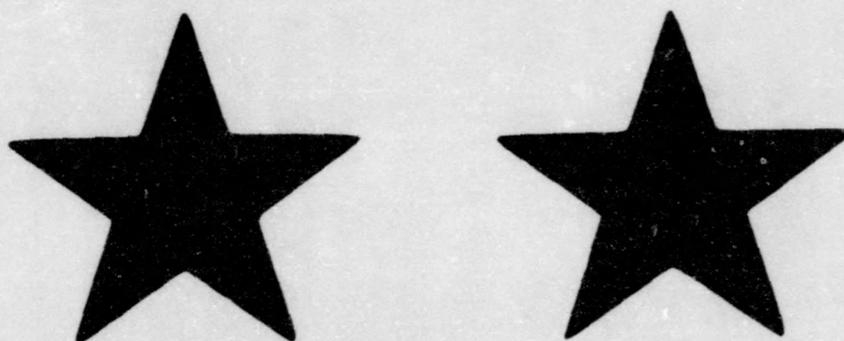
TABLE OF CONTENTS

CHAPTER	Page
I. INTRODUCTION	1
II. FACTORS AFFECTING SPONTANEOUS HEATING OF COAL	3
Intrinsic Coal Properties	3
External Factors	6
III. EXPERIMENTAL METHODS USED TO PREDICT SELF HEATING POTENTIAL	13
IV. EXPERIMENTAL PROCEDURE	17
V. RESULTS	20
VI. DISCUSSION	21
BIBLIOGRAPHY	24

LIST OF FIGURES

FIGURES	PAGE
I. Cross Section of a Coal Pile	9
II. Coal Pile Construction to Inhibit Spontaneous Combustion	10
III. The Danger of Drying and Air Leaks in Storage	11
IV. Iron Uptake of 0.015 M Coal No. 82045. .	19
V. Iron Uptake of 0.001 M Coal No. 82043. .	20
VI. Iron Uptake of 0.008 M Coal No. 82040. .	21

CORRECTION



***PRECEDING IMAGE HAS BEEN
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LIST OF FIGURES

FIGURES	PAGE
I. Cross Section of a Coal Pile	9
II. Coal Pile Construction to Inhibit Spontaneous Combustion	10
III. The Danger of Drying and Air Leaks in Storage	11
IV. Iron Uptake of 0.015 M Coal No. 82045. .	19
V. Iron Uptake of 0.001 M Coal No. 82043. .	20
VI. Iron Uptake of 0.008 M Coal No. 82040. .	21

LIST OF TABLES

TABLE	PAGE
I. Ultimate Analysis of Coals No. 82040, 82045 and 82045	22

SPONTANEOUS HEATING OF COAL

Bijhan A. Naderi

May 1984

28 pages

Directed by: Norman L. Holy, John T. Riley and John W.
Reasoner.

Department of Chemistry

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A new and relatively fast method for measuring the susceptibility of coal to spontaneous heating was studied in this work.

This method is based on the ability of coal to adsorb iron(III) from aqueous solutions. The more iron taken up by the coal, the more susceptible the coal is to spontaneous heating. The relationship holds for most of the coals being analyzed during this research project and for other succeeding ones.

The experimental procedures used and results obtained are discussed. A brief literature survey of other applied methods which have been studied, including a description of many factors affecting the spontaneous combustion of coal, is presented.

CHAPTER I
INTRODUCTION

Until the mid 1800's it was generally accepted that pyrites were the main, if not the only, cause of spontaneous heating. Since 1674, when the first episode of spontaneous combustion of coal was recorded,⁽¹⁾ there have been many papers published and many studies done in an attempt to put an end to this old problem. Unfortunately, owing to the heterogeneous nature of coal and the complex interdependence of the factors, there has been no simple, successful, universally applicable test for combustibility, and no simple effective method for preventing the spontaneous heating of coal. However, several relative measures of the spontaneous combustion potential of coal have been presented in the literature and some experimental methods have been developed to predict spontaneous combustion. Since these experimental methods cannot create a real-life situation, they cannot be used directly to predict the spontaneous combustion of coal but rather can be used as a relative measure of susceptibility of different coals to self heating.*

*Self heating, "spontaneous combustion," and "spontaneous heating" can be used interchangeably.

Statement of the Problem

All coals oxidize slowly when they come in contact with air. The rate of oxidation, a very important factor, is difficult to predict because of its dependence on intrinsic coal properties as well as external conditions. Some of these properties which contribute to self heating include low rank, high pyrite content, and high moisture content. Low rank and high moisture are typical of western coals. As a matter of fact, these coals are the most troublesome in the U.S. There are an estimated 485 billion tons of subbituminous coal and 478 billion tons of lignite in the U.S.⁽¹⁾

Spontaneous heating may occur in the high walls of surface mines, in underground mines, on trains, or in storage piles. This is a major problem for coal producers, shippers and consumers. Away from possible safety hazards and loss of production in mines or shipments, consumers must consider that any oxidation of coal is a process of deterioration. The effect of oxidized coal in coking is even greater.⁽²⁾ It produces coke of inferior quality because of its inability to fuse and form coke. It produces coal bulk-density-control problems such as reduced coke production, overheated charges, carbon deposits, and oven damage. It also produces more fines and creates handling problems. It causes increased coke reactivity as well as decreased coke rate. Oxidized coal is not much of a problem for burning except for lower heating value and excessive fine formation.

CHAPTER II

FACTORS AFFECTING SPONTANEOUS HEATING OF COAL

As mentioned before, several factors related to intrinsic coal properties and some external factors are involved in promoting the spontaneous combustion of coal.

Intrinsic Coal Properties

1. Coal Reactivity toward Oxidation

The exothermic reaction of oxidation (oxidation of carbon by air) produces 94 Kcal/mol or 3-4 calories per cubic centimeter of oxygen absorbed.^(3,4,5) The mechanism of this reaction is not completely understood, but different steps have been proposed in the literature:^(6,7)

A. In the range of 15-30°C, oxygen is physically absorbed to the coal surface. The rate doubles for each 10°C rise in temperature between 50° and 75°C. After 75°C, spontaneous ignition may occur within 72 hours. The production of CO, CO₂, or CH₄ is very low in this stage.

B. In the range of 100-135°C rate of oxygen absorption increases very rapidly. At about 100°C carbon monoxide begins to evolve, and at about 135°C carbon dioxide and water vapor are driven off.

C. The actual temperature at which spontaneous combustion can take place is 230°C. This is accompanied by rapid increase in CO and CO₂ liberation.

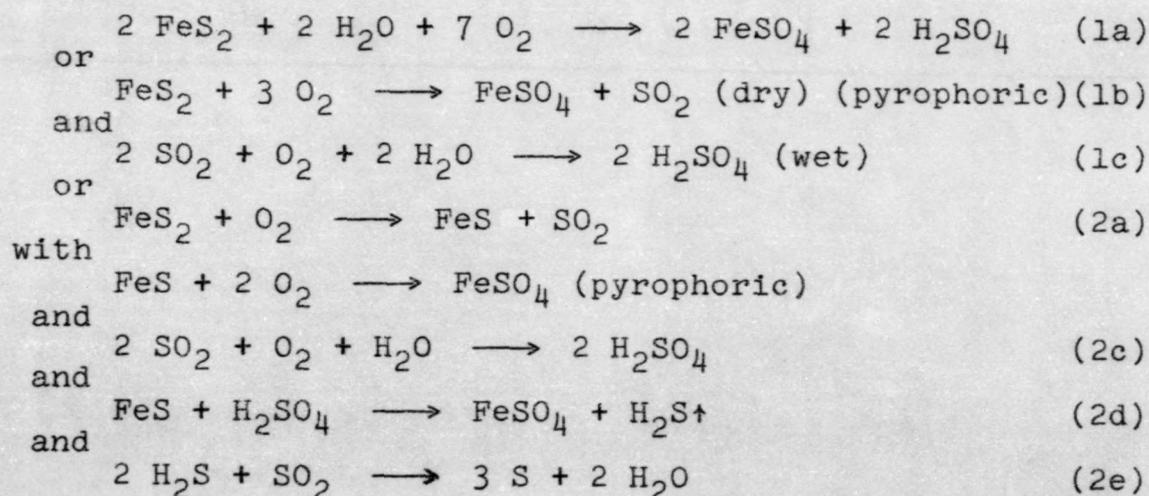
D. Near the temperature of 350°C, the coal ignites and burns vigorously.

2. Coal Type and Rank

As a rule of thumb, the rank decreases as the potential for self heating increases. This can be caused by many factors such as high moisture and oxygen content or permeable internal structure which allows more oxygen or moisture in or out.⁽²⁾ It should be kept in mind that sometimes one part of a seam may be more susceptible to self heating than another. In general, the self heating potential of maceral groups decrease in the order exinites (hydrogen rich), vitrinites (oxygen rich), and inertinites (carbon rich).^(3,1,8) The self heating potential for lithotypes decreases in the order vitrain, clarain, durain, and fusain.^(8,1)

3. Content of Pyrite and other Sulfides

Pyrite, pyrrhotite, marcasite, and other inorganic sulfides increase the self heating potential. Because of weathering, products of pyrites and marcasite are produced by exothermic reactions.^(1,9,6)



FeSO_4 formation in group a reactions is 20 times faster than in group b. Moreover, " FeSO_4 formation generates over 200 Kcal/mol or the equivalent of over 30 million calories in a ton of coal containing 2% pyrite."⁽²⁾ Morphological forms of pyrites and marcasite also contribute to self heating potentials; that is, forms having more surface area per unit volume expose more surface for oxidation. One other important factor contributed by iron sulfides is that when they weather, they start swelling and may cause the coal to disintegrate, thus exposing more sites for oxidation to occur.⁽³⁾

4. Heat of Wetting

For a given coal at temperatures below 100°C , the heat of wetting is greater than the heat of oxidation.⁽⁹⁾ This is due to the fact that wetting of coal is an exothermic reaction. Loss of moisture is endothermic, but it also exposes more oxidative sites. Wetting of coal also increases thermal conductivity in coal which helps in dissipation of the heat generated. However, there is no relationship established and details are not known. The effect of wetting is more pronounced when there is a change in moisture content, for instance, when already dried coal is introduced into a moist climate.

5. Exposed Surface Area and Porosity

Greater surface areas can provide more sites for oxidation to occur. The main factor contributing to this can be particle size; the smaller the particle size, the greater is the surface area. The rate of heating is

approximately proportional to the cube root of the external surface area.⁽⁴⁾ Therefore, dusty coals could be more prone to self heating. High porosity also has the same effect by exposing more surface area.

6. Freshness of Surfaces

Observations of carbon monoxide levels in UK mines during the work days and vacation periods have shown that fresh surfaces tend to oxidize more readily.⁽⁸⁾ However, this cannot be generalized for the other coals since different experiments result in an inconsistent situation.

7. Ash Content

The U.S. Bureau of Mines (U.S.B.M.) investigations indicate that a washed coal has a greater tendency to heat spontaneously than does run-of-mine coal.⁽¹⁰⁾ One should consider the fact that more ash content probably means more sulfides. Then, if a particular high ash coal has some other properties contributing to the self heating potential (such as excessive fines or high ash content), it would not work as an inert diluent as in other cases.

8. Methane Content

The emission of methane or its presence inside the coal structure can create an inert atmosphere near the surface of coal which blocks oxygen absorption. Low rank coals being more permeable tend to lose the methane content rapidly, thus becoming more susceptible to self heating.

External Factors

1. Change in Moisture Content

As stated earlier, wetting of coal is an exothermic

reaction, and heat generated by this reaction under 100°C can be more than heat generated by oxidation. Therefore, if a low rank coal with a high moisture content is dried for shipment, it can readily ignite if exposed to a humid climate.

2. Temperature

The rate of oxidation is a direct function of temperature. Oxidation rate increases very sharply in temperatures above 75°C.⁽⁶⁾ Increase in temperature also causes an increase in the permeability of coal to oxygen.⁽¹¹⁾

3. Availability of Air

This is a very simple but important external factor in the spontaneous combustion of coal. Air tends to oxidize coal but at the same time can carry away the heat generated by oxidation. Therefore, if the air flow is too little, heat generated by oxidation can accumulate and cause ignition. On the other hand, if a good flow of air is provided, coal oxidizes more rapidly but the heat generated can be dissipated. If access of air can be completely prevented, there can be no danger of spontaneous heating; however, this is not economically feasible.

4. Oxygen Concentration

Experiments done by the U.S.B.M.^(8,10) shows that an increase in oxygen concentration increases the oxidation of coal (particularly above 50°C).

5. Shipping and Storage Practices

When coal is dropped from a grab bucket high above the pile, many lumps will be broken, causing accumulation of

finer in the center, while larger particles will roll down the sides of the pile. This will allow some amount of air to pass through the pile creating a chimney effect and promoting spontaneous heating (See Figure 1).

To prevent these kinds of problems caused by the formation of unnecessary fines, coal should be handled and moved about as little as possible. If the segregation of particle size cannot be avoided, a roll packing is suggested.⁽¹²⁾ This method requires laying down layers of coal (not over three feet deep) and compaction of each layer before another layer is emplaced (See Figure 2). Recommended sealants to prevent air leakage through the sides are⁽²⁾ (a) compaction, (b) asphalt or road tar, (c) clay, (d) oil, (e) ethylene glycol dust suppressants, or (f) plastic tarps. This should also increase storage capacity by about 30 percent.

In the cases where one side of a coal container is warmer than the other side, one part of the coal will be drier than the other part and will be more prone to spontaneous heating if exposed to air flow (Figure 3). To avoid this problem, containers should be kept away from any heat sources in the area and they should be sealed properly to avoid air leakage.

Successive drying and wetting should be avoided as much as possible before or during shipments. It is advisable to cover the coal with plastic or road tar, etc. During shipping and storage, a monitoring of the temperature and gases given off by the coal should be helpful.

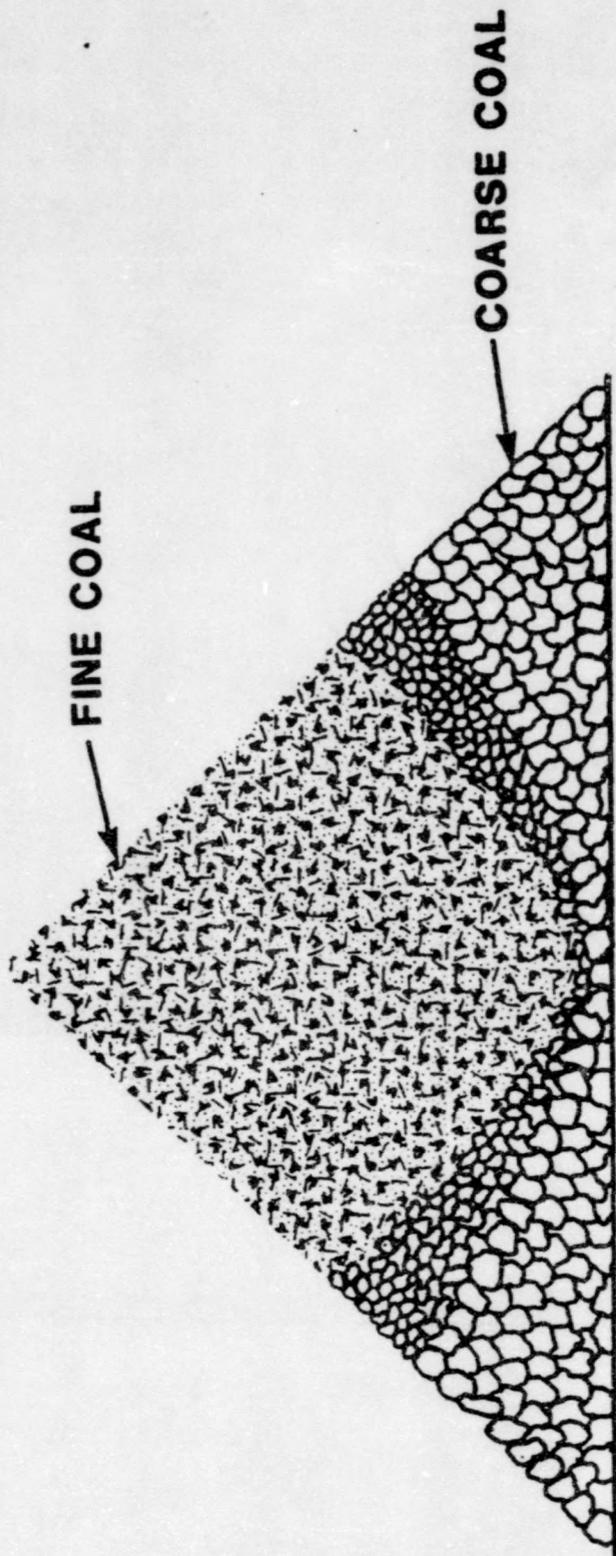


FIGURE 1 ^(1,10)

CROSS SECTION OF A COAL PILE CREATED FROM A POINT SOURCE. NOTE UNEVEN DISTRIBUTION OF FINES IN THE CENTER WITH LARGER PARTICLES SEGREGATED ON THE OUTSIDE. THIS SEGREGATION ALLOWS AIR TO FLOW THROUGH THE PILE CREATING A "CHIMNEY EFFECT" AND PROMOTES SPONTANEOUS COMBUSTION.

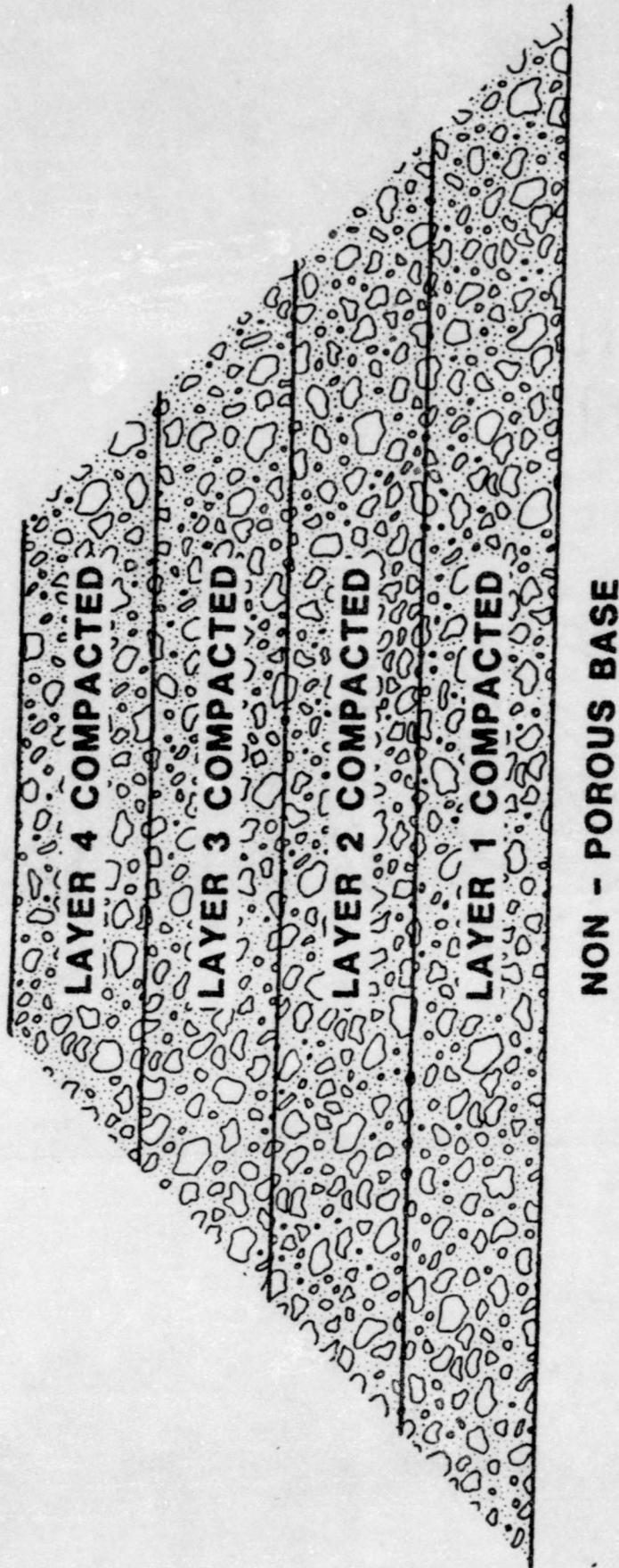
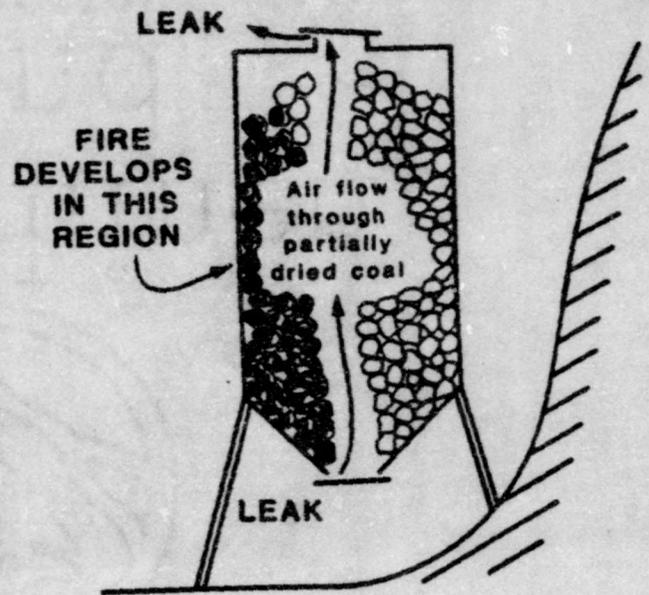
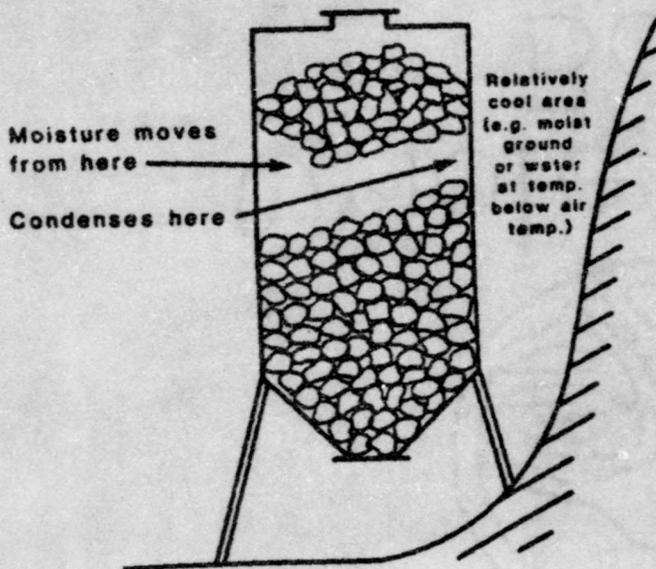


FIGURE 2
(1,10)

COAL PILE CONSTRUCTION TO INHIBIT SPONTANEOUS COMBUSTION. LAYERS SHOULD BE NO MORE THAN A FEW FEET IN THICKNESS AND COMPARED BEFORE EMPLACEMENT OF OVERLYING LAYERS. CARE SHOULD BE TAKEN TO COMPACT AND SEAL SIDES OF THE PILE TO PREVENT AIR INFLOW. A GOOD MIXTURE OF COARSE AND FINE PARTICLES WILL ELIMINATE AIR VOIDS AND LOWER PERMEABILITY.

 **TRANSFER OF MOISTURE AND PARTIAL DRYING IN ABSENCE OF AIR**
SOURCE OF HEAT

 **LEAKAGE OF AIR THROUGH PARTIALLY DRIED COAL LEADS TO SPONTANEOUS HEATING**



○ COAL PARTICLE CONTAINING NATURAL MOISTURE CONTENT

● PARTIALLY DRIED COAL PARTICLE

FIGURE 3 ^(1,10) THE DANGER OF DRYING AND AIR LEAKS IN STORAGE.

In 1973, a series of laboratory experiments were conducted to show that some chemicals like calcium chloride (Montan powder) and some borates significantly inhibit the oxidation of coal.⁽⁷⁾ However, these experiments were discontinued because of high cost and health hazards related to these chemicals.

CHAPTER III

EXPERIMENTAL METHODS USED TO PREDICT SELF HEATING POTENTIAL

Throughout more than 100 years, various experiments and methods have been developed to test the coal susceptibility for self heating. Yet, none of these methods have been able to suggest a simple, universally accepted and reliable way to predict self heating. The principle reason for the failure of these methods is the variation in factors known to contribute to the spontaneous heating susceptibility of coal. In addition, conditions under which these methods were developed are most often quite different than the actual conditions used in the mining, storing and transporting of coal.

The only large-scale tests ever made have been done on South African coals.⁽¹³⁾ In these tests, approximately 10 tons of coal were placed inside thermally isolated bunkers and the temperature rise monitored. This test gives the initial rate of heat generation, the temperature coefficient, and the decay constant for each individual coal.⁽¹³⁾ These large-scale experiments have been successful in predicting the behavior of many different coals, but the problem is its cost.

Four of the most popular laboratory experiments are listed below:

Experiment 1 - Adiabatic Calorimetry^(3,14,15)

In this method, a coal sample is heated inside an insulated container or bath so that the temperature of the

coal and surrounding material stay the same. Then air or oxygen is allowed to reach the sample, causing an increase in the temperature of the coal due to oxidation. The oxidation can be monitored along with the time required for it, thus providing the heating rate and the heat generated by the coal.

Experiment 2 - Isothermal Calorimetry⁽¹⁶⁾

The coal sample is held at a constant temperature in a large bath. Heat generated by the coal due to oxidation or wetting can be measured by thermocouples and is dissipated in a large heat sink. The measured heating rate can be correlated with the combustibility of the coal.

Experiment 3 - Oxygen Sorption⁽¹⁷⁾

Air or oxygen is added to a coal sample in a closed system; gaseous products are removed periodically. The amount of air or oxygen needed to keep the system at a constant pressure can be used to evaluate the amount of oxygen absorbed. The temperature increase per unit volume of oxygen consumed is used to predict the coal's susceptibility for self heating.

Experiment 4 - Temperature Differential⁽¹⁾

The coal sample is heated in a bath at a constant rate. The differences between the coal's temperature and the bath is measured. The coal's temperature starts rising behind the temperature of the bath, and when it starts self heating, its temperature will coincide with, and then pass, the temperature of the bath. Some variant of a temperature differential-time relationship indicates the combustibility of the coal.

Indexes of Combustibility

Following are the most popular indexes of combustibility described in the literature.⁽⁹⁾ These can be derived from previously mentioned experimental methods. Care must be taken in using these indexes since they can only give a relative measurement of combustibility, and they are most effective when used in combination with one another and in combination with other factors effecting the spontaneous combustion of coal.

1. Heating Rate

The heating rate is simply the temperature increase under controlled conditions which is measured in °C/hr/g, or quantitatively in cal/hr/gr. This rate can be used relative to the heating rate of some standard sample or it can be used with respect to the temperature of the coal's surroundings within a given range.

2. Crossing-Point Temperature

Crossing-point temperature is the temperature at which the temperature of the coal and heat bath coincide and can be determined by the temperature differential experiment.

3. Ignition Temperature

Ignition temperature is the temperature at which the coal ignites under experimental conditions and is determined by observation.

4. CO Index

The Carbon Monoxide Index is obtained by dividing CO measured (evolved) by changes in oxygen concentration.

As the temperature of coal goes up, more CO is emitted and more oxygen is absorbed. This method is very popular in the U.S., probably because of the simplicity and ease with which it can be used, particularly in monitoring the air in underground mines. However, it is important to know that all coals can form CO at near-ambient temperature without necessarily any self heating.⁽⁹⁾

Using an adiabatic calorimeter, the U.S. Bureau of Mines has developed a good correlation between the temperature of self heating of coal and the inherent moisture and oxygen (daf) content of coal:⁽⁴⁾

$$T(\text{SH}) = 139.1^{\circ}\text{C} - 4.7 (\% \text{ inherent moisture}) - 4.8 (\% \text{ oxygen-daf})$$

This formula indicates that the lower the temperature of self heating, the higher the danger of spontaneous combustion. The results of these experiments by U.S.B.M. have not yet been published. When these indices are used along with other important factors (rank, moisture content, etc.), one should get a relative idea of how a particular coal might behave under identical field conditions. Comparing various indices would be inaccurate and possibly misleading.⁽²⁾ None of these indices are in general use.⁽⁹⁾

CHAPTER IV
EXPERIMENTAL PROCEDURE

The following experimental procedures and conditions were used for all runs.

Coal samples were prepared according to American Society for Testing and Materials (ASTM) Method D 2013. Each coal was first air dried. The sample was then successively crushed and pulverized to -8, -20, and -60 mesh. This process was accompanied with a reduction in sample size. After obtaining a -60 mesh coal, 100 grams were taken for analysis.

Proximate and ultimate analyses were performed according to ASTM standard methods as listed below.

- For determining moisture, a drying oven was used as described in ASTM Method D 3173.
- To determine the ash content, the dried coal from the moisture determination was heated gradually in a muffle furnace as described in ASTM Method D 3174.
- For volatile matter measurements, a vertical electric tube furnace was used according to ASTM Method D 3175.
- For obtaining the gross calorific value, an isothermal-jacket bomb calorimeter was used according to ASTM Method D 2015.
- Carbon and hydrogen content were determined using a three zone furnace as described in ASTM Method D 3178.

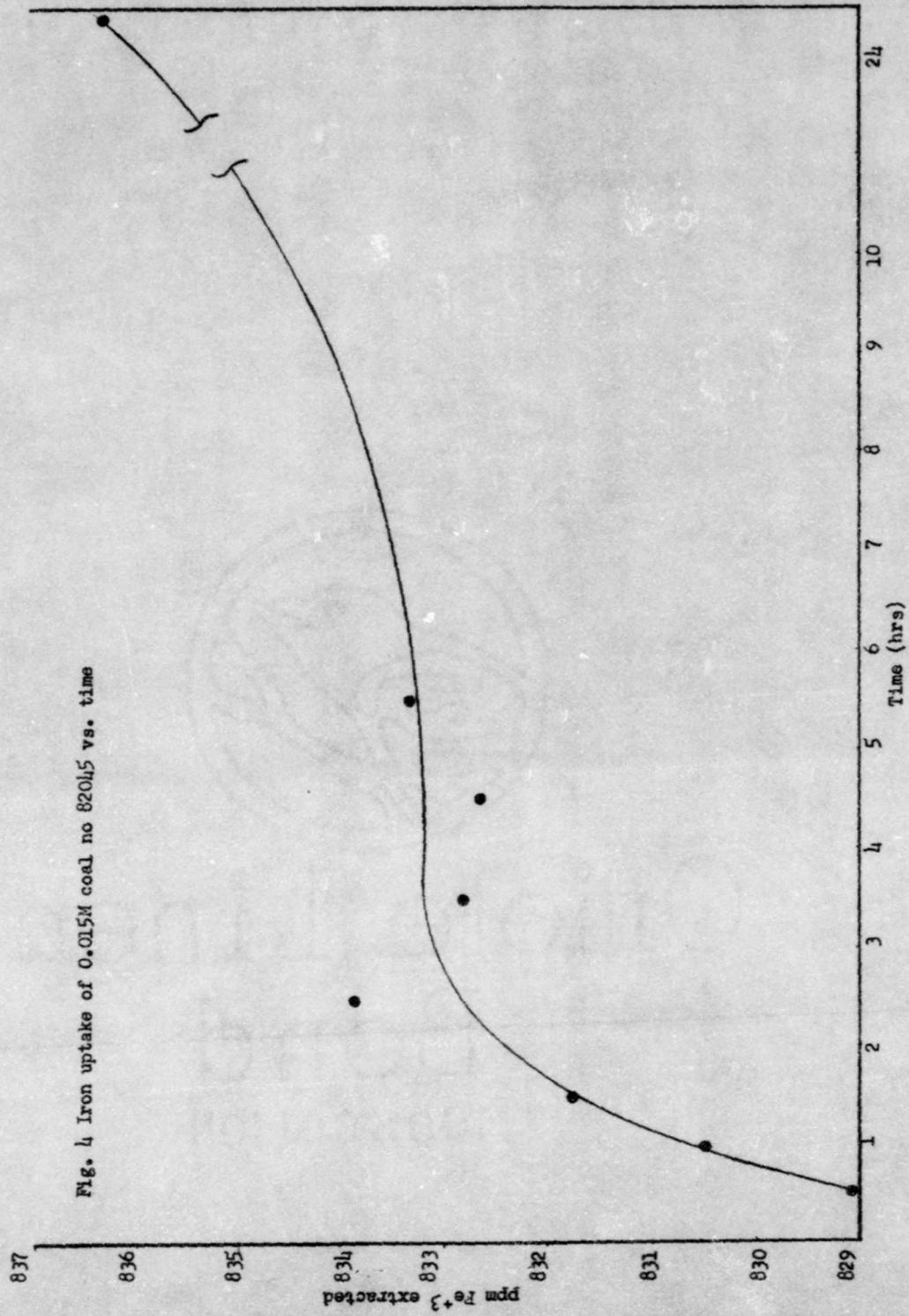
- To obtain the value of nitrogen, the Kjeldahl method was used according to ASTM Method D 3179.
- ASTM Method D 2492 was used to determine forms of sulfur.

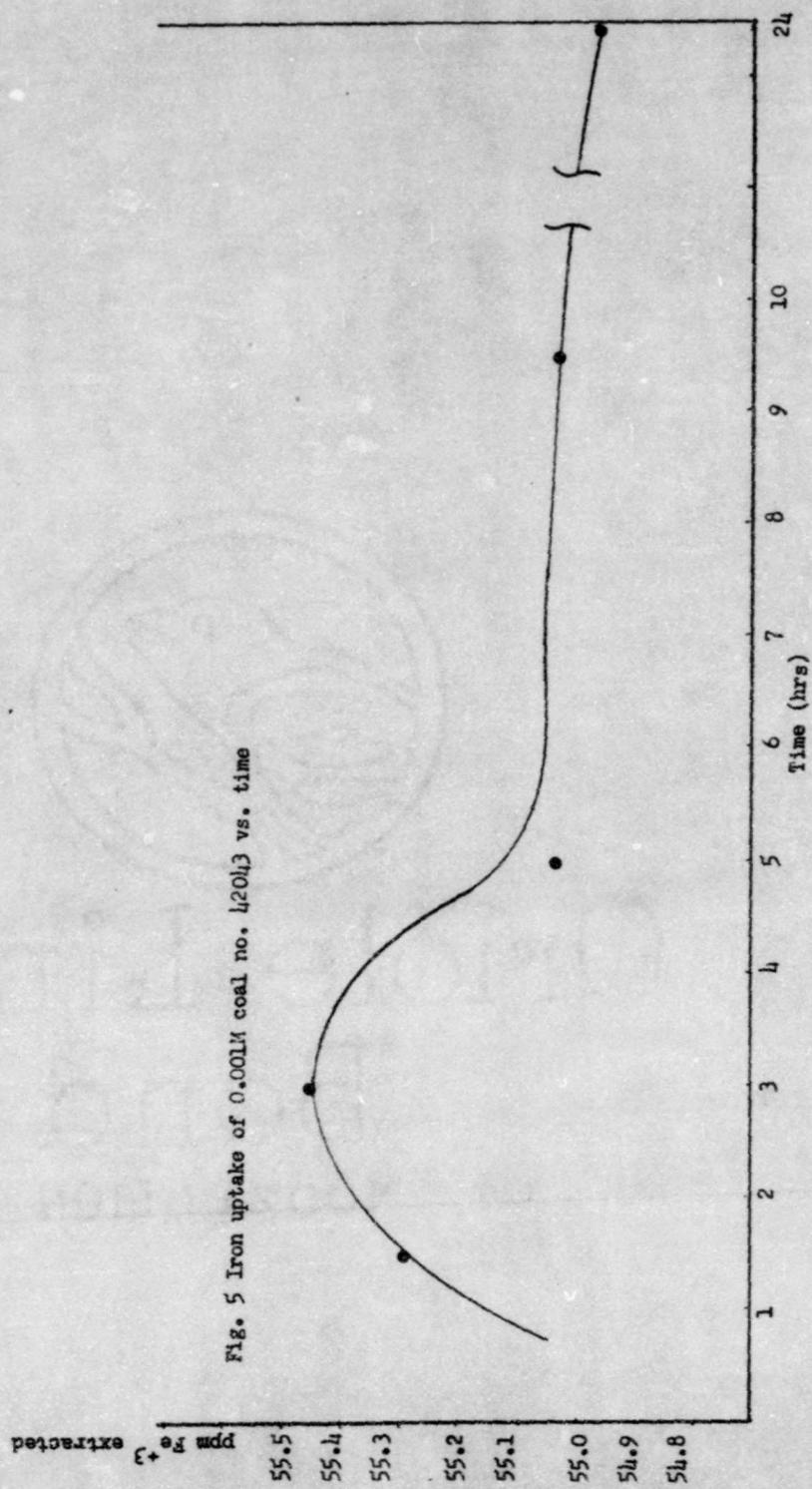
As-determined results are summarized in Table 1.

Iron(III) solutions were prepared using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ from Matheson, Coleman & Bell in D.I. water. Duplicate samples of coal, 5 grams each, were mixed with 50 ml of the iron solution of desired concentration, then the mixture was evacuated with a vacuum pump for two minutes to remove gases from the pores of the coal. To maintain a good contact between coal and solution the mixtures were agitated continuously by means of a wrist action shaker from Burrell. Five milliliter aliquots were taken with a pipet at the end of each hour and then filtered through No. 1 filter paper and diluted to 100 milliliter. All runs were conducted at room temperatures.

The diluted increments were analyzed using a 303 Perkin-Elmer Atomic Absorption Spectrometer to determine iron concentration. The instrument was used in the double beam mode, at a wavelength of 248.3 nm. The standard solutions were prepared by diluting the original solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

The results were plotted as ppm Fe^{+3} extracted vs. time in hours. Figures 4, 5, and 6.





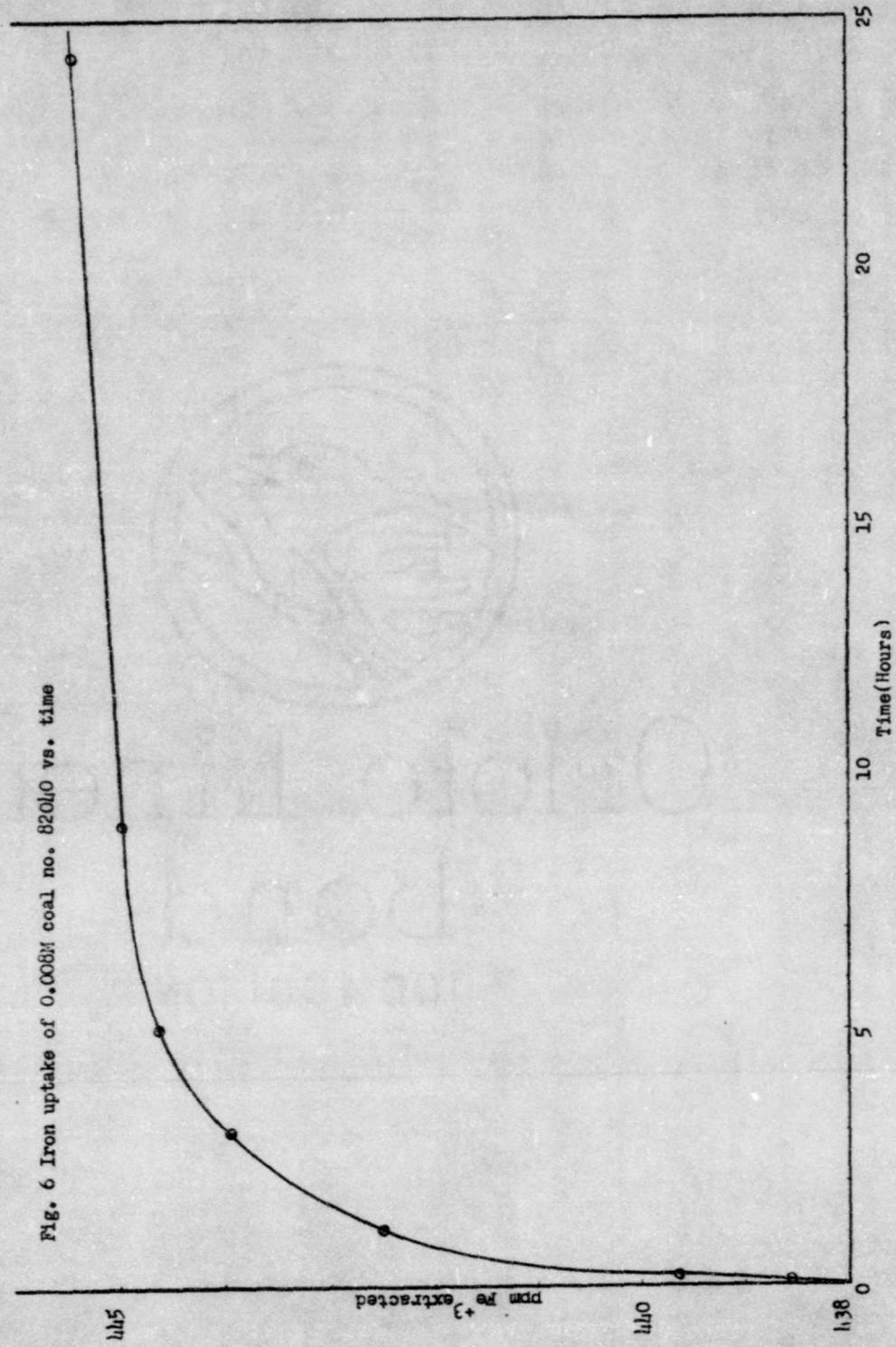


TABLE I
Analytical Values for Coals*

Coal No.	82040	82043	82045
<u>Proximate Analysis</u>			
Moisture	7.72	5.42	27.58
Ash	10.71	7.42	4.50
Volatile Matter	41.0	40.7	31.20
Fixed Carbon	40.6	46.4	36.72
Btu/pound	11630	12756	8724
<u>Ultimate Analysis</u>			
Carbon	63.26	70.92	44.80
Hydrogen*	4.43	5.08	3.41
Nitrogen	1.12	1.13	0.70
Sulfur	3.41	1.53	0.27
Oxygen* (by diff.)	9.35	8.50	18.74
FORMS OF SULFUR			
Pyritic	1.19	0.75	0.06
Sulfate	0.08	0.02	0.01
Organic	2.14	0.76	0.20
Total	3.41	1.53	0.27
ASTM RANK	HIGH VOLA- TILE BITUMINOUS C	HIGH VOLA- TILE BITUMINOUS B	SUBBITUMINOUS C

*All values are reported on an as-determined basis.

CHAPTER V

RESULTS

The different coals designated 82040, 82043 and 82045 were used for this experiment. Coal no. 82040 is a high-volatile bituminous C which is considered a reactive coal. Coal no. 82043, a high-volatile bituminous B, is a moderately active coal and the other coal, no. 82045, is a more reactive subbituminous C. The results obtained for these three coals parallels the predicted reactivities.

The main problem confronted in establishing the experimental procedure was using the right concentration of iron(III) solution for each coal, since different coals with different activity levels could adsorb no iron or too much iron. The problem in the latter case was that a concentration gradient for iron adsorbed could not be established. The only way to overcome this problem was to try different concentrations of iron solution to ascertain the right concentration needed for each coal.

Results are shown in Figures 4, 5, and 6.

CHAPTER VI

DISCUSSION

Among the different factors that effect the spontaneous heating potential of coal, rank, moisture, oxygen and pyrite content seem to be the most important. Apparently heat generated by oxidation and wetting contribute to spontaneous heating.

Due to the complex interplay among intrinsic coal properties and variations in shipping and storage practices, no successful experimental method that can predict spontaneous combustion susceptibility in coal has been developed. Nevertheless, the existing methods have been used in combination with other factors effecting the liability of coal to self heating to establish relative measures.

The iron uptake method is promising in that it is fast, does not consume a large amount of sample, and can be performed in a laboratory without any sophisticated instrumentation. Results obtained using this method might not seem to be very consistent or reproducible, but as more different coals are analyzed some modifications may improve the method.

The iron uptake method is based on the well known fact that lower rank coals adsorb metal ions from aqueous solutions.⁽¹⁸⁾ This process takes place by ion exchange depending on the kind of metal involved. As mentioned earlier,

the coals with higher oxygen contents absorb greater amounts of the metal ion from the solution. If most of the oxygen is in the phenolic form, then the metal ion can coordinate to the phenolic oxygen if proper contact is provided. Vacuum pumping eliminates the problem of proper contact or, namely, wetting to a greater extent. However, the use of a wetting agent might improve the wetting process even more. In terms of choosing the right metal, it is believed that a metal ion forms a coordination complex after being adsorbed. Thus, the metal of choice should have high coordinating capability. Use of nickel for this purpose has been reported in the literature.⁽¹⁹⁾ Nickel is a good coordinating metal and can be traced easily when adsorbed by coal since it has a very low concentration in the original coal. For this study iron(III) was chosen to provide a better coordinating capability.

The results show that the postulated theory is in agreement with the experimental results, although more work is needed to clarify the matter and to support the data. As shown in Table I and Figures 4, 5 and 6, coal number 82045 has the highest amount of oxygen and moisture and lowest amount of carbon (lower rank). A 0.015 molar solution of iron(III) (highest concentration used) was used for this coal. For coal number 82043 a 0.001 molar solution was used; for coal number 82040, a 0.008 molar concentration of iron solution was used. Taking into account the heterogeneous nature of coal it is not surprising that one coal, namely coal number 82040, shows better results than others. The

origin of the problem is not yet known. There is a possibility that it might be related to the experimental procedure used. The project is still under investigation.

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ELECTROCHEMICAL MEASUREMENTS OF CORROSION RATES

Part Two

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Presented to

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Bijhan A. Naderi

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TABLE OF CONTENTS

CHAPTER	Page
I. INTRODUCTION	2
II. THEORY	10
Electrode Kinetics	11
Exchange Current Density	12
Activation and Concentration Polarization . .	12
Mixed Electrodes	17
Corrosion Rate Measurements	17
III. EXPERIMENTAL	20
Instrumentation	20
Procedure	26
IV. RESULTS AND DISCUSSION	
BIBLIOGRAPHY	55

LIST OF FIGURES

FIGURES	Page
1. Schematic diagram of the SRC-1 plant. . . .	4
2. SRC 1 atmospheric fractionation column(T-105)	5
3. Weight loss measurement cell used for coal liquids.	7
4. Hydrogen-hydrogen-ion exchange current densities.	15
5. Activation-polarization curve of a hydrogen electrode.	15
6. Concentration polarization curve (reduction process).	16
7. Effect of environmental variables on concentration polarization curve	16
8. Electrode kinetic behavior of pure zinc in acid solution	19
9. Applied current anodic & cathodic polarization curves of a corroding metal showing Tafel extrapolation	19
10. Electric circuit for cathodic polarization measurements	21
11. Schematic diagram of the potentiostat and related circuitry (see also Fig. 12) Designed and made by A.A. Sagues, IMMR . .	22
12. Schematic diagram of the potentiostat and related circuitry	23
13. Three electrode system used for corrosion rate measurements	25
14. Instantaneous ohmic drop & depolarization curve as seen on the scop	27
15. Carbon steel in 50 ppm aniline hydrochloride, IX scale	31
16. 0.055M sulfuric acid and 10X scale calibration	32

FIGURE	Page
17. Carbon steel in 1000 ppm chloride as aniline hydrochloride deaerated medium, 10X scale	34
18. Carbon steel in 1000 ppm chloride as aniline hydrochloride deaerated medium, 10X scale	36
19. Pure iron in 1000 ppm chloride as aniline hydrochloride deaerated and filtered medium, 10X scale.	39
20. Pure iron in 2000 ppm chloride as aniline hydrochloride deaerated and filtered medium, 10X scale.	40
21. Pure iron in 4000 ppm chloride as aniline hydrochloride deaerated and filtered medium, 10X scale.	41
22. Pure iron in 1000 ppm chloride as aniline hydrochloride deaerated and filtered medium, 10X scale.	42
23. Pure iron in 2000 ppm chloride as aniline hydrochloride deaerated and filtered medium, 10X scale.	43
24. Pure iron in 4000 ppm chloride as aniline hydrochloride deaerated and filtered medium, 10X scale.	44
25. Pure iron in 2000 ppm chloride as aniline hydrochloride deaerated and filtered medium, 10X scale.	45
26. Initial corrosion rate as a function of test temperature for carbon steel coupons exposed in water containing 1000 ppm chloride as aniline hydrochloride.	47
27. Non agitated corrosion rate by weight measurement carbon steel in 1000 ppm chloride as aniline hydrochloride	48
28. Weight loss vs. time, stagnant aniline hydrochloride.	50
29. Weight loss vs. time agitated aniline hydrochloride.	51
30. Weight loss vs. time agitated and stagnant aniline hydrochloride.	52

LIST OF TABLES

TABLE		Page
1.	Exchange Current Densities	13
2.	Table of Results	46

ELECTROCHEMICAL MEASUREMENTS OF CORROSION RATES

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54 pages

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Major coal liquefaction pilot plants have reported severe instances of chloride-related corrosion in the distillation areas. Weight loss measurements have been the most popular laboratory technique for measuring or predicting the corrosion rates.

Recently there has been new interest in developing faster and easier means of measuring corrosion rates. Most of this attention has been focused on electrochemistry. The information reported here provides a description of electrochemistry of corrosion and how the Tafel extrapolations are used to predict corrosion rates. A discussion of the related problems and the reliability of this method is also included.

CHAPTER I
INTRODUCTION

With increasing usage of coal as an alternate source of energy and development of multi-ton demonstration and pilot plants to produce synfuels from coal, a new and active area of research has developed. Some of the problems in this new area have been encountered before through research and development in the petroleum industry and related technologies. However, new problems unique to the nature of coal have appeared. One of the problems which seems to be the center of attention at the present time is corrosion. All four major direct coal liquefaction pilot plants have experienced unexpectedly severe corrosion in the order of 100 - 1000 mils per year (MPY)* in the distillation areas. Most of the research related to the subject of this paper has been done in connection with the Solvent Refined Coal-I (SRC-I) pilot plant of Wilsonville, Alabama.

Three months after switching from low chloride feed coal (0.02 wt%) to a much higher one (0.2 wt%), the distillation tower developed leaks and severe internal damage due to corrosion. The damage was so pronounced that the 316 stainless steel lined tower had to be replaced. The operators of the SRC-1 pilot plant could reduce the corrosion to a considerably lower rate by adding forty pounds of sodium carbonate to

*A mil is 1/1000 of an inch.

every two tons of feed coal (a slight excess to the molar equivalent of chloride in the coal).⁽¹⁾ This addition proved to be an effective way of minimizing the problem. However, it is not applicable to a large commercial plant. As an example, high levels of sodium cannot be tolerated by a gasifier which is usually included in a direct liquefaction plant.

A simplified schematic of SRC-I plant is given in Figure 1. In the process coal is mixed with a recycled solvent and heated, under 1500-2000 psig hydrogen pressure, at around 454°C (850°F) in a reactor called a dissolver. Next, low and high boiling fractions are separated in a high pressure separator. Up to 50% of the chloride entering the dissolver may be transported through a high boiling stream to the atmospheric distillation tower T-105⁽²⁾ (where most of the corrosion occurs). The T-105 tower is shown in Figure 2. The re-boiler is maintained at around 315°C (600°F) and the overhead temperature is at 171° - 204°C (340 - 400°F) range. The tower has twenty trays. The zone of high corrosivity is between trays 9 and 15. The typical chemical makeup of the coal liquids in this zone is 25 to 50 weight percent phenols, predominantly m + p - cresol, 3,5-dimethylphenol, and 3,4-dimethylphenol. Two to six percent consist of basic nitrogen compounds, roughly equal amounts of anilines and pyridines. The remainder is composed of neutral oils.⁽³⁾

A significant amount of research has been done on the subject in order to find the major cause or causes of the problem. As stated before, it was easy to pinpoint the increased

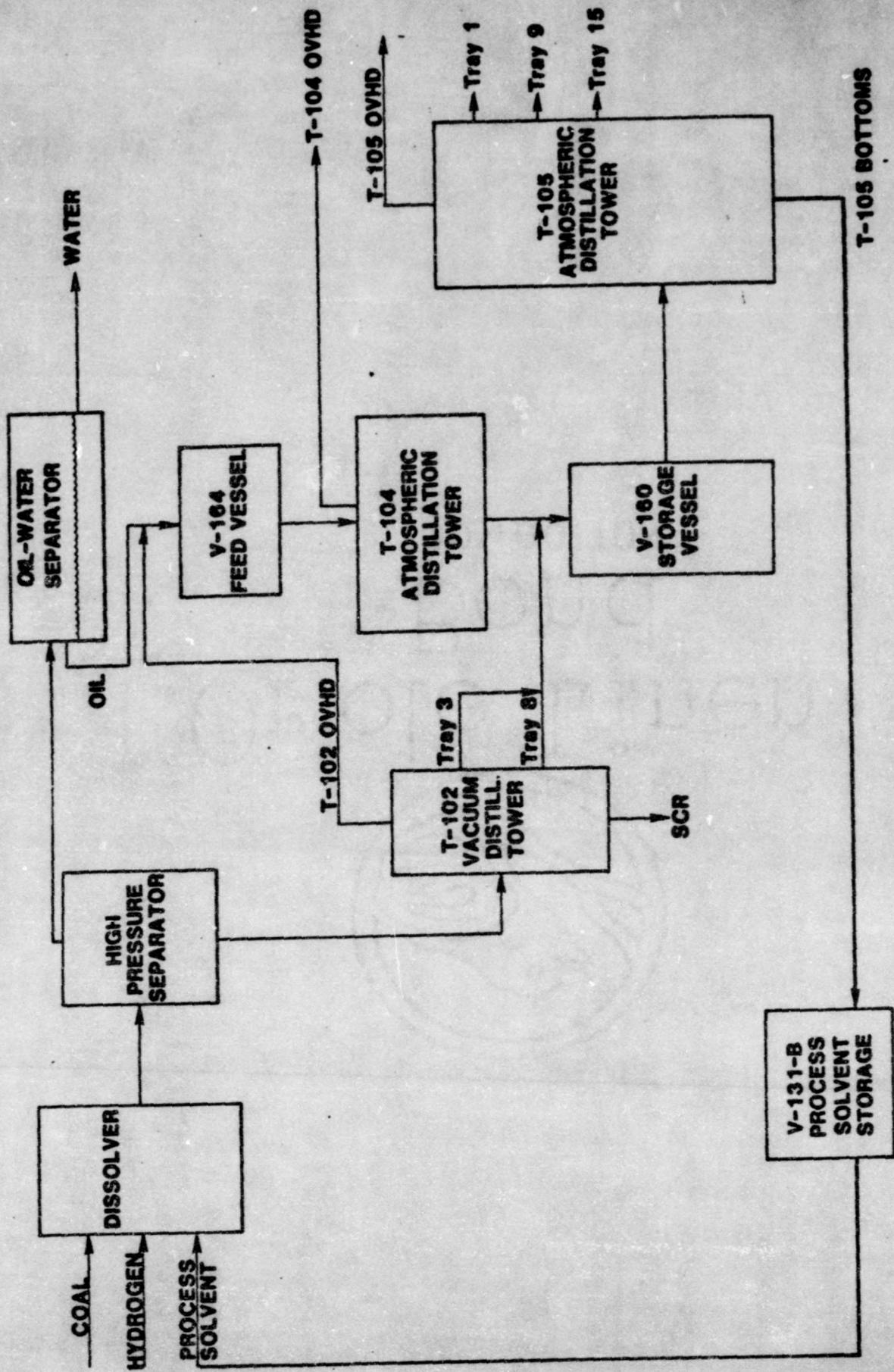


Fig. 1 Schematic diagram of the SRC-1 plant. (2)

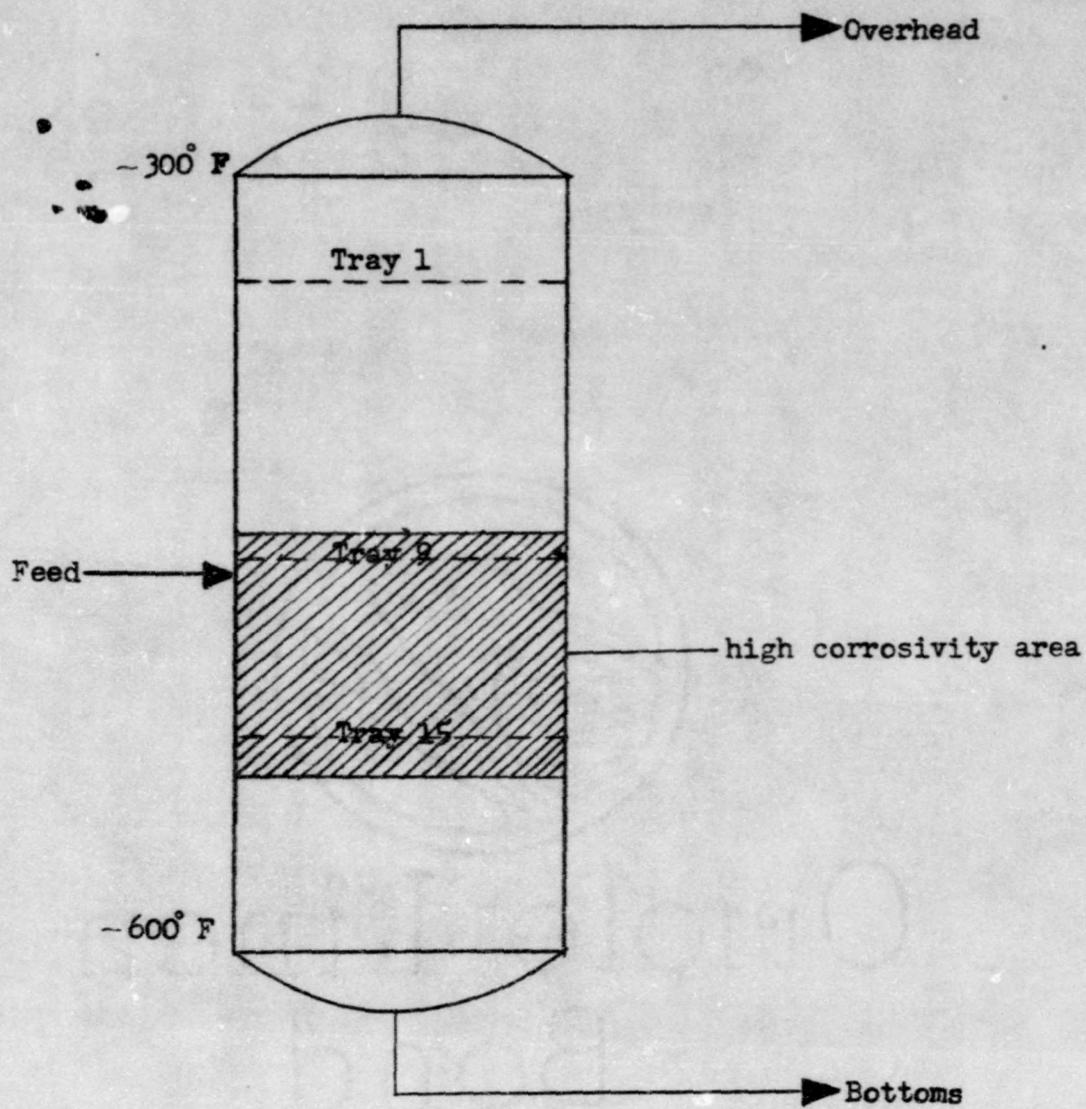


Fig.2 SRC 1 atmospheric fractionation column(T-105).⁽¹¹⁾

amount of chloride in the feed coal as the corroding species but there still existed many problems to be solved. A number of papers have been published on the subject to which the reader can refer (see Bibliography).

Corrosion experiments in coal liquids were carried out using pot measurements where a carbon steel coupon was suspended in coal liquid. The weight loss of the coupon would be measured periodically after washing ultrasonically in acetone. The schematic of the cell used for pot measurements is given in Figure 3. These investigations revealed a synergistic effect among ionic chloride, basic nitrogen compounds and phenols.

The basic nitrogen compounds were found to be responsible for chloride transport and concentration mechanism.⁽⁴⁾ Some of the other findings that would be relative to this work are given below:

1. Chloride additions in the order of 100 - 1000 ppm result in a very large increase of the corrosivity of the distillation column coal liquids (water soluble inorganic chloride).⁽²⁾
2. The presence of phenols and basic nitrogen compounds in the liquid is necessary for the increase of corrosivity to be observed in an open system upon introduction of chloride.⁽³⁾
3. The weak-base anilines and pyridines usually present in coal liquids produce a conjugate acid with pKa normally in the 4-7 range.⁽²⁾

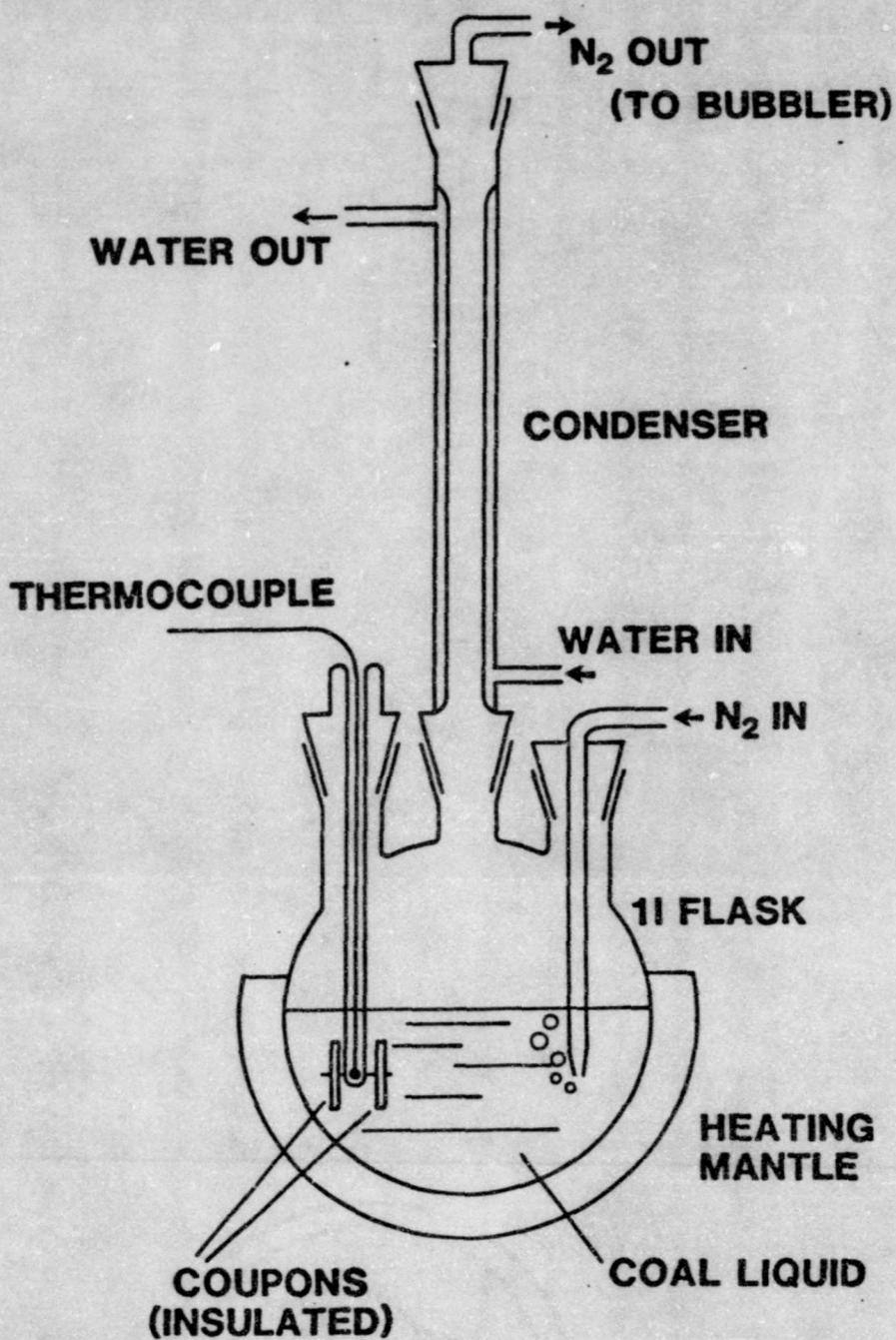


Fig. 3 Weight loss measurement cell used for coal liquids.⁽²⁾

4. Addition of dicyclohexylamine (DCHA) greatly reduces the corrosion rate. As a strong base DCHA would produce a conjugate acid with pK_a in the 10-11 range and it would limit the amine salt solubility, thus lowering the conductivity of the solution.⁽²⁾

The fact that the chlorides responsible for the corrosion were in a water-soluble form suggested water washing as a means of corrosion control in the coal liquids. Although the water washing seemed to be a good solution to the corrosion problem, it was seen later that wash waters could be very corrosive.⁽⁵⁾ This new finding created additional interest to determine what parameters contribute to the corrosivity of wash waters. The purpose of this dissertation is to conduct additional exploratory research in that area.

To approach this problem, aniline hydrochloride was chosen to simulate the wash waters of coal liquid. Aniline was one of the basic amine compounds expected to be responsible for carrying the corrosive chloride. A concentration range of 100 - 4000 ppm of chloride would be similar to the concentration range expected in the actual wash waters. Two different techniques, namely--electrochemical and weight loss measurements, were used to study the corrosivity of simulated wash waters. All these experiments were conducted at room temperature.

Although the weight loss measurements provided valuable information, they were slow and time consuming. For this

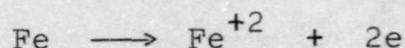
reason the main body of research was directed to exploring the electrochemical method as a faster alternative to the wieght loss measurements.

CHAPTER II

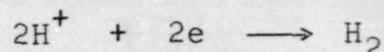
THEORY

Although the conventional pot measurements provided fairly reliable results, there has been added interest in different electrochemical methods since it takes as long as one week of daily measurements before results can be well established by weight loss measurements. The following is a brief discussion of the theory behind the electrochemistry of corrosion.

Corrosion* is the result of a basic chemical interaction of metal with its surroundings. This interaction is divided into two parts: the loss of electrons by metal, namely oxidation,



and a reduction part which involves gain of electrons, like a hydrogen evolution reaction



The overall reaction is the summation of oxidation and reduction reactions,



With the application of thermodynamics, one can predict the direction of a corrosion reaction. Such a prediction is possible by calculating the change in free energy of a system

$$\Delta G = -nFE$$

where ΔG is the free energy change, n is number of electrons

*metallic corrosion.

involved, F is the Faraday constant, and E is the cell potential. E can be calculated from the EMF series and half cell potentials for a given system. A negative value for ΔG indicates a spontaneous reaction.

I - Electrode Kinetics

Faraday's Law relates chemical charge and electrical energy. "For every equivalent of chemical reaction 96,500 coulombs must pass through the cell." Faraday's Law allows one to express the rates for electrochemical reactions in terms of electrical currents.

Before proceeding any further, one should keep in mind the following terms:⁽⁶⁾

Anode refers to the electrode at which a net oxidation process occurs.

Cathode refers to an electrode at which a net reduction process occurs.

Anodic reaction is synonymous with an oxidation reaction.

Cathodic reaction is synonymous with a reduction reaction.

Polarization can be defined as the displacement of electrode potential resulting from a net current or deviation from equilibrium potential.

Overvoltage, usually abbreviated η , is a measure of polarization with respect to the equilibrium potential of an electrode.

The discussion is based largely on the mixed potential theory of electrode kinetics as stated by Wagner and Traud.⁽⁷⁾ The basic assumptions of the theory are as follows:

(A) The kinetics of the various partial reactions can be treated separately.

(B) No net current flows from an electrode which is in equilibrium or at steady state, that is when the total rate of oxidation must equal the total rate of reduction.

II - Exchange Current Density

Equilibrium is a dynamic situation. Reactants and products jump back and forth at a very real rate, but since there is no accumulation of product, direct measurement of this rate is difficult. In the case of an electrochemical reaction, this exchange rate at equilibrium is called exchange current density. The relationship between exchange reaction rate and current density can be directly derived from Faraday's Law.⁽⁶⁾

$$r_{\text{oxid}} = r_{\text{red}} = \frac{i_0}{nF}$$

where r_{oxid} and r_{red} are the equilibrium oxidation and reduction rates and i_0 is the exchange-current density.

Depending on the metal electrode used, the exchange current density can vary as illustrated in Figure 4. A logarithmic scale for current density allows a wide range of points to be plotted. Table (I) lists some experimentally determined exchange current densities.

III - Activation and Concentration Polarization

Electrochemical reactions can be controlled by a slow step in the reaction sequence such as the electron-transfer step during hydrogen evolution. Activation polarization refers to these types of electrochemical reactions. The Tafel equation

TABLE 1
Exchange Current Densities⁽¹⁰⁾

Reaction	Electrode	Solution	i_0 , amp/cm ²
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Al	2N H_2SO_4	10^{-10}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Au	1N HCl	10^{-6}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Cu	0.1N HCl	2×10^{-7}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Fe	2N H_2SO_4	10^{-6}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Hg	1N HCl	2×10^{-12}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Hg	5N HCl	4×10^{-11}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Ni	1N HCl	4×10^{-6}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Pb	1N HCl	2×10^{-13}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Pt	1N HCl	10^{-3}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Pd	0.6N HCl	2×10^{-4}
$2\text{H}^+ + 2\text{e} = \text{H}_2$	Sn	1N HCl	10^{-8}
$\text{O}_2 + 4\text{H}^+ + 4\text{e} =$ $2\text{H}_2\text{O}$	Au	0.1N NaOH	5×10^{-13}
$\text{O}_2 + 4\text{H}^+ + 4\text{e} =$ $2\text{H}_2\text{O}$	Pt	0.1N NaOH	4×10^{-13}
$\text{Fe}^{+3} + \text{e} = \text{Fe}^{+2}$	Pt		2×10^{-3}
$\text{Ni} = \text{Ni}^{+2} + 2\text{e}$	Ni	0.5N NiSO_4	10^{-6}

shows the relationship between reaction rate and overvoltage for activation polarization: (16)

$$\eta_a = \pm \beta \log \frac{i}{i_0}$$

where η_a is overvoltage, β is Tafel constant, and i is the rate of oxidation or reduction in terms of current density.

If a logarithmic current scale is used, the relationship between overvoltage or potential and current density is a linear function. (6) Figure 5 shows an activation polarization curve of a hydrogen electrode. The reaction rate changes by one order of magnitude for each 100 mv or 0.1 volts change in overvoltage. This gives beta a value of 0.1 volts which should normally be observed.

Concentration polarization occurs when one of the reactants is consumed at an electrode faster than it can be supplied from the bulk of the solution. The rate of the reaction is limited by diffusion from the solution to the electrode surface.* Since there is an unlimited supply of metal atoms during metal dissolution, concentration polarization is observed usually only during the cathodic reaction. This phenomenon is illustrated in Figure 6. Figure 7 shows the effects of different parameters on the concentration polarization curve.

*limiting diffusion current density i_L

$$i_L = \frac{DnFC_B}{x}$$

D is diffusion coefficient of the reacting ions, C_B is the concentration of reacting ions in the bulk solution, x is the thickness of the diffusion layer. (6)

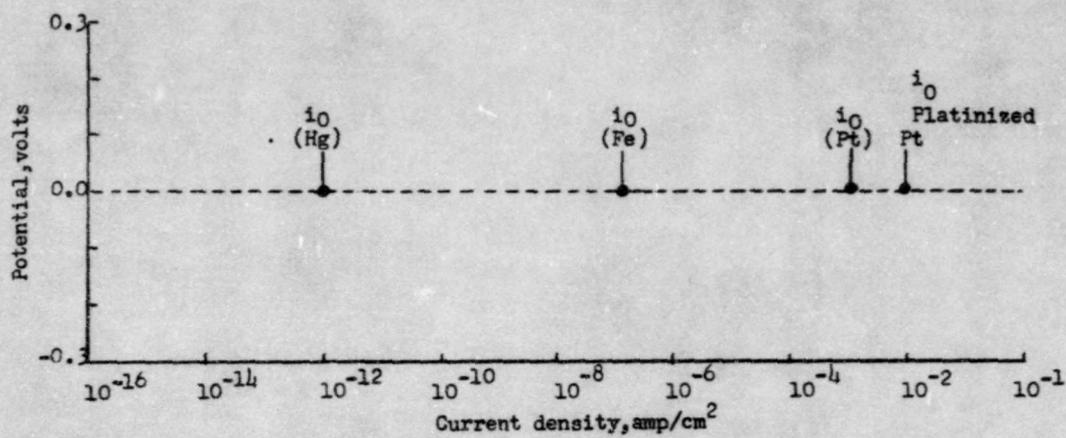


Fig.4 Hydrogen-hydrogen-ion exchange current densities. (6)

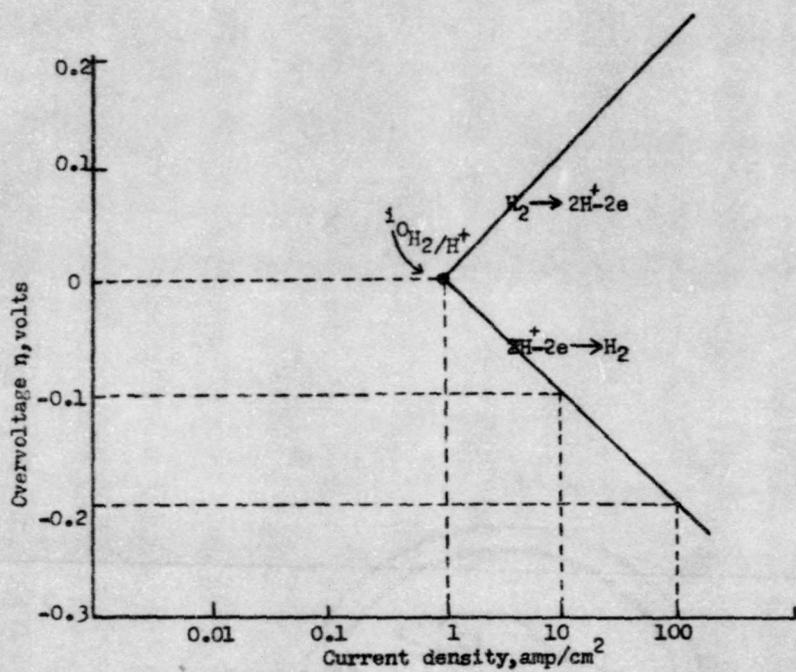


Fig.5 Activation-polarization curve of a hydrogen electrode. (6)

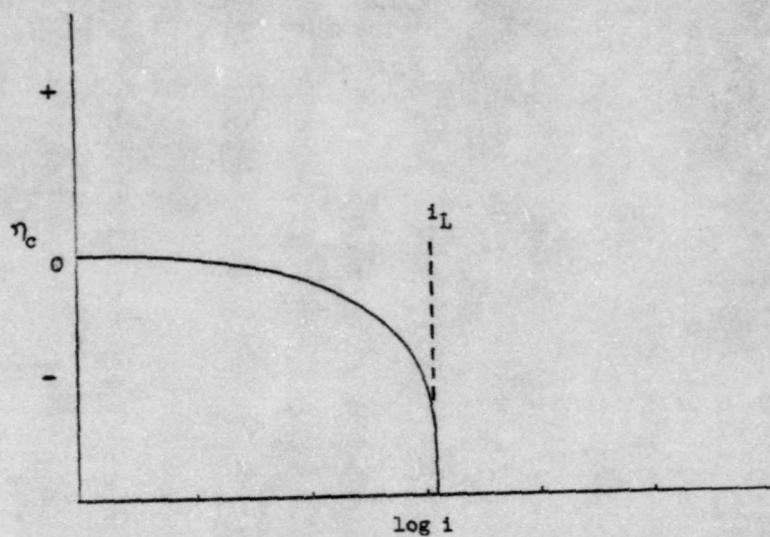


Fig. 6 Concentration polarization curve (reduction process).⁽⁶⁾

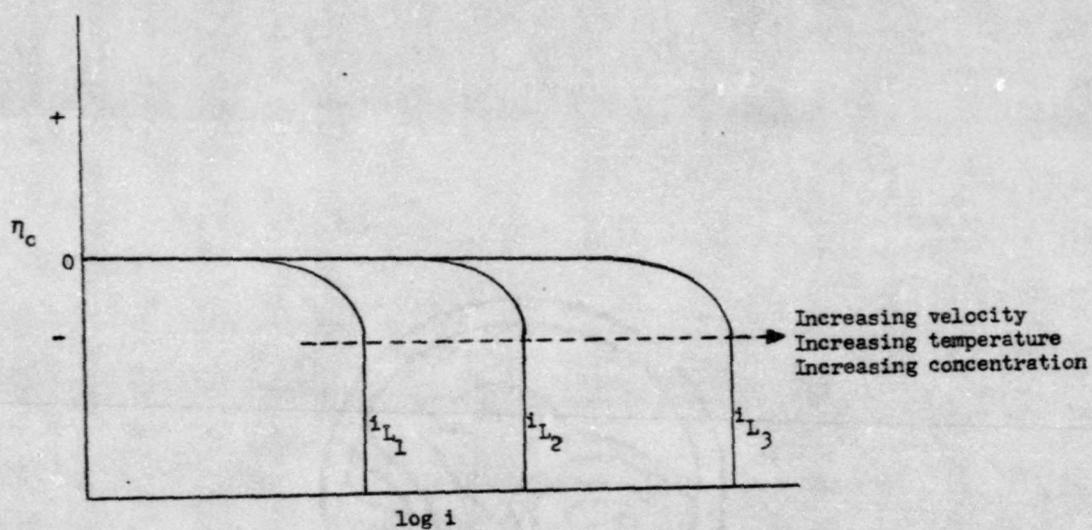


Fig. 7 Effect of environmental variables on concentration polarization curve.⁽⁶⁾

IV - Mixed Electrodes

Unlike a reversible system, in a corroding system more than one oxidation reduction system is in contact with an electrode. Consider dissolution of a metal in acidic solution. If the metal electrode is in equilibrium with its ions, then we can show this by a reversible potential: metal - metal - ion electrode reaction. Also, under equilibrium conditions, we can show the hydrogen-electrode reaction on a metal surface by another reversible potential (Figure 8). Now if the second hypothesis of the Wagner Theory holds, there must be a point where the total rate of oxidation equals the total rate of reduction. The only point that this can happen is at the intersection represented by the corrosion potential, E_{corr} . At this point the rate of metal dissolution is equal to the rate of hydrogen evolution expressed in terms of current density. This current density is referred to as corrosion current density, i_{corr} , since it represents the metal dissolution rate. Using Faraday's Law, this current density can be converted to the corrosion rate of the metal in the acidic solution.

V - Corrosion Rate Measurements

Based on mixed-potential theory, corrosion rate can be measured electrochemically. During the course of this project, one of these electrochemical methods, namely Tafel extrapolation, has been used. Below is a brief description of the method.

Cathodic or anodic polarization, or both, can be used to obtain data for corrosion rate measurement as shown in Figure 9. The actual applied-current potential curves do not follow a semi-logarithmic form near the corrosion potential because the applied current is the difference between the rates of the anodic and cathodic reactions. The linear region is referred to as the Tafel region and is used for extrapolation (to the corrosion potential). At the corrosion potential, the rate of hydrogen evolution is equal to the rate of metal dissolution and corresponds to the corrosion rate of the system.

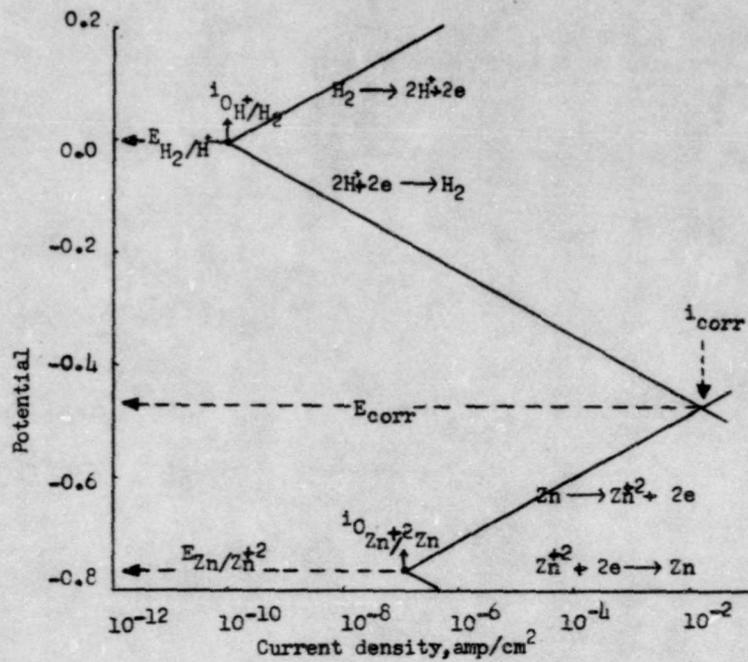


Fig. 8 Electrode kinetic behavior of pure zinc in acid solution.(6)

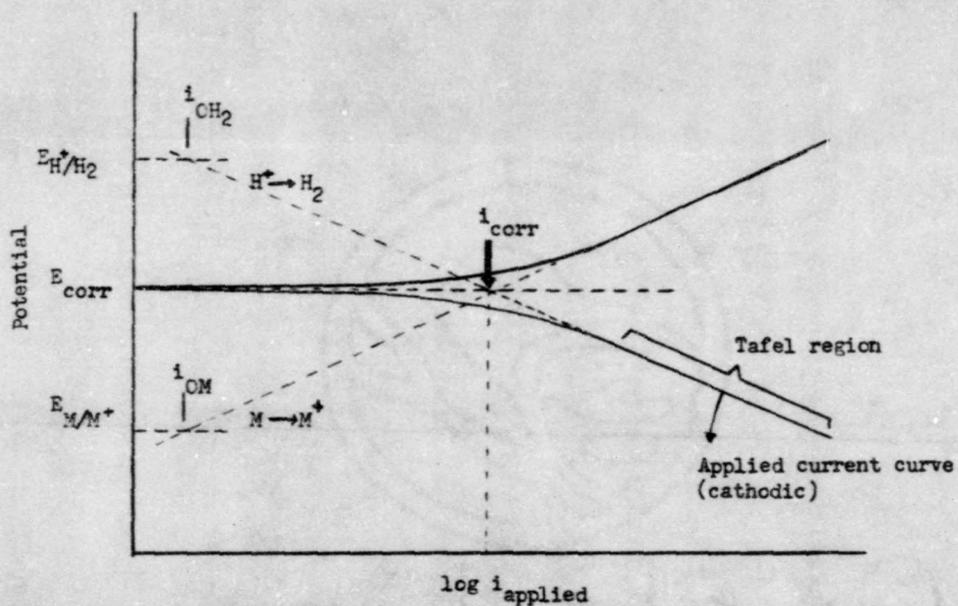


Fig. 9 Applied current anodic & cathodic polarization curves of a corroding metal showing Tafel extrapolation.

CHAPTER III
EXPERIMENTAL

I - Instrumentation

The instrumentation described below is the result of many modifications used, up to this date, to eliminate many problems encountered.

The cell consists of a glass container which holds the electrolyte and three electrodes. The metal sample is termed the "working electrode." An auxiliary or counter electrode supplies a cathodic current to the working electrode. The auxiliary electrode is usually made of some inert material like platinum or graphite. The potential of the working electrode is measured with respect to a reference electrode by a potentiometer-electrometer circuit. Current is measured by an ammeter. A simplified diagram is shown in Figure 10. In practice, reducing the value of the variable resistance, R , increased the current.⁽⁶⁾ It should be mentioned that the actual potentiostat is much more complex. It can range from a homemade unit like the one used for this study (Figures 11 and 12) to a very sophisticated and expensive version. Some of the features of the unit used in this project are (a) capability of two current scales, 1x covering from 0.01 microamp to 100 microamp and 10x covering from 0.01 microamp to 1.0 milliamp; (b) an interrupter switch to determine the ohmic-resistance of the solution;

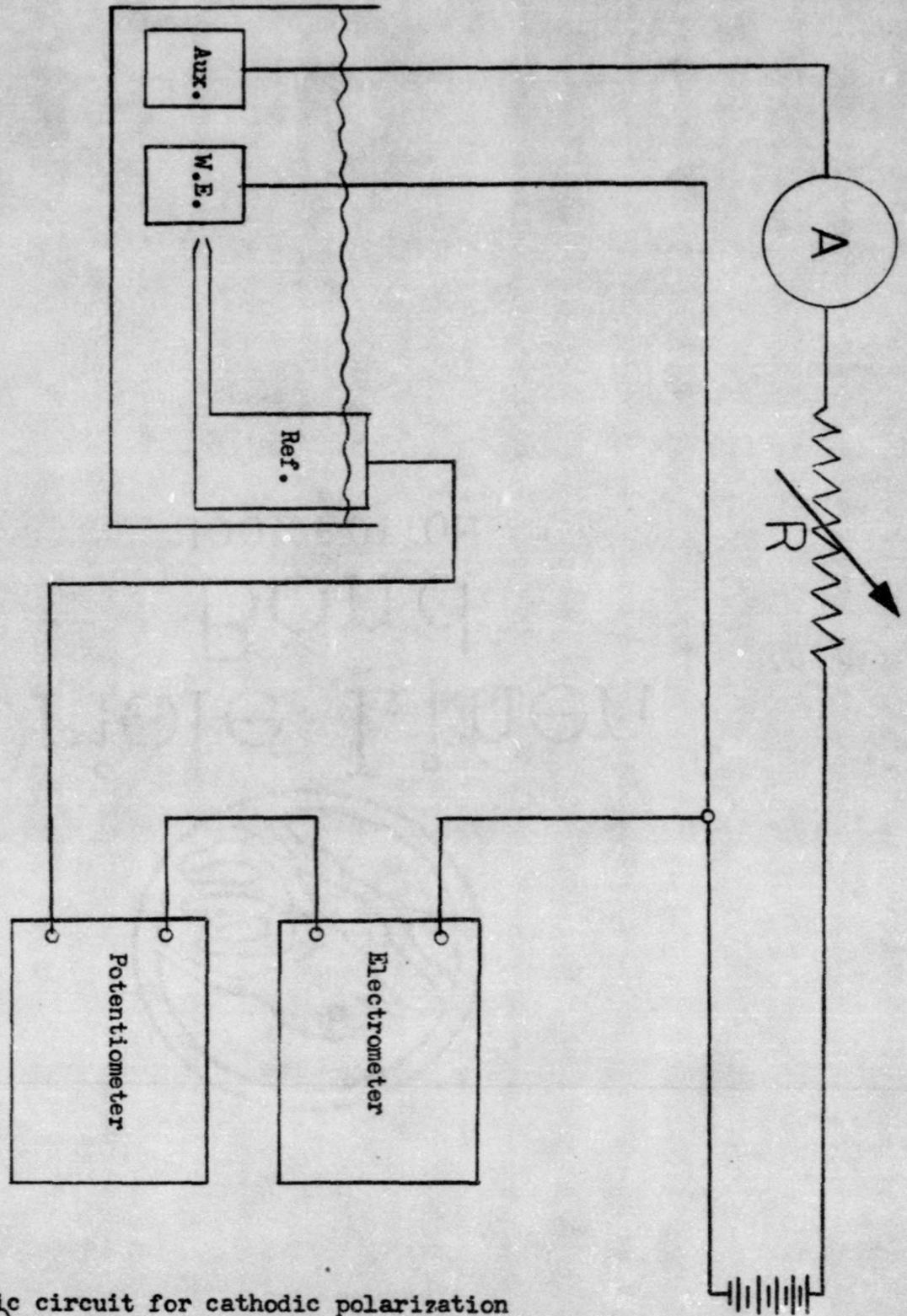


Fig. 10 Electric circuit for cathodic polarization measurements. (6)

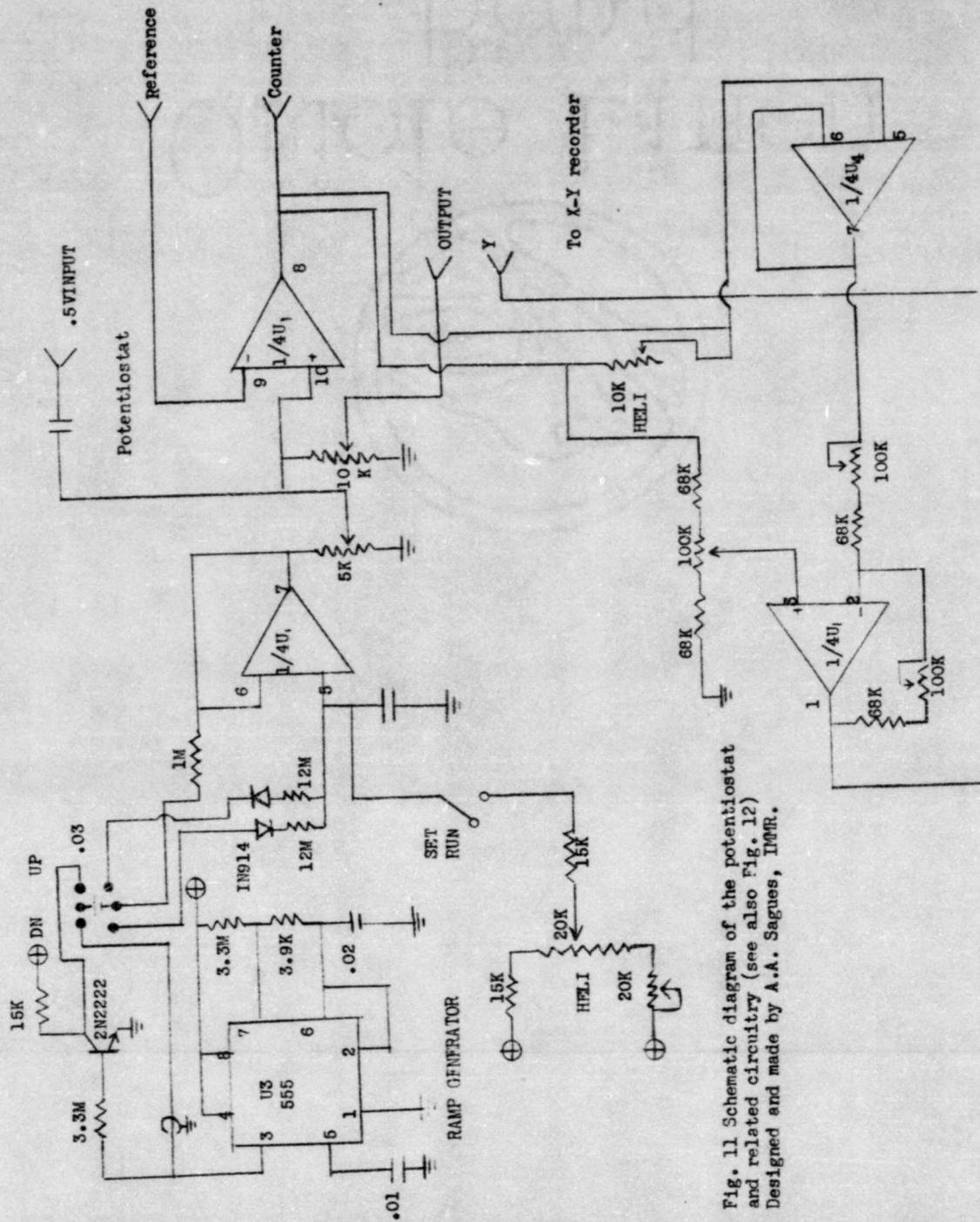


Fig. 11 Schematic diagram of the potentiostat and related circuitry (see also Fig. 12) Designed and made by A.A. Sagues, IMMR.

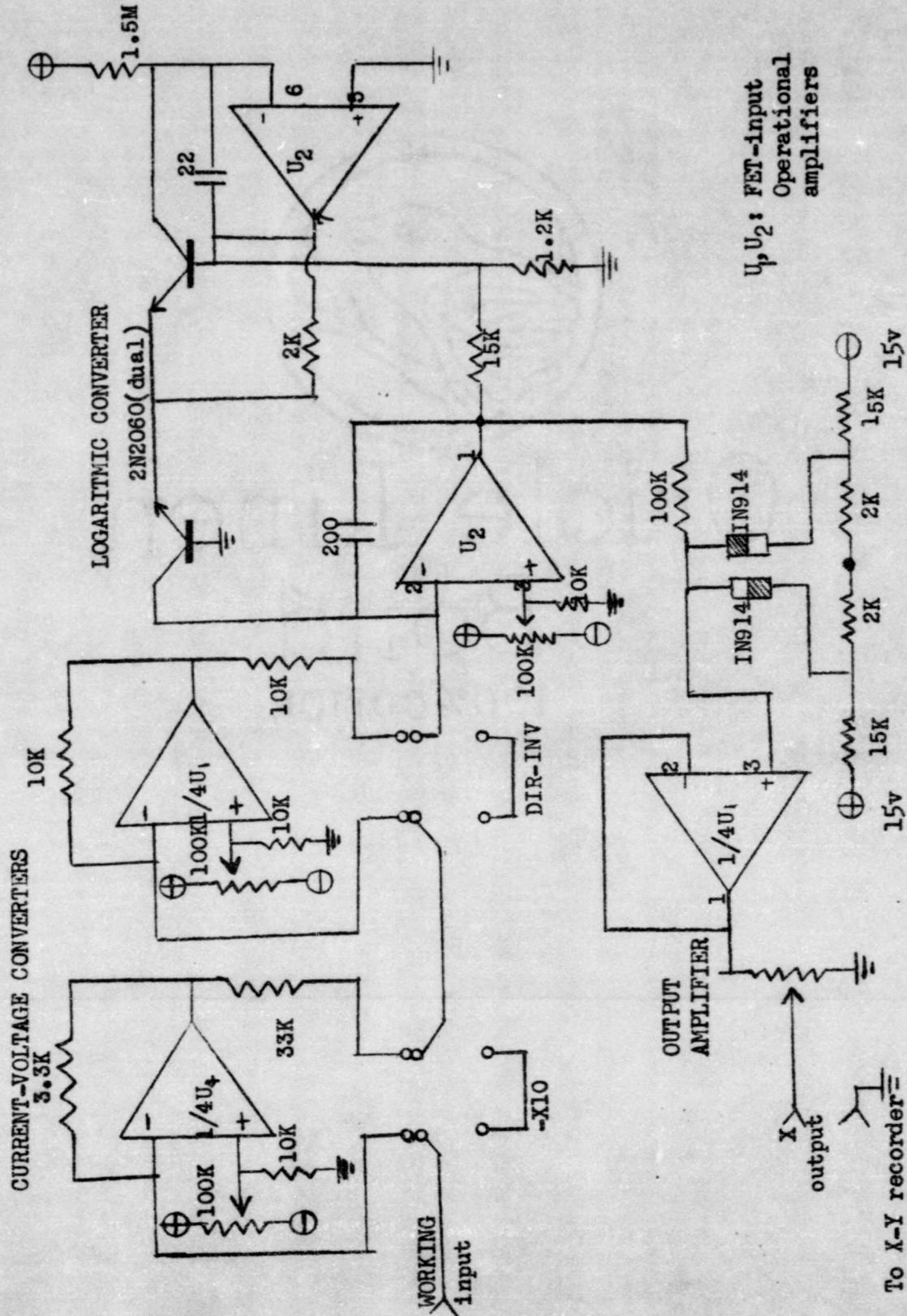


Fig. 12 Schematic diagram of the potentiostat and related circuitry.

(c) a circuit to compensate for ohmic drop (which later proved to be useless); (d) a switch to choose the direction of the run, whether it started from a low potential upwards or from a high potential downwards. The scan rate of this unit was roughly 0.2 mv/sec.

The cell used in this study is shown in Figure 13. A Ferrovac E, pure iron screw with the surface area of approximately 0.42 cm^2 was used as the metal sample. The iron screw was attached to the tip of a teflon rod to make up the working electrode. The auxiliary or counter electrode was composed of a circular platinum disc, and a silver chloride electrode was used as a reference electrode. As it is shown in Figure 13, there is a probe attached to the reference electrode. This probe is called a Haber-Luggin capillary and it extends from the reference electrode to the working electrode. The purpose for using this probe was to decrease the resistance caused by the electrolyte between two electrodes. This resistance results in an ohmic or IR drop. High values of IR drop are encountered in solutions with low electric conductivity, especially during high cell currents.

Although the Luggin probe is necessary to decrease IR drop, it does not compensate for the resistance of the solution completely which resulted in a non-linear Tafel region. In an attempt to overcome this problem an additional electronic circuit was used to compensate for the resistance of the solution. However, this change did not produce acceptable results and interfered with other unit functions causing other problems. It was learned that the best way to compensate

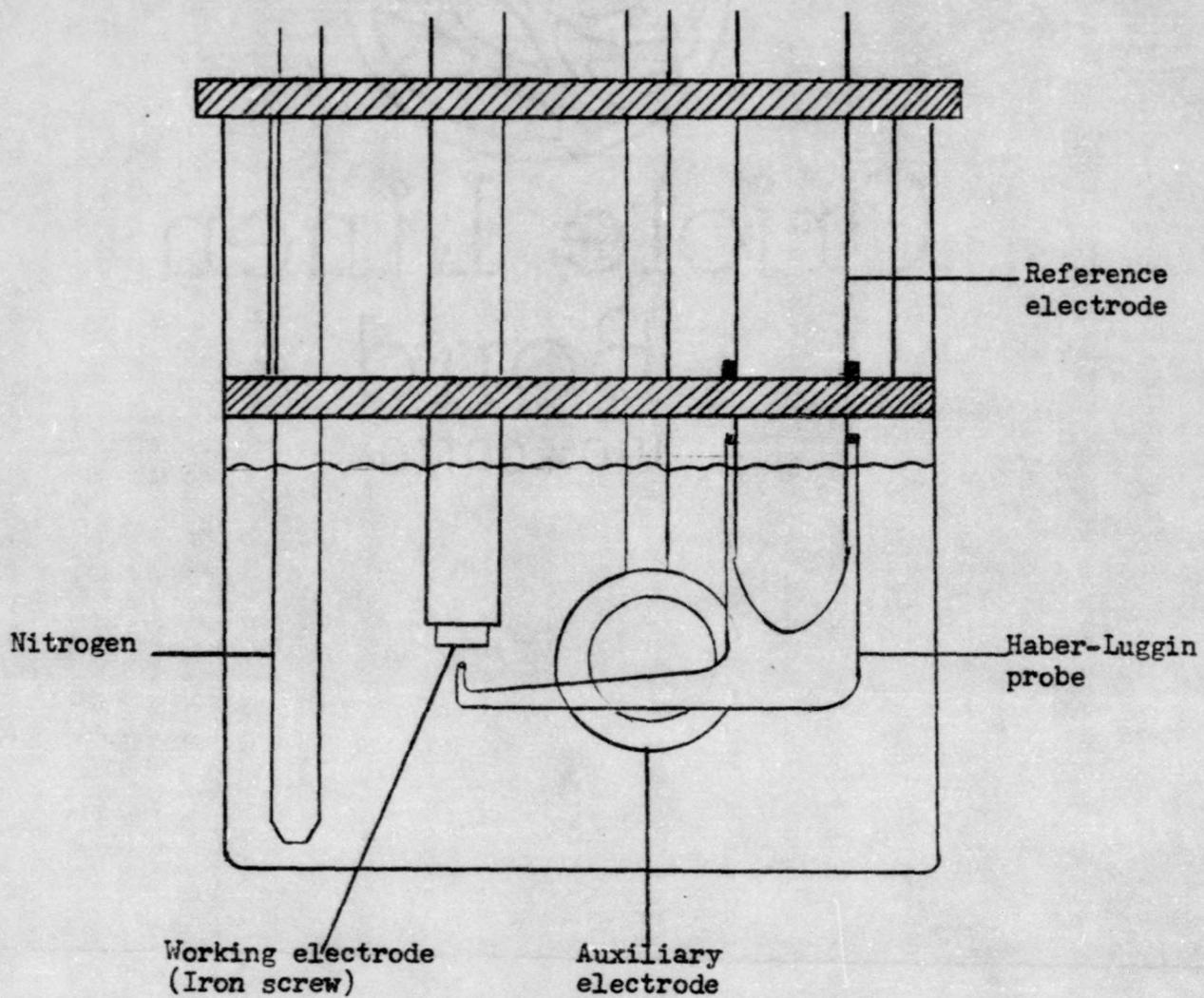


Fig. 13 Three electrode system used for corrosion rate measurements.

was to measure the ohmic drop. The measurement was made by means of the so-called "interruption method" which is based on periodical short-timed interruption of the polarization current by switches, assuming that ohmic drop disappeared instantaneously after the interruption of current.⁽⁸⁾ The polarization current, on the other hand, decayed slowly with time. A time delay oscilloscope with a memory was used to register the pattern during each interruption (Figure 14). Interruptions were done every 50 mv along the way.

To keep the oxygen out of the solution it was deaerated with nitrogen gas at the rate of approximately one bubble per second. The plots were recorded by means of an x-y recorder. For weight loss measurements mason jars were used. The specimens were M-1044 carbon steel and had surface area of approximately 0.5 square inches. A glass rod hanging from the top of the jar was used to suspend the coupons in 500 ml of solution. A magnetic stirrer was used for agitation.

II - Procedure

The iron specimen was removed, sanded with a 600 grit sandpaper, and cleaned with acetone before each run to remove the corrosion products and any possible film that might have formed on the surface. Each solution* of interest was filtered with a number one quantitative filter paper to remove the oxidized species and other impurities before

*Aniline hydrochloride was obtained from Aldrich Chemicals and was dissolved in D.I. water to give the simulated solutions.

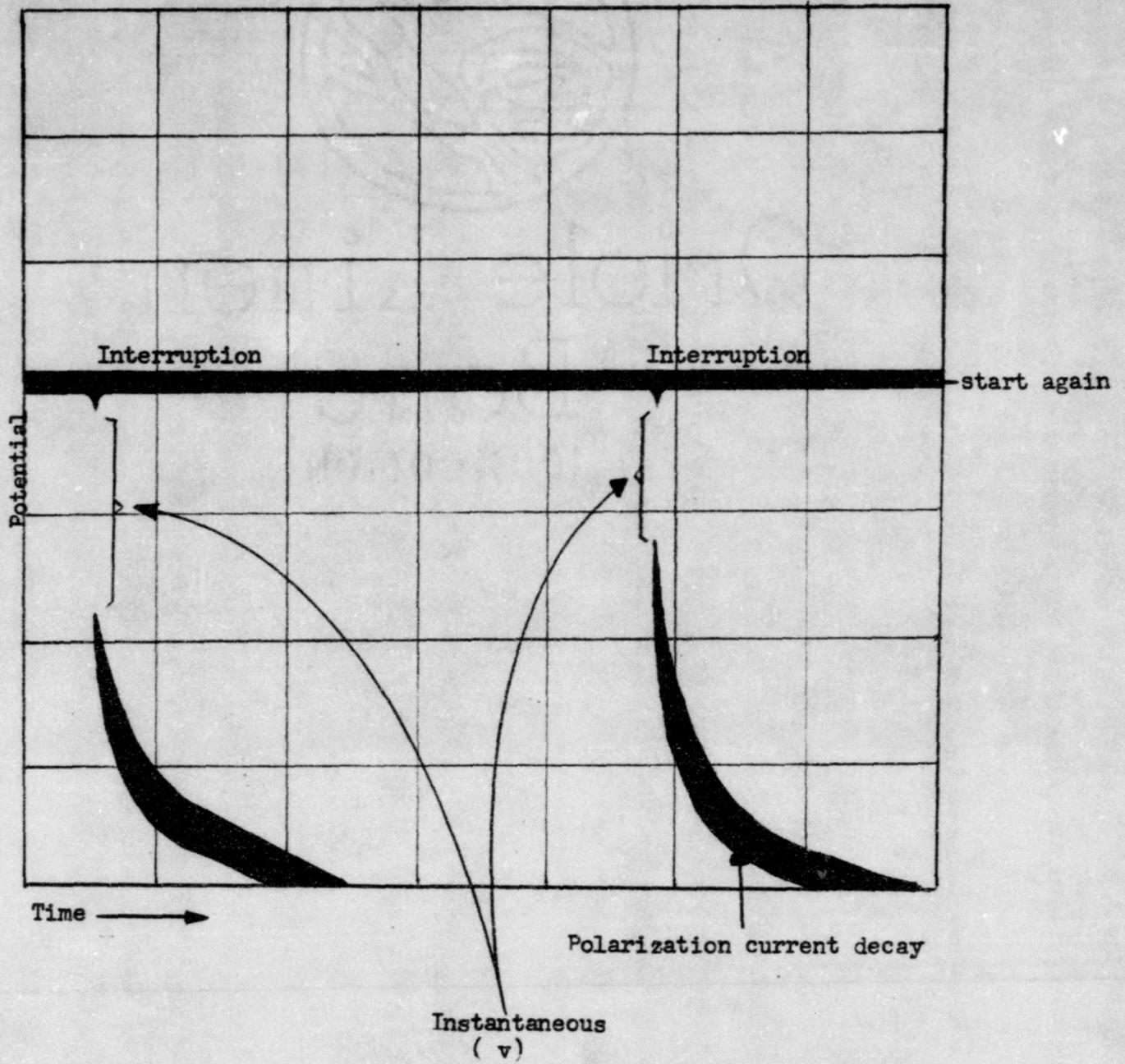


Fig. 14 Instantaneous ohmic drop & depolarization curve as seen on the scop.

deaerating for at least half an hour with nitrogen gas. Before each run the working electrode was soaked in the solution with no current running for at least ten minutes. It was necessary to determine E_{corr} before starting each run. E_{corr} was determined by disconnecting the counter electrode and measuring the potential after it reached a stable value.

For weight loss measurements, each coupon was ground with 200, 400, and finally with a 600 grit sandpaper and cleaned with acetone before each run. For periodical measurements, each coupon was cleaned ultrasonically in acetone and dried with a paper towel.

CHAPTER IV
RESULTS AND DISCUSSION

Although the electrochemical method for measuring the corrosion rates is known and has been in practice since the 1950's, it is difficult to find a good literature reference that shows the usage of the method in a clear and inclusive way. Most of the papers written on the subject were produced in the 50's and 60's which, of course, does not include the current developments in solid state technology. Another time related problem concerns the usage of coal to produce synthetic fuels. In other words, none of the papers searched during the course of this project were related to the application of this method in coal liquids or other similar systems. This lack of current literature presented the researcher with the problem of determining many unknown factors by using the "trial and error" approach as the project proceeded. The work was primarily of an exploratory nature. For this reason most of the effort was spent in removing the obstacles encountered during the short time period of the project. It should be mentioned that some manufacturers can now provide the researcher with state-of-the-art electronic equipment that utilize microprocessors and microcomputers that minimize many of the problems encountered using the homemade unit. The question as to how they perform is not in the scope of this paper; however, the interested reader can refer to any future papers produced by IMMR in relation to the same project (electrochemical measurements by corrosion rates).

From the 120 plus Tafel plots produced, only a few showed behavior amenable to simple interpretation. Figure 15 shows one of the early plots obtained by using a carbon steel specimen in 50 ppm of aniline hydrochloride solution. (No Luggin probe was being used at the time.) This solution was chosen since aniline hydrochloride was expected to be present in the wash waters as the basic nitrogen compound carrying the corrosive chloride. An examination of this plot shows that the apparent Tafel region was very steep. The slope of this region for acid solutions is usually about 100 mv per decade of the current scale. This steepness could be the result of a number of different factors. Most of the time the mass transfer effects or concentration-polarization (refer to the theory section) were blamed, but it should be noted that many other factors--such as (a) the resistance of the solution, (b) the IR drop, (c) the presence of dissolved oxygen which could be reduced and therefore interfere with the reduction process, or (d) a combined effect of all mentioned above could have resulted in a complex behavior in the Tafel region.

After other less acceptable results were obtained, two modifications were applied. First a Luggin probe was used which would extend from the reference electrode to the working electrode, thus minimizing the effects of the IR drop. Second, the current scale was expanded to 1 mA or 1000 μ A, allowing the researcher to have more extended plots in the case of high corrosive medium which would shift the i_{corr} to higher current densities. The results are shown in Figure 16.

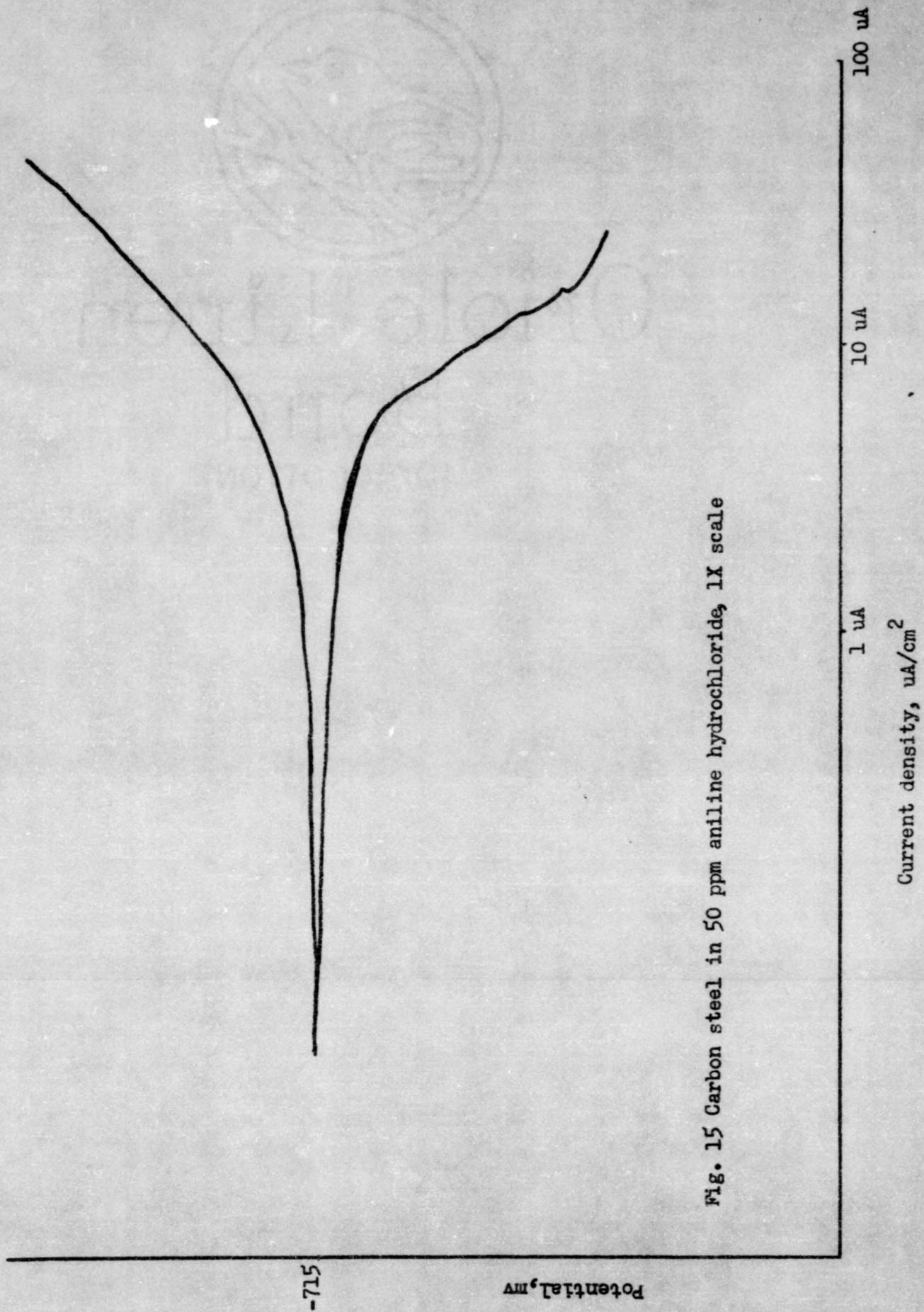


Fig. 15 Carbon steel in 50 ppm aniline hydrochloride, 1X scale

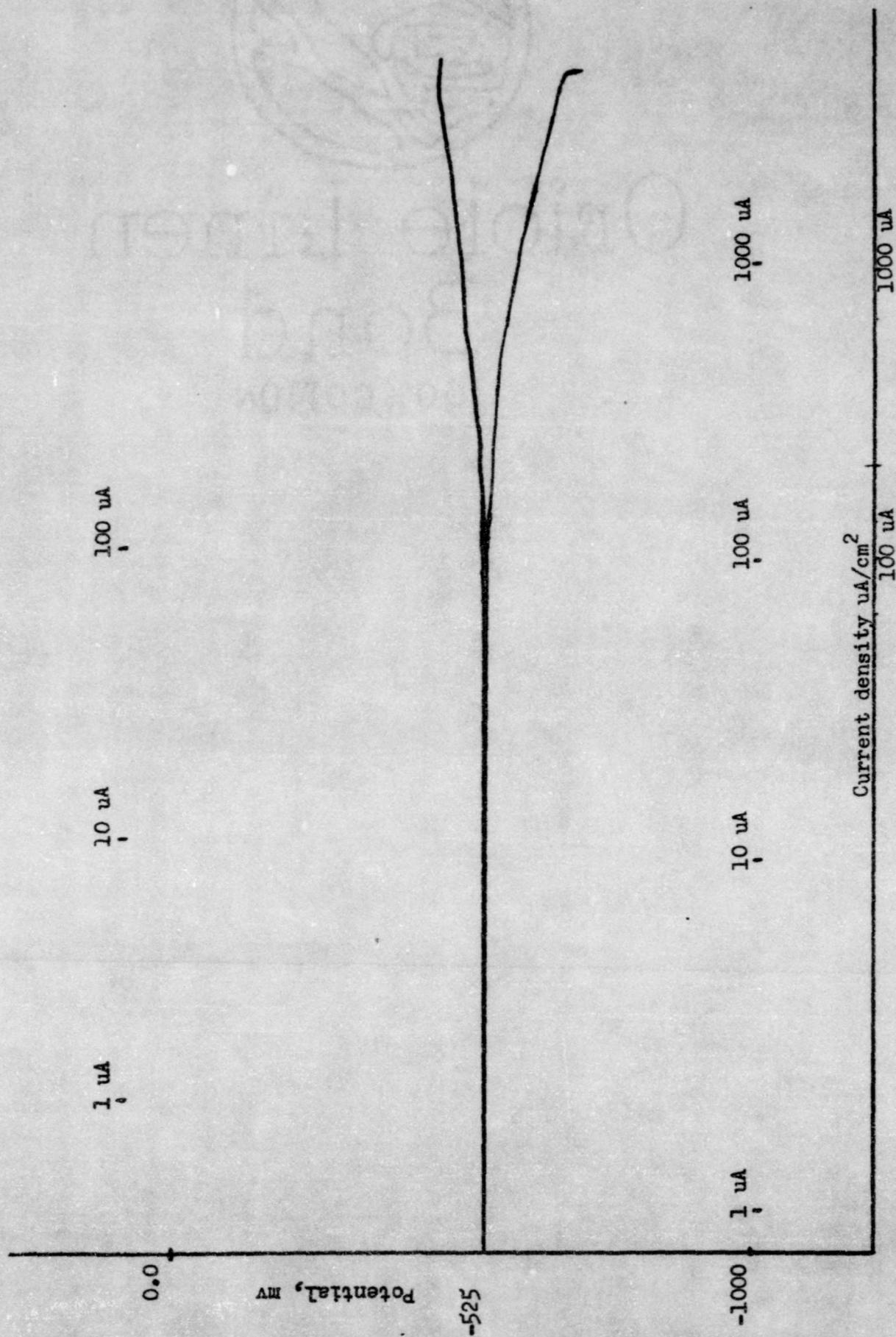


Fig. 16 0.055M sulfamic acid and 10X scale calibration.

This solution was used to test the experimental arrangements by comparing the results with published data for a carbon steel specimen in 0.055 M sulfuric acid.⁽⁹⁾ The calibration of the new current scale is also shown in this Figure. A symmetrical plot with a slope of 100 mv/dec on the cathodic portion and 60 mv/dec on the anodic portion is an acceptable Tafel plot, although it is apparent that because of high corrosivity of sulfuric acid, a greater expansion of the current scale is needed. Since this study was conducted on systems less corrosive than sulfuric acid, the lack of another current expansion scale did not present any problems. Moreover, with the amine hydrochloride medium used, results were complex and interpretation of the data was difficult.

The presence of oxygen in the solution as mentioned above could be another source of error due to interference in the reduction process. To minimize the problem, the D.I. water was boiled before dissolving the aniline hydrochloride in it and then deaerated with nitrogen gas bubbling for one to two hours. The result was a much smoother and more linear plot which is shown on Figure 17. The solution was a 1000 ppm chloride as aniline hydrochloride, and the specimen was a new carbon steel screw. The extrapolation of Tafel region intersected E_{CORR} at about 18.50 microamp which is roughly equal to 19.20 mils per year (MPY).

One problem which persisted during the course of this project was the formation of bubbles on the surface of the working electrode. Although one would guess that these bubbles were formed during the hydrogen reduction process, in actuality the hydrogen reduction process takes place mostly

during the anodic part of the plot. These bubbles were only present in the cathodic portion of the run and toward the higher current end. No explanations could be found to describe the nature of this problem. Moreover, no solutions could be found to eliminate the problem. However, use of one modification in the potentiostat proved to be useful. The unit was provided with the ability of scanning in the reverse direction--that is, instead of going from the high cathodic current end of the plot to the corrosion potential, it could start at the corrosion potential and scan toward high cathodic current end. Since most of the bubbles were formed at the high current end, the interference introduced by bubble formation was minimized. Another useful aspect of using a reverse scan was that most of the reaction products were formed on the surface of the working electrode toward the high current end. A reverse scan would minimize any interference presented by these products. Results are shown on Figure 18. Another carbon steel screw was used in a 1000 ppm chloride as aniline hydrochloride. The solution was deoxygenated and the reverse scanning was conducted in cathodic portion. The corrosion rate calculated by this plot was about 50 MPY.

Up to that point the specimen used as the working electrode was a 1080 type carbon steel screw. This type of material contained a certain percentage of other metal impurities which can cause a galvanic coupling effect. Galvanic coupling takes place when an electrical contact exists between two dissimilar metals. It was noted that the possible redox

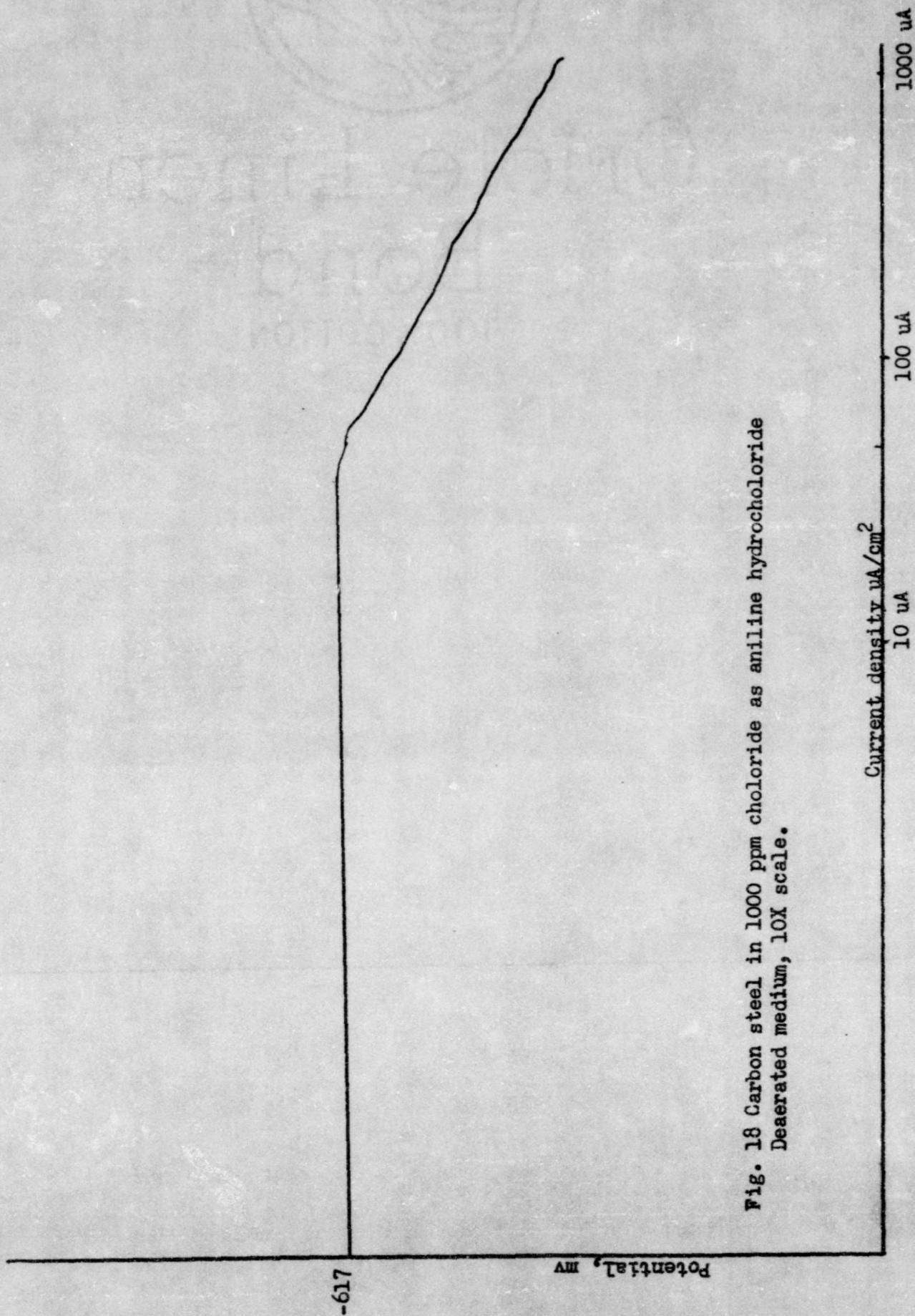


Fig. 18 Carbon steel in 1000 ppm aniline hydrochloride
Deaerated medium, 10X scale.

process that could take place within the carbon steel specimen could interfere with the redox process under study. To eliminate this problem a Ferrovac E pure iron screw was built and used instead of the carbon steel screw.

As mentioned in Chapter III, the interruption method was adapted for dealing with the IR drop of the solution. The interruptions were applied every 50 mv. The instantaneous part could be registered and measured on the scope and then subtracted from the voltage at the time of the interruption. The new potential value was then marked on the plot, and a straight line was drawn through these points to intercept the corrosion potential--as illustrated in Figure 19.

Another important point which is shown in Figure 19 is that the vertical scale was expanded by a factor of two so that every division on the graph paper would be 50 mv instead of 100 mv, allowing for a more extended Tafel region.

An experimental procedure that produced acceptable results was established, and a series of Tafel plots were measured in the following fashion:

A pure iron specimen with the surface area of 0.422 cm^2 was used in three different concentrations of aniline hydrochloride solution. These solutions were deaerated with nitrogen gas bubbling and were filtered. A reverse scan was used for all cathodic parts. The current scale was 0.001 to 1 milliamp and the potential scale was 50 mv per division.* The

*Each division was equal to one centimeter in the graph paper.

cathodic parts are illustrated in Figures 19 through 21. After the anodic portions of the curves were obtained, they were put together and reduced in size and are illustrated in Figures 22 through 24. The corrosion rates obtained by these extrapolations of 1000, 2000, 4000 ppm chloride solutions are respectively 8.55 MPY, 31.5 MPY, 21.1 MPY.

The corrosion rate of 2000 ppm solutions seemed to be unusually high compared with the other two solutions. The comparison of this plot with an earlier plot, Figure 25, showed that this high rate was not unexpected since Figure 25 showed a corrosion rate of 36 MPY. Some of the results obtained in the course of this project are summarized in Table 2.

To compare the results obtained by electrochemical technique with weight loss technique, a series of weight loss measurements were conducted. The solution used for these measurements was not deoxygenated. The other factors were kept similar to the test conditions for the electrochemical method. Earlier studies using weight loss measurements showed the dependence of corrosion rates on the temperature.⁽⁵⁾ As illustrated in Figure 26, the corrosion rate for a carbon steel coupon in 1000 ppm chloride (as aniline hydrochloride) dropped to approximately 147 MPY at 23°C. This drop seems to be very high; however, these are the initial corrosion rates.

The first experiment in this investigation involved a carbon steel coupon in 1000 ppm chloride (as aniline hydrochloride) at room temperature. As shown in Figure 27, the

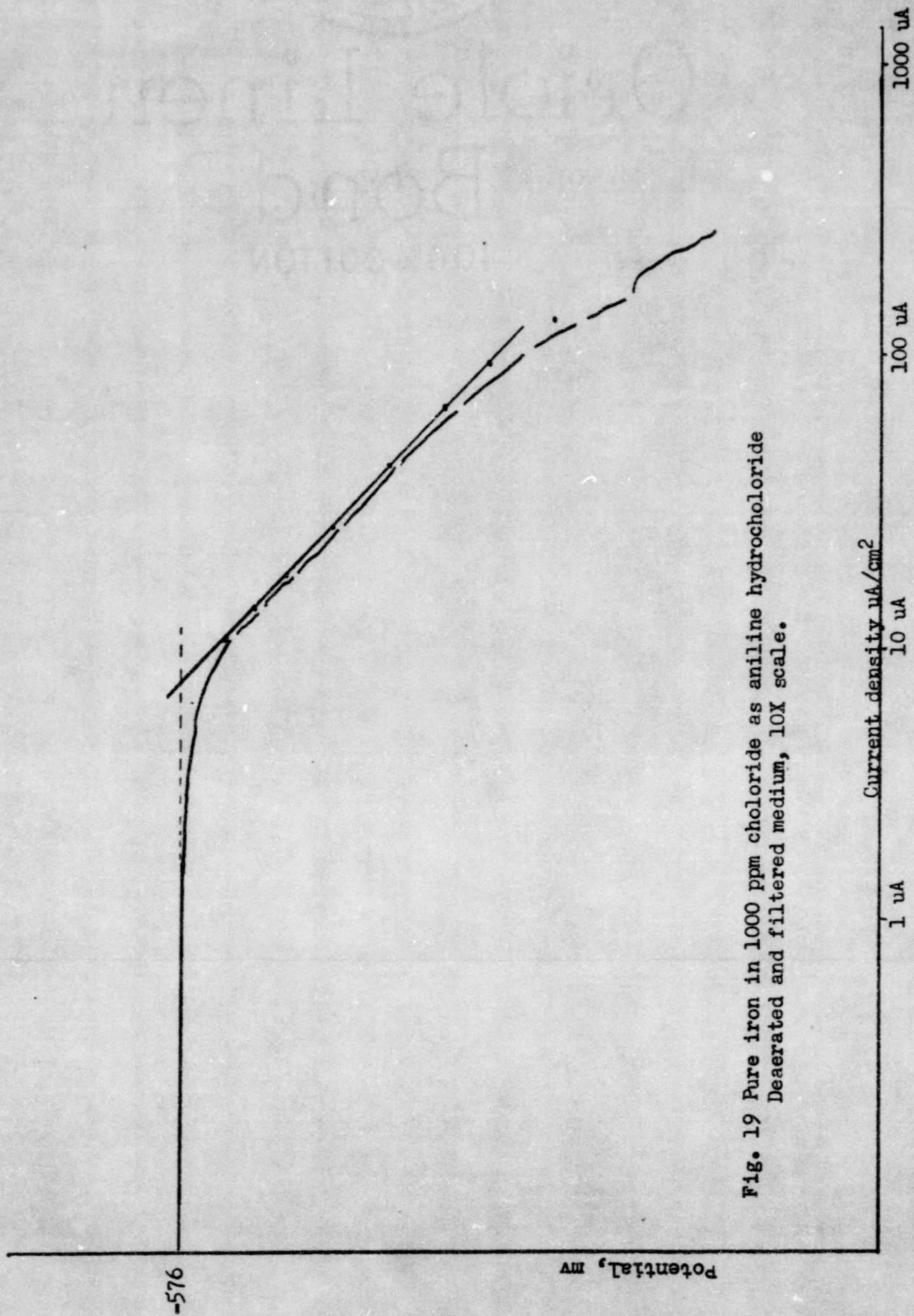


Fig. 19 Pure iron in 1000 ppm chloride as aniline hydrochloride
Deaerated and filtered medium, 10X scale.

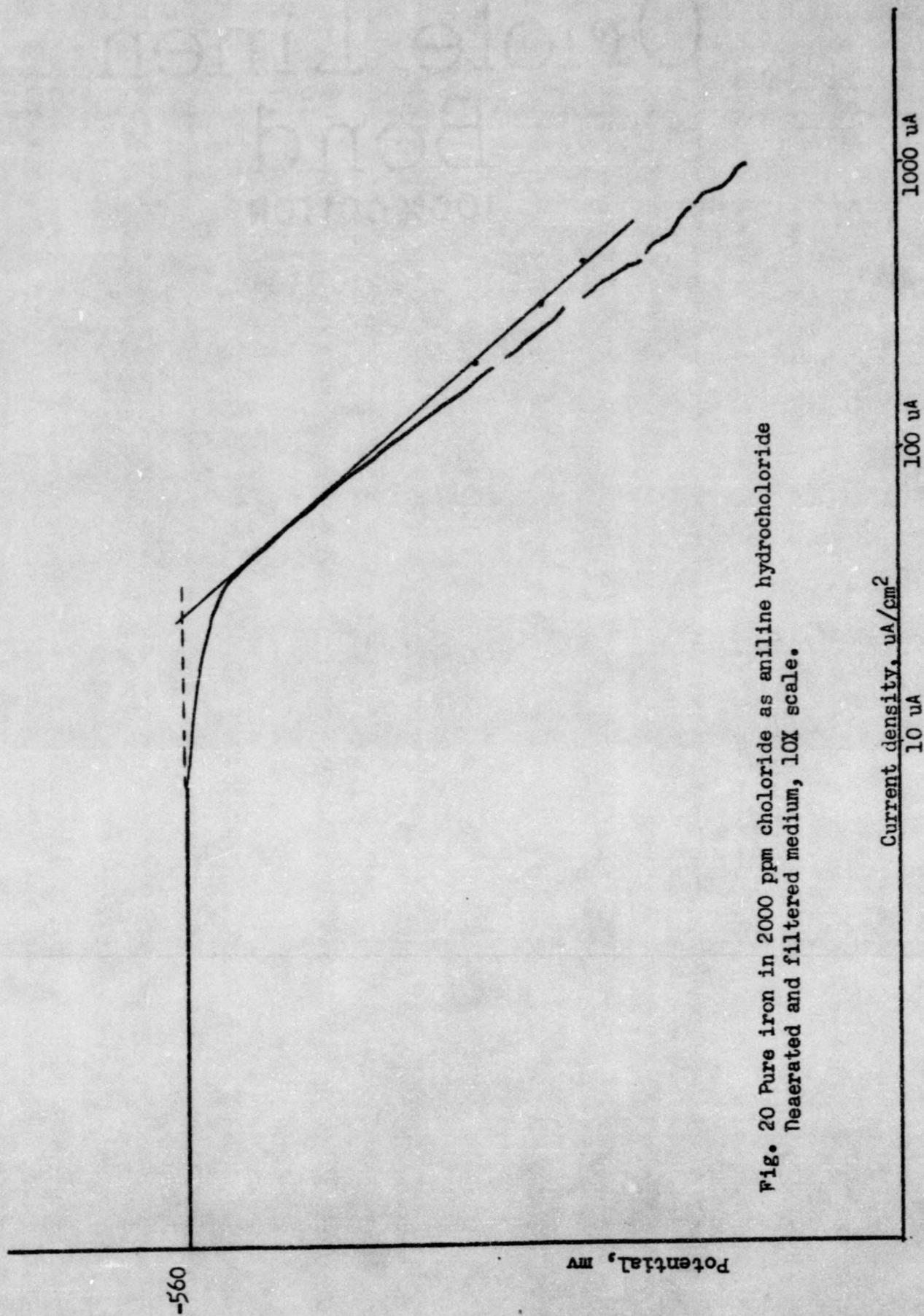


Fig. 20 Pure iron in 2000 ppm chloride as aniline hydrochloride
Deaerated and filtered medium, 10X scale.

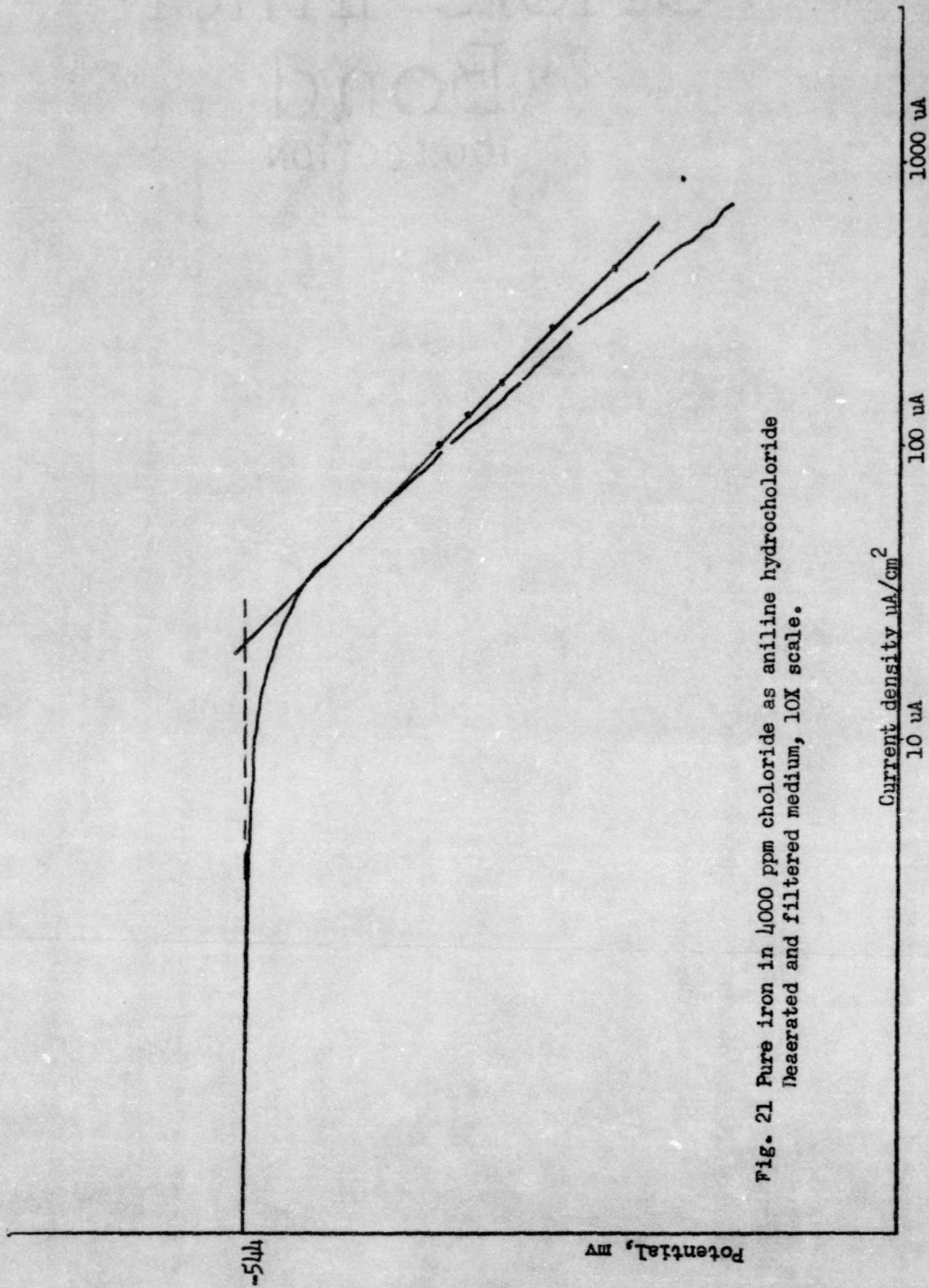


Fig. 21 Pure iron in 4000 ppm chloroform as aniline hydrochloride
Deaerated and filtered medium, 10X scale.

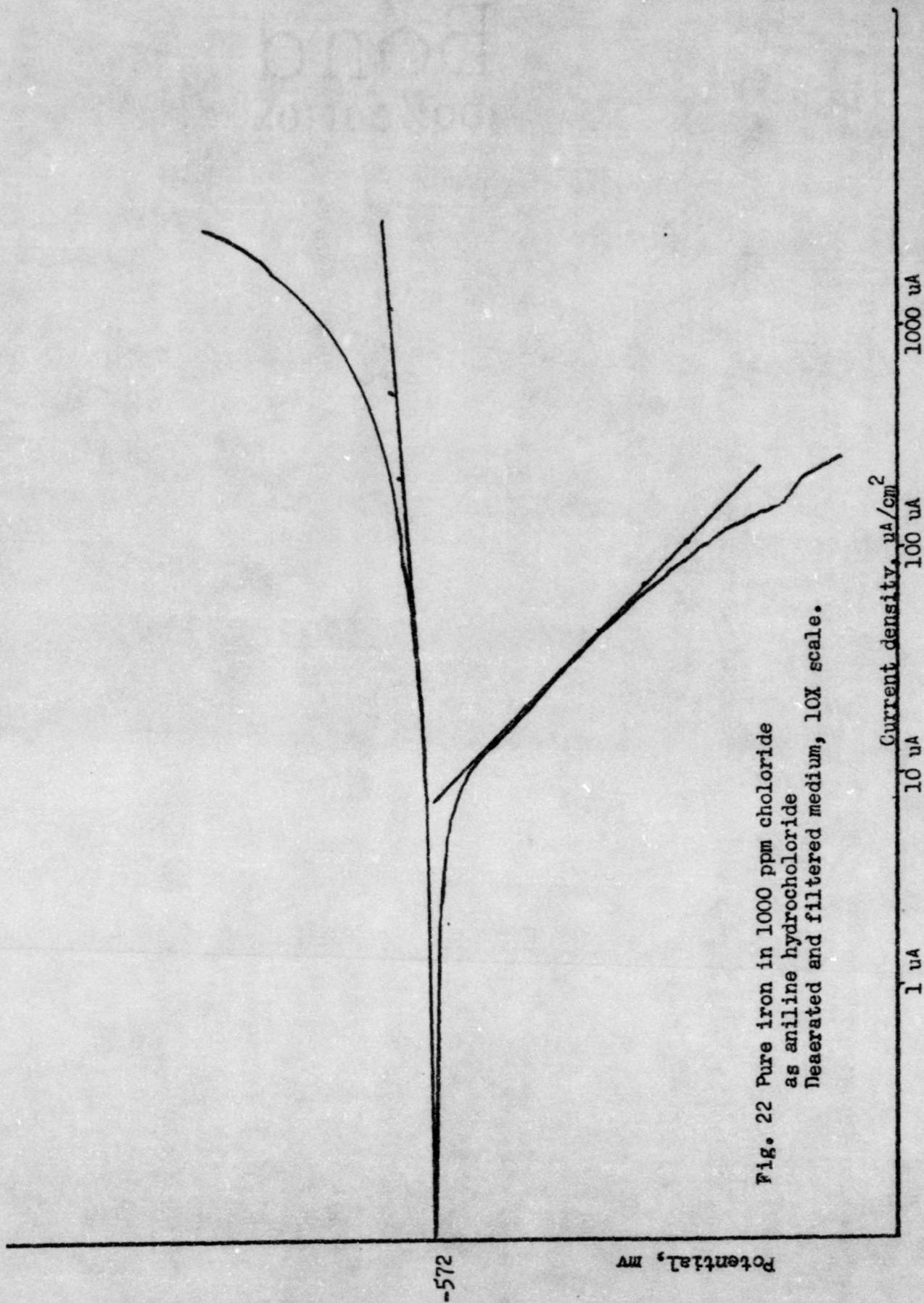


Fig. 22 Pure iron in 1000 ppm chloroform
as aniline hydrochloride
Deaerated and filtered medium, 10X scale.

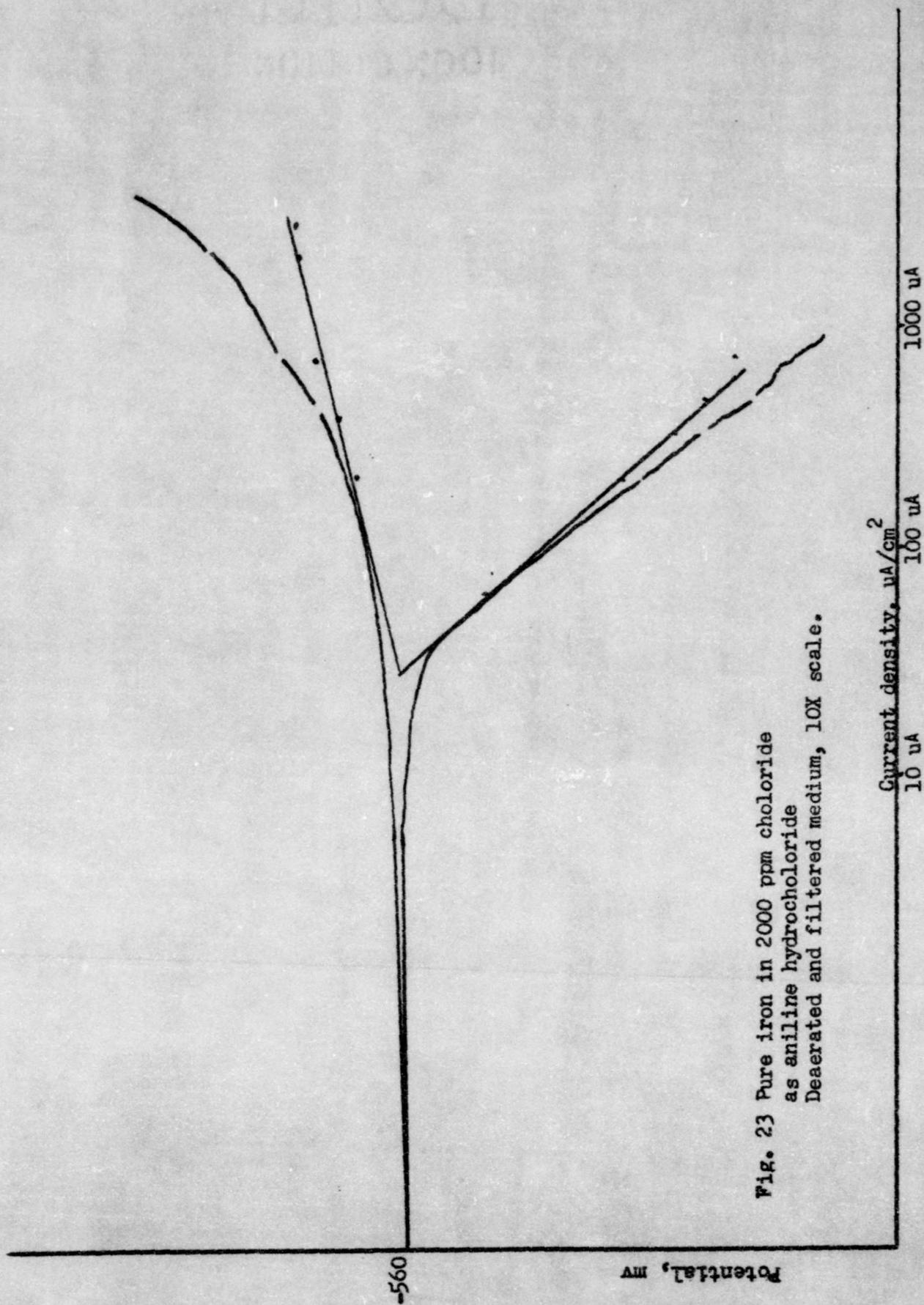


Fig. 23 Pure iron in 2000 ppm chloroform
as aniline hydrochloride
Deaerated and filtered medium, 10X scale.

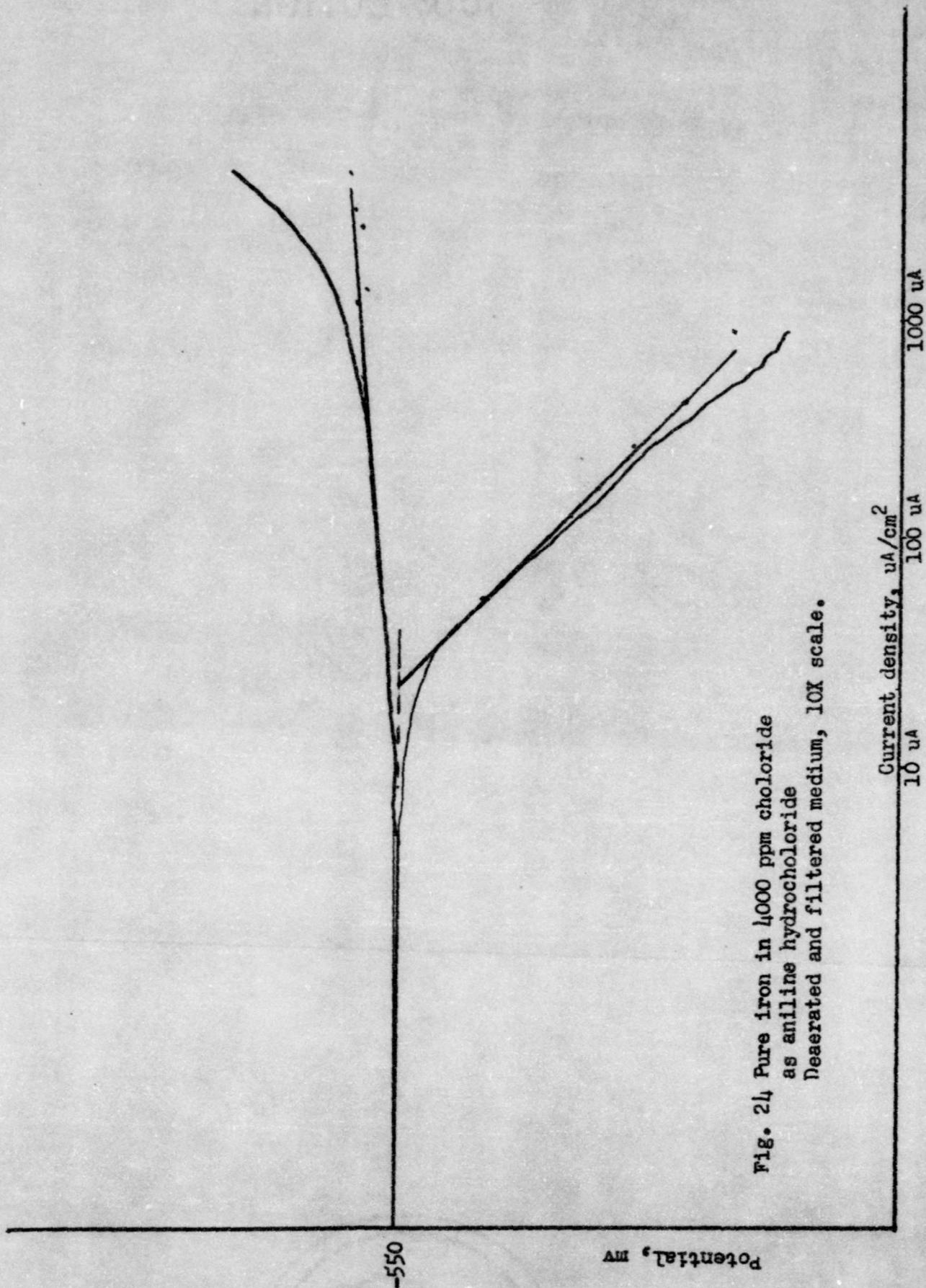


Fig. 24 Pure iron in 4000 ppm chloroform
as aniline hydrochloride
Deaerated and filtered medium, 10X scale.

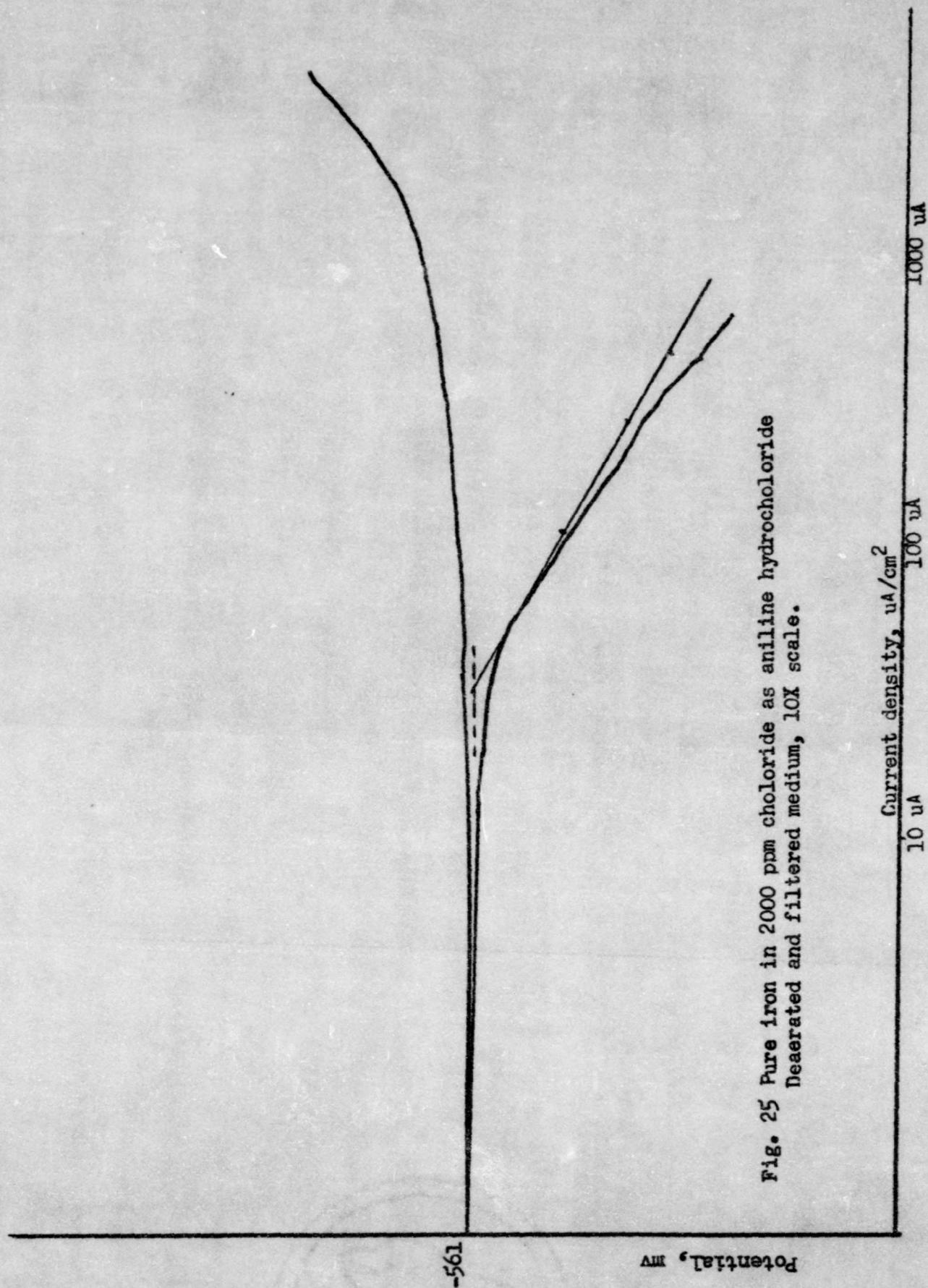


Fig. 25 Pure iron in 2000 ppm chloroform as aniline hydrochloride
Deaerated and filtered medium, 10X scale.

TABLE 2

TABLE OF RESULTS^a

SOLUTION	SCALE	WORKING ELECTRODE	IR COMPENSATED	DEOXYGENATED SOLUTION	E(mv) corr	MPY	OTHER
100 ppm aniline HCl	1X	C.S.			-440	26	Agitation, no luggin probe
0.55M H ₂ SO ₄	10X	C.S.			-525	200	
1000 ppm Cl ⁻ (b)	10X	C.S.		x	-604	60	
1000 ppm Cl ⁻	10X	C.S.		x	-584	25	Cathodic curve only, started from E _{corr} downward
1000 ppm Cl ⁻	10X	C.S.	x		-607	21	The same as above
1000 ppm Cl ⁻	10X	C.S.			-576	83	The same as above
1000 ppm Cl ⁻	10X	Ferrovac		x	-562	15	The same as above
2000 ppm Cl ⁻ (c)	10X	Ferrovac	x		-559	32	
8000 ppm Cl ⁻	10X	Ferrovac		x	-539	30	Cathodic curve only, started from E _{corr}
1000 ppm Cl ⁻	10X	Ferrovac	x		-572	9	Expanded potential scale
2000 ppm Cl ⁻	10X	Ferrovac	x		-560	32	The same as above
4000 ppm Cl ⁻	10X	Ferrovac	x		-550	23	The same as above

(a) All runs are conducted at room temperature.

(b) Chloride is in the form of aniline hydrochloride

(c) From this plot on a filtered solution was used, also IR compensation was done by means of the Interruption Method.

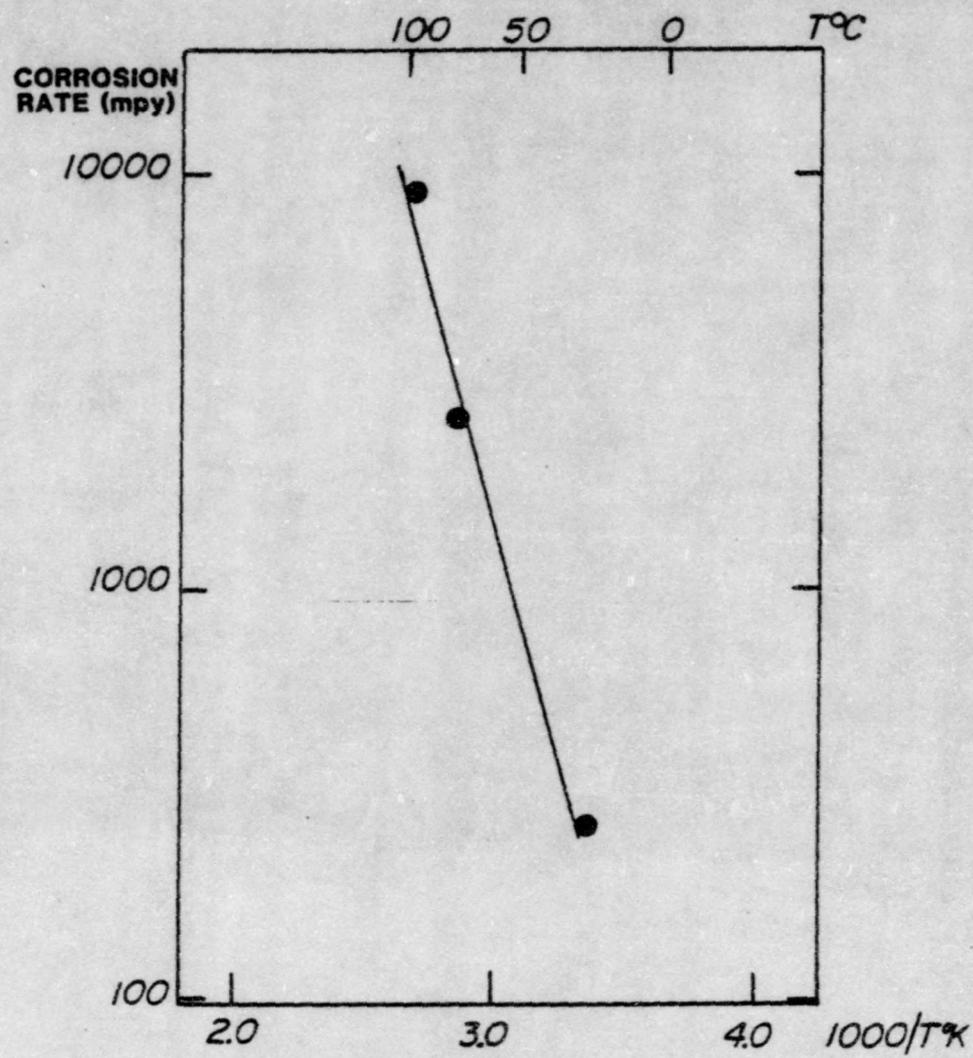


Fig. 26 Initial corrosion rate as a function of test temperature for carbon steel coupons exposed in water containing ~1000 ppm chloride as aniline hydrochloride.⁽⁵⁾

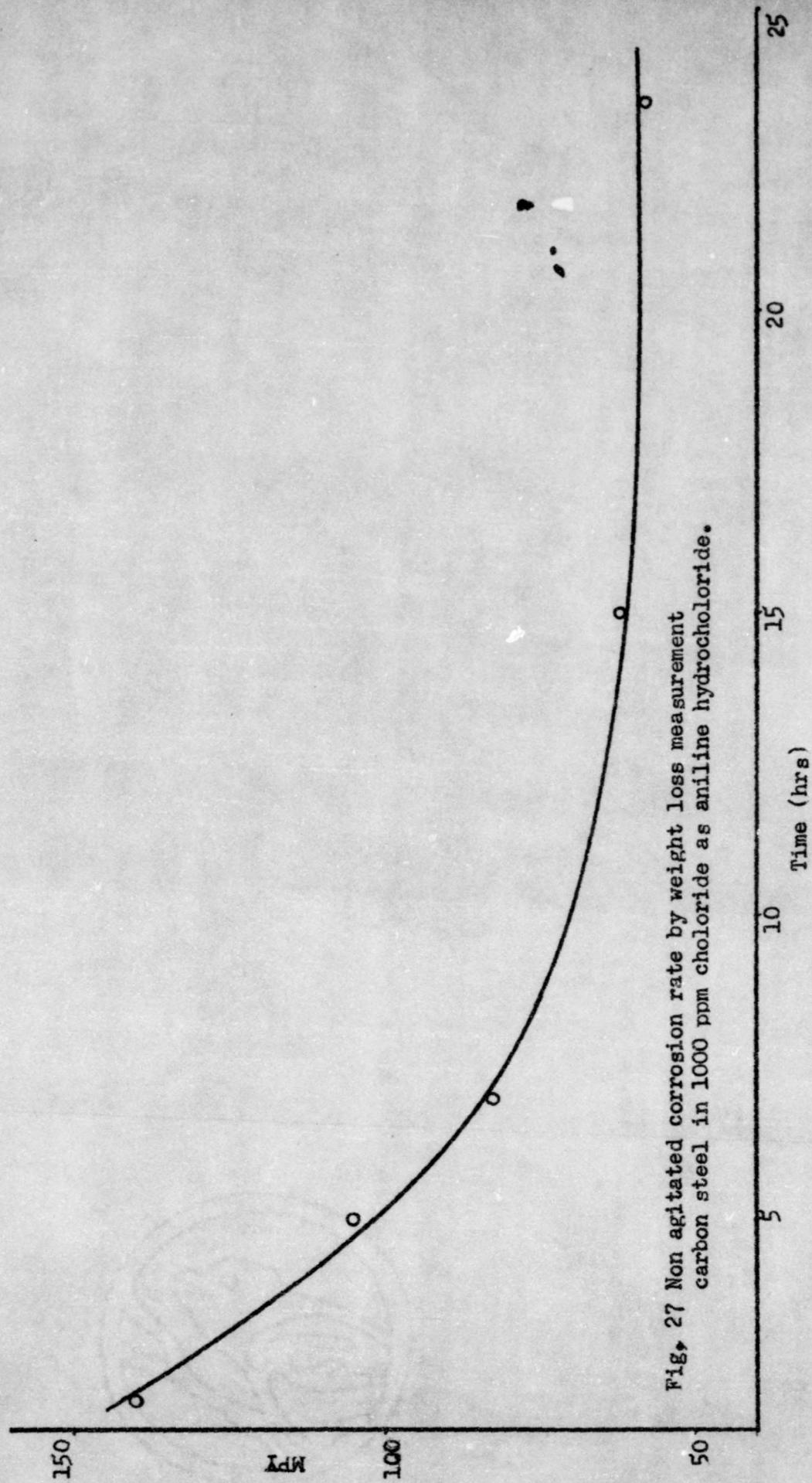


Fig. 27 Non agitated corrosion rate by weight loss measurement carbon steel in 1000 ppm chloride as aniline hydrochloride.

corrosion rate for this run reached a steady rate somewhere between 50 and 60 MPY which is actually closer to the rates measured by the electrochemical method. Obviously more data is needed to draw a definite conclusion in comparing these two methods.

Additional experiments were then conducted to determine the concentration and velocity effects. Figure 28 shows weight loss measurements conducted in stagnant 1000, 2000, and 4000 ppm chloride solutions as aniline hydrochloride for a carbon steel coupon at room temperature. Figure 29 shows the results for an agitated system with the concentrations and conditions the same as mentioned above. When these two sets of results were put together in Figure 30, it was obvious that the corrosion rates for the agitated system were an order of magnitude higher than the stagnant system. Apparently many of the mass transport barriers can be eliminated in an agitated medium. The different concentrations used did not seem to have a dramatic effect on the corrosion rates.

The following is a list of the more important conclusions drawn during the course of this study.

- 1) The electrochemical method is a faster and more reliable method as an alternative to weight loss measurements.
- 2) The effect of the Cl^- concentration of simulated wash waters on corrosion rates is not dramatic.
- 3) Increasing velocity rapidly increases the rate of corrosion in simulated wash waters.

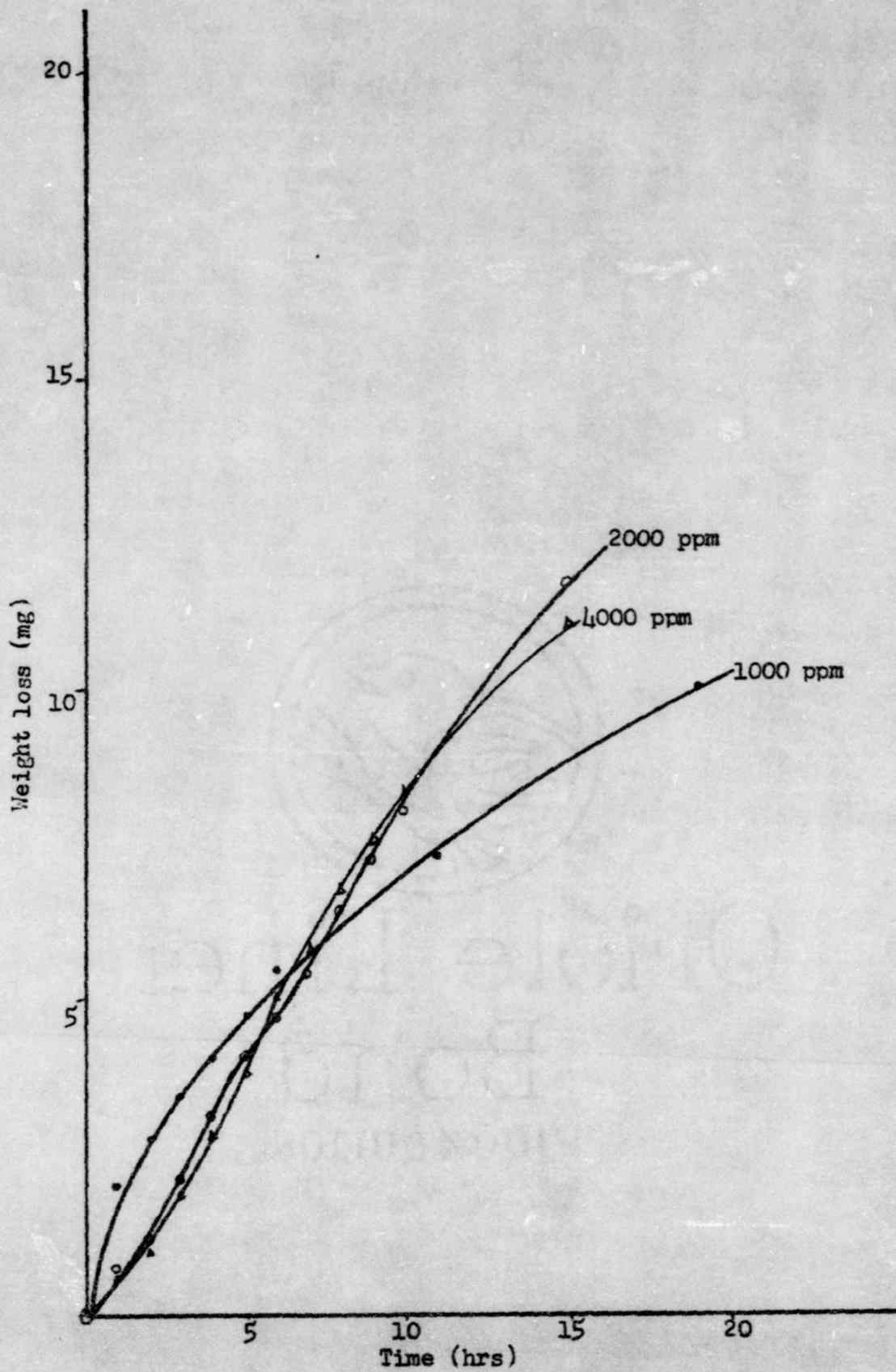
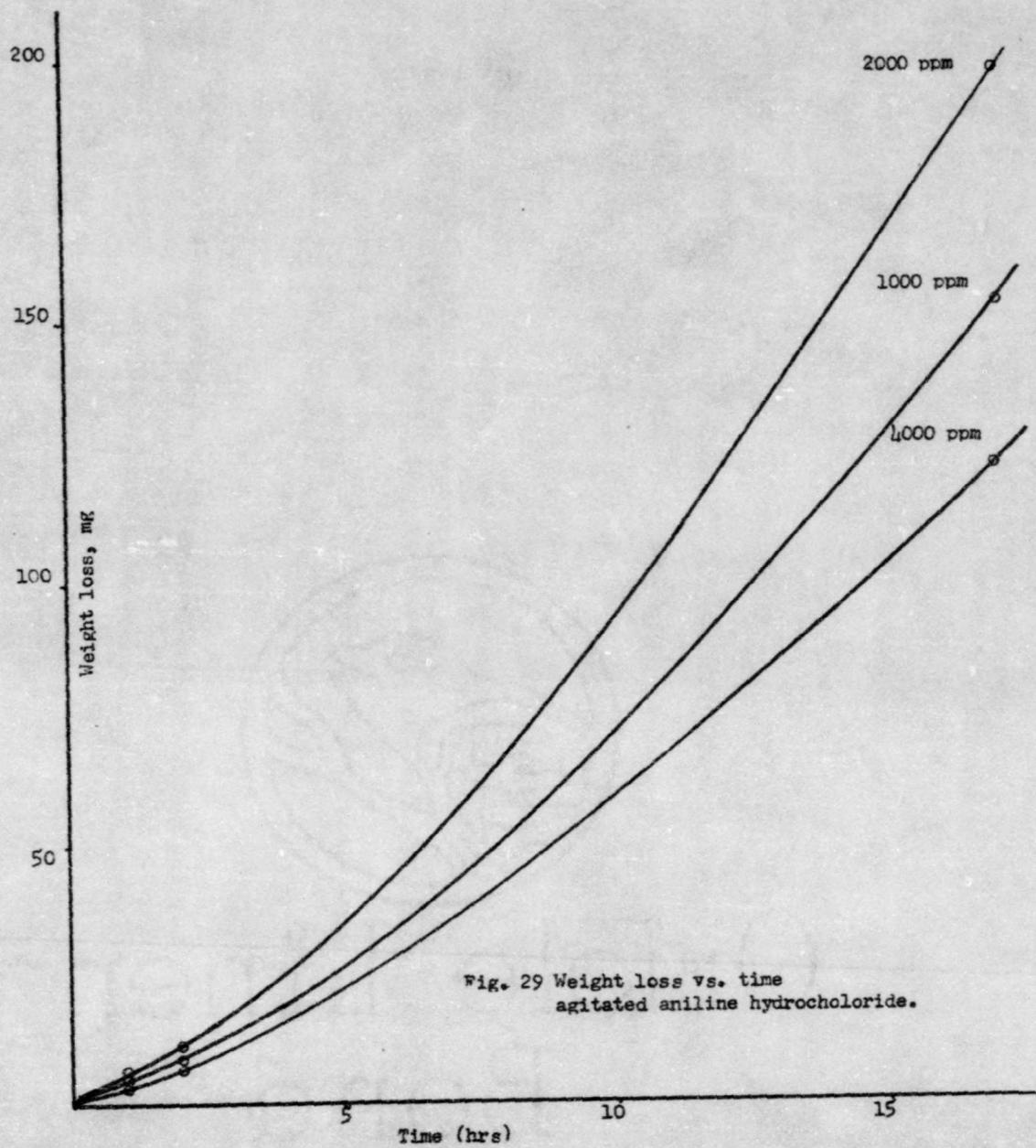
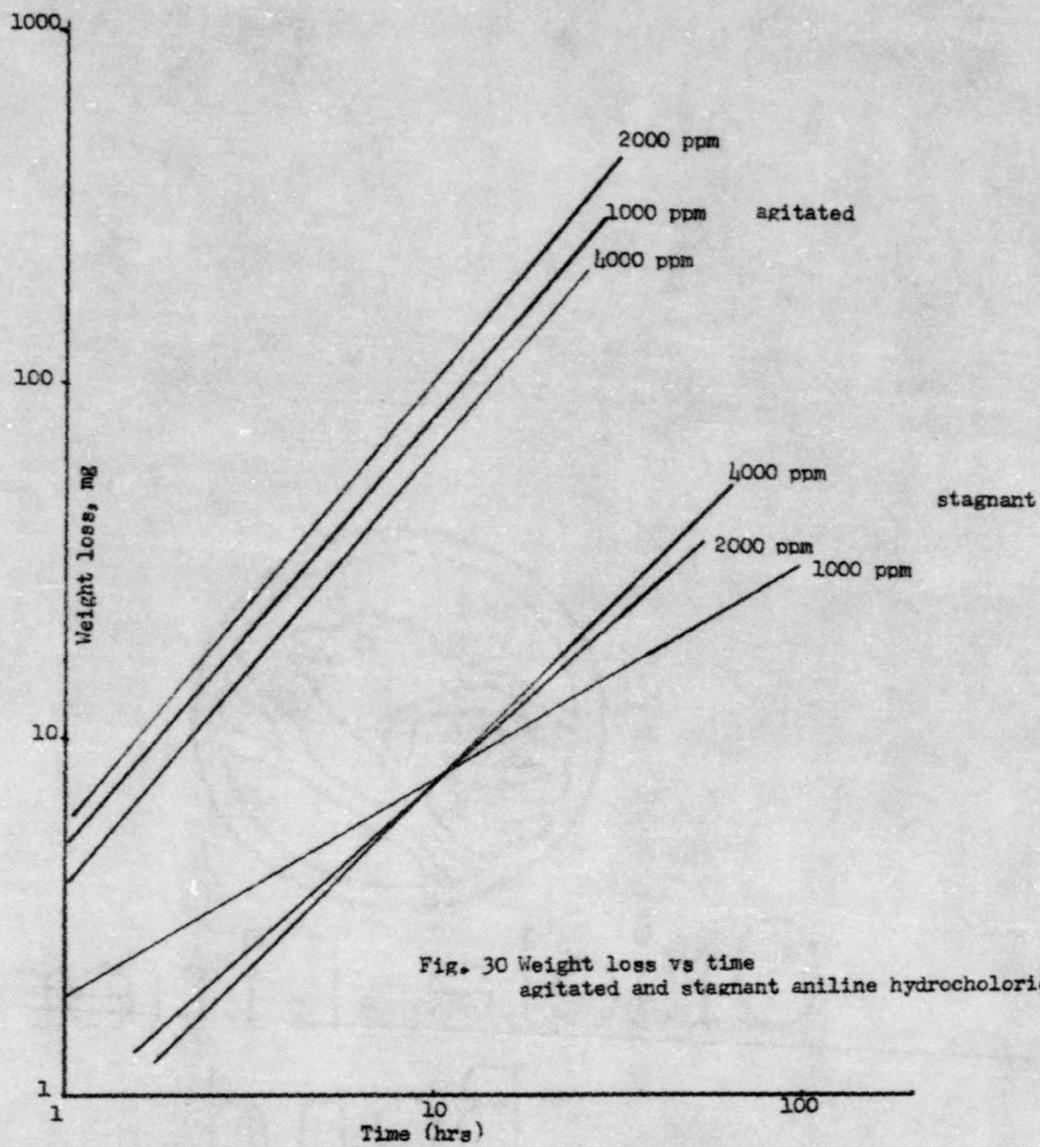


Fig. 28 Weight loss vs. time, stagnant aniline hydrochloride.





4) Effects of oxygen and ohmic drop are very important in corrosion rate measurements.

In summary, with the Tafel extrapolation technique it is possible to rapidly measure very low corrosion rates. There are, however, numerous restrictions which should be met before this method can be used successfully. To ensure reproducible results, one must keep in mind the extreme sensitivity of this method. It should be performed under exactly the same conditions. The interference from any concentration polarization, IR drop, electronic noise, or other extraneous effects could cause a non-linear Tafel region. The use of the Tafel extrapolation would be restricted to systems having one reduction process since the Tafel region is usually distorted if more than one reduction process occurs.

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