CORROSION BEHAVIOR OF THE ALUMINUM ALLOY - TYPE 347 STAINLESS STEEL GALVANIC COUPLE IN FUMING NITRIC ACID SOLUTIONS AT 160°F

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of the Ohio State University

By

JAMES F. WILLGING, B.S., M.S.

The Ohio State University

1953

Ohio State University Approved by:

[Signature] Advisor
ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. M.G. Fontana, Chairman of the Department of Metallurgy, for having given the author the opportunity to perform this investigation and for his guidance given during the course of this work. The encouragement and aid tendered to the author by Dr. F.H. Beck, Assistant Research Professor, Engineering Experiment Station, is greatly appreciated.

The investigation was sponsored and supported by the Air Material Command, Wright-Patterson Air Force Base, Dayton, Ohio by means of a contract with the Ohio State University Research Foundation. The interest and co-operation of these two agencies is hereby gratefully acknowledged.
Dedicated to my wife, Audrey R. Willging, without whose unswerving loyalty this work could not have been performed.
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I. INTRODUCTION

One of the more serious limitations on the use of a metal is its resistance to corrosion. The improvement of the corrosion resistance of a metal or the prevention of corrosion has become a subject of vital importance. Since such improvements or preventions must be founded on a knowledge of the process by which metals corrode, a great deal of research has been done on corrosion. Many major developments in corrosion theory have already been accomplished. The electrochemical nature of corrosion, the role of polarization, and the applicability of thermodynamic treatment are widely accepted. There remains, however, the application and modification of the generalized theory to specific cases. Such a specific case is the subject of this investigation.

The corrosion of metals in fuming nitric acid has recently become of interest since the acid is used in certain types of rockets. More specifically, the corrosion behavior of the galvanic couple aluminum - stainless steel is the subject of this investigation.

Standard investigational methods have been used to accumulate knowledge of the behavior of such couples in fuming nitric acid. Some of the information to be gained from this investigation can be summarized as follows:

(1) The nature and mechanism of the corrosion process with a view to corrosion prevention.
(2) The applicability of standard research methods to the subject galvanic couple.

(3) The polarization characteristics of aluminum and stainless steel in fuming nitric acid.

(4) The possibility of application of cathodic protection to mitigate the galvanic current.

(5) A knowledge of the type of inhibition necessary, and the acquisition of a criterion for selection of inhibitors.
II. SUMMARY AND CONCLUSIONS

1. The primary anodic reaction is the solution of the aluminum as the $\text{Al}^{3+}$ ion.

2. The air-formed oxide film initially present on the aluminum is removed by solution of the oxide and conversion of the oxide to the nitrate. This removal allows the solution of aluminum to occur.

3. The oxide film is partially repaired through chemical oxidation of the aluminum by nascent oxygen in the fuming nitric acid. This effect is large in relation to the dissolution rate of the aluminum caused by the potential difference between local anodes and cathodes, and it is small in relation to the dissolution rate of the aluminum caused by the difference in potential between aluminum and the stainless steel cathode.

4. The anodic polarization is affected by impressed current density. The polarization consists of solution-formed oxide film at low current densities and hexahydrated aluminum nitrate deposit added to the oxide film at higher current densities.

5. The water content of the fuming nitric acid exerts an important influence on the anodic polarization of aluminum. High water content (9.2 - 11.2%) eliminates the nitrate polarization through solution of the nitrate. Intermediate water content (5.2 - 7.2%) has an intermediate effect and produces a
polarization which is stable over a large range of current densities.

6. Water in intermediate concentrations acts as an anodic inhibitor in the galvanic couple in question, but produces an undesirable type of inhibition.

7. Cathodic protection by means of impressed current is not practicable in the galvanic couple under consideration.

8. The addition of a cathodic inhibitor is indicated as a method for mitigating the galvanic corrosion of this couple.

9. The cathodic reaction at the Type 347 stainless steel cathode of the galvanic couple is the reduction of nitric acid to nitrous acid at all acid concentrations tested.

10. The cathodic reaction is essentially insensitive to cathodic current density within the range of current densities tested and therefore polarizes only slightly.

11. The relative area of the stainless steel cathode to the aluminum alloy anode has an important effect on the corrosion of the anode, namely, increasing the relative cathode area increases the anodic corrosion of aluminum in a non-linear fashion.

12. The galvanic couple in question operates under mixed control.

13. The distance of separation between the anode and the cathode is a controlling factor in the galvanic corrosion of such a couple. Increasing the distance of separation decreases the anodic corrosion.
14. Increased temperature of testing increases the anodic corrosion of the galvanic couple non-linearly.

15. The equipment and techniques developed are applicable to the studied galvanic system and are useful tools for investigating the behavior of metals in fuming nitric acid and other media.
III. LITERATURE SURVEY

A. Electrochemistry of Corrosion

1. General Theory of Electrochemical Corrosion

The nature of the process of corrosion of metals has long been a subject of investigation. The idea that corrosion of metals is largely electrochemical in nature was first postulated by de la Rive\(^1\) and was later supported by Whitney\(^2\). Whitney and others\(^{3,4}\) concluded that the corrosion of iron and steel in aqueous solution is essentially an electrochemical process. The presence of "local" anodes and cathodes on the surface of a corroding metal and flow of local currents between them was established by Müller\(^5,6\). He assumed that a metal in solution was covered by a porous film. The bare metal at the bottom of such pores passed into solution as the metal ion (oxidation process) and then formed an anode element. The film was assumed to possess conductivity and could act as a locale for cathodic reactions (reduction processes). These two local reactions formed an electrolytic cell which was short circuited through the metal. The driving force of such a reaction was considered to be the e.m.f. of the cell or the difference in potential between the anode reactions and the cathode reactions. Neglecting reactions which might oppose the local cell, the following expression was developed according to Kirchoff's Law:

\[
E_A + (I_L \cdot R_P) + (I_L \cdot R_S) - E_C = 0 \quad (1)
\]
When:

\[ E_A = \text{anode potential} \]
\[ E_C = \text{cathode potential} \]
\[ I_L = \text{local current} \]
\[ R_P = \text{resistance of the pores} \]
\[ R_S = \text{resistant of the solution} \]

This expression is developed from the simple Ohm's Law expression:

\[ E_A - E_C = I_C \cdot R_L \]  \hspace{1cm} (2)

where \( R_L \) is the resistance of the local cell. Müller further postulated in his "Lokalstromtheorie" that the dissolution of metal from the anode should be proportional to the current, according to Faraday's Law. This assumption has been verified many times. Among the investigators who have corroborated this effect are Evans and co-workers\(^7,8\), and Brown and Mears\(^9\). The latter investigators went to great lengths to isolate the local anodes from the local cathodes so that currents and potentials might be measured. On the surface of a piece of corroding metal, the local anodes and cathodes may be so numerous and so mingled as to defy analysis\(^10\). In addition they may also continuously shift their location and so further complicate the measuring of local cell action.

2. **The Electrode Processes**

When a metal is placed in solution it develops anodes and
cathodes having potentials which may be designated as $E_A$ and $E_C$ respectively. The exact process by which these potentials are established was first given mathematical formulation by Nernst\(^{(11)}\).

He considered that a metal has a tendency to pass into solution and thus exhibits a solution pressure. By osmotic pressure, ions of the metal existing in the solution exert a tendency to return to the metal. These two opposing tendencies are then regarded as being analogous to vapor pressure and osmotic pressure respectively.

Treating these two pressures by means of the gas law, Nernst obtained an expression of the same form as that which can be derived strictly from free energy considerations for the metal-metal ion electrode. That is:

$$E = \frac{RT}{nQ} \ln C^+ - E^0$$

(3)

This expression is known as the "Nernst Equation".

A more modern theory of the phenomenon of solution potential has been developed\(^{(12)}\). As in the Nernst Theory, the metal has a tendency to pass into solution forming ions, which then have a tendency to plate out on the electrode. These processes will reach equilibrium, and at equilibrium the free electrons on the metal surface will be spatially separated from the accumulation of positive ions in the solution by a small distance and will thus have built up an electrical double layer. The potential difference across this layer is the single electrode potential. Since the process is at equilibrium, this potential is known as the reversible electrode potential\(^{(13,14)}\). The rates of the two opposing reactions
are postulated to be:

Rate of solution of ions \( = K'e^{-(1-\alpha)ZFE/RT} \)

Rate of deposition of ions \( = KC^+e^{aZFE/RT} \)

Where \( \alpha \) is the fraction of the potential drop \( E \) across the double layer which tends to discharge ions, \( Z \) is the valence of the ions, \( F \) is Faraday's constant, \( K \) and \( K' \) are rate constants and \( C \) is the concentration of ions in the solution. Since the rates of the two processes are equal at equilibrium:

\[
KC^+e^{aZFE/RT} = K'e^{-(1-\alpha)ZFE/RT} \quad (4)
\]

\[
E = \frac{RT}{ZF} \ln \frac{K}{K'} - \frac{RT}{ZF} \ln C^+ \quad (5)
\]

Since \( \frac{K}{K'} \) is constant we may write:

\[
E = \frac{RT}{ZF} \ln K - \frac{RT}{ZF} \ln C^+ \quad \text{or} \quad (6)
\]

\[
E = E^0 - \frac{RT}{ZF} \ln C^+ \quad (7)
\]

Some authors \((15,16)\) feel that this idea of electrode potential is too simple, but no more satisfactory hypothesis has yet been offered.

In a reversible cell, composed of two reversible electrodes, the chemical changes can be represented by the well-known equation

\[
aA + bB \rightarrow LlM \quad (8)
\]

By the law of mass action the equilibrium constant would be

\[
K = \frac{A^1_L \cdot A^m_M \cdots}{A^a_A \cdot A^b_B \cdots} \quad (9)
\]

Where \( A \) is the activity of the components \( A, B, \ldots L, M \ldots \) of the system, and the relative amounts of the components are \( a, b, \ldots l, m \ldots \).
In any given cell when all the components are in their standard states, that is at unit activity, the electromotive force of such a cell is designated $E^\circ$. If the reaction proceeds with the passage of $n$ Faradays of electricity, we may write the following relationship for the standard free energy change $\Delta F^\circ$ in the process:

$$\Delta F^\circ = -nFE^\circ = RT \ln K$$  \hspace{1cm} (10)

Where $F$ is the Faraday, $T$ is the temperature in degrees Kelvin, and $R$ is the gas constant. By rearranging equation (10) the standard potential of the cell is obtained.

$$E^\circ = \frac{RT}{nF} \ln K$$  \hspace{1cm} (11)

At any other states than the standard state this relationship would become:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{A_L^l A_M^m}{A_A^a A_B^b}$$  \hspace{1cm} (12)

This equation gives the algebraic sum of the potentials at the two reversible electrodes involved. The single electrode potential can be expressed:

$$E = E^\circ_n - \frac{RT}{nF} \ln A_i$$  \hspace{1cm} (13)

Where $A_i$ represents the activities only of those components involved in the single electrode reaction.

Since the determination of the activities of ions is a difficult task, another method for determining single electrode potentials has been evolved. If one sets the potential of some readily reproducible electrode arbitrarily as zero and makes up a reversible cell using
such an electrode as one of the cell electrodes, the e.m.f. of the cell will be a measure of the unknown single electrode potential according to equation (12). The potential of hydrogen gas at an atmosphere pressure bubbling through a platinized platinum electrode in a solution of hydrogen ions at unit activity has thus been designated as zero. The potentials of all other single electrodes are then assigned values on this scale. Since this standard electrode presents experimental complications, other electrodes whose potentials are well known have been often used as reference electrodes.

One such electrode is the calomel electrode.

In dealing with single electrode potentials, it is well to note that the potential depends on the reactions taking place at the metal surface. That is, the potential is a property of the reaction rather than of the cell (17). The potential of a metal will thus vary with the solution into which it is placed. Pourbaix (18) has shown that an electrochemical reaction can take place as an oxidation process only when the reaction potential of the surface on which it takes place is higher than the equilibrium Potential E, and conversely only as a reduction reaction when the reaction potential is lower than the equilibrium potential E. This point has been proven experimentally (19).

Since the potential of a metal does depend on the reactions taking place on the metal surface, inspection of equation (13) reveals that ionic concentration, as well as temperature may affect
the electrode potential. One form of corrosion known as "thermo-galvanic" corrosion arises from the fact that different potentials exist at regions of a metal under a thermal gradient\(^{(20, 21)}\). Concentration gradients can also cause potential variations\(^{(22, 23)}\) and consequent corrosion. Any factors tending to produce concentration gradients such as cracks and crevices will thus produce corrosion. Motion of the electrolyte if it provides for stagnant and turbulent areas may set up potential differences\(^{(24)}\). The single electrode potential of a metal has also been shown to be affected by the state of stress of the metal\(^{(25, 26)}\). In addition to these effects, the flow of current to or from an electrode can change the direction or magnitude of the equilibrium potential of the electrode. Such current-induced changes are known as polarization of the electrode.

3. **Polarization Theory**

Polarization can be defined according to Uhlig\(^{(27)}\) as a back e.m.f. resulting from the physico-chemical effects of products formed or concentration changes during flow of current. Two methods of graphical illustration of polarization have been developed. The method of Pourbaix\(^{(28)}\) is shown in Figure 1, and that of Evans\(^{(29)}\) is shown in Figure 2. It will be noted that the effect of polarization of an anode is to change its potential in the less anodic direction; conversely the effects of polarization upon a cathode is to change its potential in the less cathodic direction. In the Evans diagram it is possible for the anodic and cathodic polarization
curves to intersect. The current density at the point of intersection is known as the "limiting current density" and indicates the maximum amount of corrosion current that can flow between the local anode and the local cathode \((30,31)\). If the electrolyte possesses zero resistance, this equi-potential point will be attained. However, the solution will possess a finite resistance and the current will attain a value less than \(I_1\). At this point \((I_G)\) the drop through the solution equals the difference in polarized potentials between the anode and the cathode. That is:

\[
(E_A + \phi_A \frac{I}{A_a}) - (E_C - \phi_C \frac{I}{A_C}) = IR
\]

Where

- \(E_A\) = open circuit potential of the anode
- \(E_C\) = open circuit potential of the cathode
- \(\phi_A\) = polarizing function of the anode
- \(\phi_C\) = polarizing function of the cathode
- \(A_A\) = area of the anode
- \(A_C\) = area of the cathode
- \(I\) = galvanic current
- \(R\) = resistance

The polarization behaviors of anodes and cathodes give rise to a system of classifying corrosion processes according to the type of control \((32)\). If the processes taking place at the anode control the velocity of the total reaction (anode and cathode), the process is said to be under anodic control. If the cathode processes are the rate-controlling processes, the system is under cathodic control. If
both anode and cathode processes are responsible for limiting the total reaction, the process is under mixed control. In cases where no limit upon reaction velocity is imposed by either anode or cathode, the classification is that of resistance control since the only restriction is that of conductivity of the system. Cases of diffusion control where the rate controlling factor is the supply of a reagent to an electrode are also known. An illustration of these control types is shown in Figure 3.

Polarization curves are extensively used to illustrate the effect of inhibition on metallic corrosion. The fundamental use of a corrosion inhibitor is to (a) increase the anodic polarization, (b) increase the cathodic polarization, (c) decrease the difference in open circuit potential between anode and cathode or (d) perform a combination of any of these factors.\(^\text{33,34,35,36}\)

Cathodic protection theory and practice utilizes polarization - current studies as a gauge of effectiveness. Nears and Brown\(^\text{37,38}\) have made extensive use of polarization curves and have concluded that for complete cathodic protection it is necessary to polarize the cathodes in a corrosion cell to a potential which is equal to, or more anodic than, the open circuit potential of the local anodes. They have also shown that if the cathodes are essentially non-polarizing, it is virtually impossible to prevent corrosion by cathodic protection alone (See Figure 4).

4. Types of Polarization

Polarization may result from several different mechanisms.
Some of these mechanisms will be discussed.

(a) **Film Polarization**, as its name implies, occurs when the formation of a film at an anode or cathode affects its potential\(^{(39,40)}\). This effect is the basis for the mechanism of some inhibitors\(^{(41)}\). A film may have a threefold effect: (1) the presence of the film simply prevents accessibility of electrolyte to metal surface; (2) because of the decreased amount of exposed anode area, current density on the exposed anodic area increases and thus increases polarization of the exposed anodic areas; and (3) a film such as that of \(\text{Al}_2\text{O}_3\) an aluminum may offer increased ohmic resistance to electron movement\(^{(42)}\).

(b) **Concentration Polarization** occurs through accumulation of ions at an electrode. Thus at the anode, an accumulation of cations will make the anode less anodic. Ionic diffusion thus becomes a rate controlling factor\(^{(43,44,45)}\). Crevices in the electrode surface may then become locally important in polarization.

(c) **Overvoltage** may become important in some corrosion systems. It is defined by Glasstone\(^{(46)}\) as the difference between the reversible potential of an electrode and the potential at which a reaction perceptibly occurs. A familiar example is the hydrogen overvoltage phenomenon. Hydrogen will actually evolve from a metal surface at a different potential than that calculated theoretically. The amount of the overvoltage will vary with the nature of the electrode, the current density, and the surface condition of the electrode\(^{(47)}\). For example, the overvoltage for the evolution of hydrogen on a
platinized platinum electrode is 0.0 volts while for a smooth platinum electrode the value is 0.09 volts. The mechanism for overvoltage has been repeatedly investigated and several theories have been advanced \(48, 49, 50, 51\). It is sufficient to say that all agree that there is a slow, rate controlling step somewhere in the process which is responsible for the overvoltage.

5. Electrochemistry of Bi-Metallic Systems

The electrochemical character of normal corrosion has been demonstrated for several metals\(52, 63, 54\). In 1824 Humphrey Davy\(55\) noted that the corrosion of a metal is accelerated by contact with some metals and reduced by contact with certain other metals\(56\). This form of corrosion is known as "galvanic" or "bi-metallic" corrosion. The principles in the previous discussion concerning electrochemical relationships in local cells can be applied to galvanic corrosion, the only difference being in the distribution of anodes and cathodes. In galvanic corrosion one metal will function as a cathode and the other will function as an anode. Local cells may still exist on the metal surfaces but may largely be obscured in most cases by the larger effects of galvanic current.

As in the case of local cells, the potential difference between anode and cathode will be the driving force of the corrosion reaction\(57\). The electrochemical series might be used to predict corrosion reactions but is not accurate since the metals in the series are arranged according to the potentials of the metals in solutions containing
ions of the respective metals at unit activity. A somewhat more comprehensive guide has been evolved by La Que and Cox (58) for sea water electrolyte, but still one must measure potentials of metals in a given media to determine the direction of galvanic corrosion in the media. The extent of the corrosion caused by contact between two metals will not, however, be proportional to the potential difference since again polarization must be taken into account. The current flow in a bi-metallic couple is shown schematically in Figure 5. It is apparent that the polarization of the anode will be increased due to increased current density caused by the alien metal cathode, and that the cathodic polarization curve for the couple will be a composite of the alien metal cathode and the local cathodes on the anodic metal. When the galvanic anode and galvanic cathode exhibit a large potential difference, the effect of polarization of local cathodes on the anode metal will be obscured.

Galvanic cells can be classified according to type of control, precisely as has been previously discussed for local cells (59).

Inhibition and cathodic protection can be applied to galvanic cells exactly as one would apply them to local cells (60).

Polarization and current effects are somewhat easier to measure in galvanic cells than is true for local cells since (1) areas of anode and cathode are large and fixed, and (2) anode and cathode effects can be separately measured on a gross scale.

As might be expected, the greatest corrosion in a bi-metallic
system takes place near the junction of the two metals. The effect is most marked in electrolytes of low conductivity since the galvanic couple will be effective to a lesser distance.\(^{61,62,63}\).

In summation it can be said that a galvanic cell obeys the same laws and behaves generally as does a local cell.

---

**B. Chemistry of Nitric Acid**

1. **General**

Nitric acid has been classified as a strong monobasic acid and usually acts as an oxidizing agent.\(^{64}\) Nitric acid may be reduced with the production of nitrous acid, nitrogen peroxide, nitric oxide, nitrous oxide, nitrogen, ammonia, hyponitrous acid, hydroxylamine, and possibly nitrohydroxylaminic acid.\(^{65}\) Nitric acid will decompose when exposed to light\(^{66}\) or heat\(^{67}\). Franck and Schirmer\(^{68}\) found that nitric acid decomposes according to the rate law:

\[ -\frac{d\,[\text{HNO}_3]}{dt} = k \frac{[\text{HNO}_2]^2}{[\text{H}_2\text{O}]} \]  \hspace{1cm} (15)

or in terms of the \(N_2O_5\) concentration of the acid:

\[ 2\text{HNO}_3 = N_2O_5 + H_2O \quad K = \frac{[N_2O_5][H_2O]}{[\text{HNO}_3]^2} \]  \hspace{1cm} (16)

It is therefore thought that the \(\text{HNO}_3\) decomposition passes through \(N_2O_5\) and that the rate controlling process is the reaction:

\[ N_2O_5 = N_2O_3 + O_2 \quad \frac{d\,[N_2O_5]}{dt} = k_{N_2O_5} [N_2O_5] \]  \hspace{1cm} (17)

The overall rate would then be:

\[ \frac{d\,[\text{HNO}_3]}{dt} = k_{N_2O_5} \cdot K \cdot \frac{[\text{HNO}_3]^2}{[\text{H}_2\text{O}]} \]  \hspace{1cm} (18)
This reaction points to the possibility that the presence of water is a deterrent to the breakdown of nitric acid. C.K. Ingold and co-workers (69,70,71,72,73,74,75) have made a study of the addition of nitrating agent to fuming nitric acid. They believe that the acid decomposes according to the following reactions:

\[
2\text{HNO}_3 = \text{H}_2\text{NO}_3^+ + \text{NO}_3^- \text{ (rapid)}, \quad K_3 = \frac{[\text{H}_2\text{NO}_3^+][\text{NO}_3^-]}{[\text{HNO}_3]} \quad (19)
\]

\[
\text{H}_2\text{NO}_3^+ = \text{NO}_2^+ + \text{H}_2\text{O} \text{ (slower)}, \quad K_4 = \frac{[\text{NO}_2^+][\text{H}_2\text{O}]}{[\text{H}_2\text{NO}_3^+]} \quad (20)
\]

Overall:

\[
2\text{HNO}_3 = \text{NO}_2^+ + \text{NO}_3^- + \text{H}_2\text{O}, \quad K_3K_4 = K_5 = \frac{[\text{NO}_2^+][\text{NO}_3^-][\text{H}_2\text{O}]}{[\text{HNO}_3]^2} \quad (21)
\]

The effect of water is believed to be the deprotonating of the nitric acidium and nitronium ions as follows:

\[
\text{NO}_2^+ + 2\text{H}_2\text{O} = \text{HNO}_3 + \text{H}_3\text{O}^+ \quad (22)
\]

\[
\text{H}_2\text{NO}_3^+ + \text{H}_2\text{O} = \text{HNO}_3 + \text{H}_3\text{O}^+ \quad (23)
\]

These reactions go completely to the right, and nitronium ion is undetectable at 5% water. The water content also has a rather complicated effect on the nitrate ion concentration. The net effect is that nitrate ion concentration decreases as water increases up to 2.5 per cent water; thereafter water and nitrate ion increase together. The effects in acid containing more than 5 per cent water are different since the reaction

\[
\text{HNO}_3 + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{NO}_3^- \quad (24)
\]
begins to assume greater importance. The anticatalytic effects of water will become less and less potent as dilution increases above 5% water.

2. Action of Nitric Acid on Metals

(a) General

Among the earliest investigators of the action of nitric acid on metals was R. Boyle\(^{76}\) who noted that many metals remain inert towards concentrated nitric acid but are readily attacked by dilute nitric acid. The earliest opinion of the mechanism of attack was that the metal was oxidized directly by the acid\(^{77,78}\). It was later discovered that very high purity nitric acid in any concentration attacks very few metals; the reaction occurs only when a trace of free nitrous acid is present\(^{79}\). This observation was confirmed by Veley\(^{80}\). Veley states: (1) the primary reaction is between the metal and nitrous acid; (2) no gas is evolved at first from the surface of the metal; (3) the amount of nitrous acid increases to a constant and maximum proportion; and (4) those conditions which increase the amount of metal dissolved per unit time are equally those which increase this proportion of nitrous acid. Given a small initial content of nitrous acid, the process can then be represented as follows: (1) the metal dissolves in nitrous acid to form the metallic nitrite and nitric oxide; (2) the nitrite formed is decomposed by the excess of nitric acid to reproduce the nitrous acid; and (3) the nitric oxide formed in (1) is not evolved as such but reduces the nitric acid or the nitrate to
produce further nitrous acid. For example:

\[ \text{Cu} + 4\text{HNO}_2 = \text{Cu(NO}_2)_2 + 2\text{H}_2\text{O} + 2\text{NO} \quad (25) \]

\[ \text{Cu(NO}_2)_2 + 2\text{HNO}_3 = \text{Cu(NO}_3)_2 + 2\text{HNO}_3 \quad (26) \]

\[ 2\text{NO} + \text{H}_2\text{O} + \text{HNO}_3 = 3\text{HNO}_2 \quad (27) \]

Burch and Veley\(^{(81)}\) introduced copper, silver, and bismuth respectively into nitric acid to form a galvanic cell with platinum. The e.m.f. of such cells increased gradually to a maximum value. This maximum could be attained immediately upon the addition of nitrous acid. Conditions favoring the production of nitrous acid, i.e. temperature increases, impurity of the acid with respect to nitrous acid, and concentration of the acid tended to increase the e.m.f. of such cells. Any additives which destroy nitrous acid decreased the e.m.f. of such cells. Urea is an example of the latter.

Bancroft\(^{(82)}\) objected to the assumption that metal dissolves in nitrous acid to form the nitrite. Ihle\(^{(83)}\) said that the action of nitrous acid is that of a catalyst.

Acworth\(^{(84)}\) and Bancroft\(^{(85)}\) are proponents of the "hydrogen theory". This theory assumes that a nitrate of the metal and nascent hydrogen are first formed. The hydrogen then reduces the nitric acid to nitrous acid. The reaction is as follows:

\[ \text{M} + 2\text{HNO}_3 = \text{M(NO}_3)_2 + 2\text{H} \quad (28) \]

This hydrogen is not evolved, but acts on the free acid on the metal nitrate reducing it to nitrous acid, hyponitrous acid, hydroxylamine, and ammonia after the work of Whitney\(^{(86)}\) on the electrochemical nature of corrosion. Bancroft\(^{(87)}\) said that the attack of nitric
acid on metals can be considered as electrolytic corrosion. In support of the electrochemical theory, Evans\(^{(88)}\) postulated the following reactions: At the anode: divalent metal

\[
M = H^{++} + 2e
\]

At the cathode the three step reaction

\[
\begin{align*}
HNO_3 + H^+ + e & = NO_2 + H_2O \\
NO_2 + H^+ + e & = HNO_2 \\
HNO_2 + H^+ + e & = NO + H_2O
\end{align*}
\]

Reactions (30), (31), and (32) may be written ionically:

\[
\begin{align*}
NO_3^- + 2H^+ + e & = NO_2 + H_2O \\
NO_2^- + e & = NO_2^- \\
NO_2^- + 2H^+ + e & = NO + H_2O
\end{align*}
\]

Evans feels that reaction (31A) is likely to occur most smoothly for it involves the fewest number of particles and does not require the approach of a negatively charged particle to the negative electrode.

Considering the work of Ellingham\(^{(89)}\), Evans divides metals into two classes: (1) metals active enough to evolve hydrogen at the local cathodes; the hydrogen may be evolved or may react with the nitric acid; magnesium, zinc, and cadmium belong to this class of metals; and (2) the noble metals which reduce nitric acid to nitrous acid at the local cathodes; evolution of gas, chiefly NO\(_2\), will occur; silver, mercury, and gold are examples of this class of metals.

The products of reaction between metals and nitric acid are many. Hydroxylamine as a reduction product of nitric acid by magnesium, zinc, aluminum, and manganese, has been observed by Divers\(^{(90)}\) and others. Divers also observed production of ammonia
in the cases of zinc, aluminum, lead, iron and sodium. Smith(91) confirmed ammonia production in the cases of aluminum and iron as reducing agents for nitric acid. Nitric acid is usually monobasic and forms a series of nitrate salts by action on metals, metal hydroxides, oxides, and carbonates. The great number of metallic nitrates in which the number of water molecules is some multiple of 3, as for example 3, 6, 9 or 12, has led observers(92) to assume that the hydrates can be regarded as addition products of the base with one of the hypothetical nitric acids such as orthonitric acid, \( \text{H}_2\text{NO}_5 \), mesonitric acid, \( \text{H}_3\text{NO}_4 \), and metanitric acid, \( \text{HNO}_3 \). Aluminum for example yields an enneahydrate by the mechanism:

\[
\text{Al(OH)}_3 + 3\text{H}_2\text{NO}_5 = \text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}
\]  

(33)

A discussion of the products of reduction by metals pertinent to this research will be offered in a later section.

(b) Behavior of Aluminum in Nitric Acid

Early references to the effect of aluminum are few and inaccurate. Seligman and Williams(93) in 1916 performed some experiments on the reduction of nitric acid by aluminum and corrected many inaccuracies by previous investigators(94,95). At about the same time Trillat(96), working independently, published a paper which essentially agreed with Seligman and Williams. These investigators found that: (1) temperature is the most important factor governing the rate of dissolution of aluminum in nitric acid; (2) next to temperature the most prominent factor in controlling corrosion rate is concentration of the nitric acid; (3) some impurities,
such as Fe ion, increased the rate of dissolution, others decreased the rate; (4) lower oxides of nitrogen stimulate the attack.
The effect of temperature was shown to increase sharply between 56°C and 80°C. The rate of solution of aluminum also showed a sharp increase which centered at about 4.5% water.

The fundamental nature of the solution of aluminum in strong nitric acid is in doubt. Callendar believed that at an aluminum anode the nitrate ion is discharged and breaks down forming first an oxygen polarizing layer and then the oxygen combines with the metal to form a solid film, the pores of which are filled with a resistant layer of oxygen gas. McKee and Brown state that the mechanism of solution of aluminum in dilute solution of nitric acid is similar to its solution rate in dilute sulfuric acid except that there is no hydrogen evolution in the case of nitric acid. Bryan states that aluminum passes into solution in strong acids as the positive ion Al. He postulates the following reactions:

$$2\text{Al} = 2\text{Al}^{3+} + 6\text{e} \quad (34)$$
$$2\text{Al}^{3+} + 6\text{Cl}^- = 2\text{AlCl}_3 \quad (35)$$
$$6\text{HCl} = 6\text{H}^+ + 6\text{Cl}^- \quad (36)$$

Although Bryan does not specifically discuss nitric acid, he does classify it as a strong acid. Presumably the nitrate ion could be substituted for the chloride ion in the anode reactions. Reschke and Geier investigated the dissolution rate of aluminum in high purity nitric acid. They found that pure aluminum corrodes less than any of its alloys in 99.6% nitric acid. A work hardened piece
of aluminum was found to corrode less than an identical sample which had been heated at 500°C for one hour and air cooled. Aluminum was found to be more passive in concentrated nitric acid than in dilute nitric acid. Some recent investigations have been made to evaluate materials suitable for handling fuming nitric acid (101, 102). Pure aluminum and aluminum alloys of low alloy content were judged sufficiently resistant to fuming nitric acid for industrial usage.

No information was found concerning aluminum as an anode in bi-metallic corrosion in fuming or strong nitric acid.

The products of corrosion of aluminum in nitric acid have been investigated. Several nitrates of aluminum are known. Mellor (103) states that the enneahydrate \( \text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) is stable in 73% or less nitric acid, the octohydrate \( \text{Al(NO}_3\text{)}_3 \cdot 8\text{H}_2\text{O} \) is stable in nitric acid of 73 – 81% concentration, and the hexahydrate \( \text{Al(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \) is stable in nitric acid more concentrated than 81%. Seligman and Williams (104) confirm that only the hexahydrate is stable in nitric acid of 1.5 specific gravity. This precipitate was obtained by the action of commercially pure aluminum on nitric acid of 1.5 specific gravity. The limit of solubility of the hexahydrate in nitric acid of 1.5 specific gravity was found to be 0.0177 gm of Al – equivalent to 0.21 gm of the hexahydrate in 100 ml of the acid at 20°C. It was also observed experimentally that as the metal slowly dissolves at 20°C, the acid becomes saturated with the nitrate which deposits in large crystals until the aluminum has been dissolved or the acid has been exhausted.
(c) **Behavior of Stainless Steel in Nitric Acid**

Very little information is extant on the behavior of stainless steels in strong nitric acid. Evans\(^{105}\) has experimented with iron in nitric acid and states that iron is a borderline case in his classification of metals according to the cathode reaction involved. Watts\(^{106}\) believes that, since stainless steels contain metals which are transition elements, both types of cathodic reaction are possible. In nitric acids more concentrated than 65%, however, the reduction of nitric acid to nitrous acid is stated to be the cathodic reaction.

Nitric acid is considered to be a strong oxidizing agent. Since at least one theory attributes the passivity of stainless steels to an oxide film, it might be reasonable to suppose that stainless steels were inert to fuming nitric acid. The opposite has been found to be true. Fontana, Beck, and Holzworth\(^{107}\) found that the resistance of stainless steel to fuming nitric acid varies with the composition of the steel, the temperature of testing, and with the heat treatment of the steel. They find that corrosion rates of 100-250 M.P.Y. (mils per year) are possible in the case of type 347 stainless steel. Kaplan and Andrus\(^{108}\) and Sands\(^{109}\) have tested various stainless steels in fuming nitric acid and found appreciable corrosion rates.

No information has been found concerning the behavior of type 347 stainless steel as a cathode in bi-metallic corrosion in fuming nitric acid.
3. Electrolytic Behavior of Nitric Acid

Faraday observed that in the electrolysis of dilute nitric acid between platinum electrodes, hydrogen was evolved at the cathode, but with concentrated solution no hydrogen evolution occurred, the cathodic products being nitrous acid and apparently nitric oxide. By increasing the voltage, however, hydrogen could be liberated even from concentrated solutions: the greater the concentration, the higher was the voltage needed for this purpose. Ellingham did detailed work on this subject. Ellingham states that the primary cathode reaction in nitric acid solutions under all conditions is

\[ \text{H}^+ + e = (\text{H}) \]  \hspace{1cm} (37)

Where \((\text{H})\) is atomic hydrogen occluded in the platinum. This process may be followed by either of the alternative secondary reactions

\[ \text{HNO}_3 + 2(\text{H}) = \text{HNO}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (38)
\[ 2(\text{H}) = \text{H}_2 \text{ (gas)} \]  \hspace{1cm} (39)

Reaction (39) will proceed only if reaction (38) cannot proceed at a rate sufficient to remove \((\text{H})\) as fast as it is formed in reaction (37). Reaction (38) is very slow for even moderately concentrated solutions, unless nitrous acid is present as a catalyst. The current density which can be maintained by reaction (38) is therefore mainly determined by the concentration of nitrous acid which is established in the layer of solution next to the cathode. When reaction (38) is insufficient to maintain the current density being applied, a sudden transition is made to reaction (39) as the current density is increased. It is therefore understandable that in more concentrated acid solutions
the critical current density for the transition to hydrogen evolution is more difficult to attain. As the concentration of the acid increases so does the concentration of nitrous acid in the nitric acid. This mechanism also explains the variation in behavior of different metals. The very basic metals will carry out the reaction of

\[ M + 2H^+ = M^{++} + 2(H) \]  

more vigorously than the nobler metals. The rate of supply of atomic hydrogen will be too great for reaction (38) and reaction (39) will ensue. With nobler metals the activity of atomic hydrogen will be lower in the layer of solution adjacent to the cathode and conditions will correspond to electrolysis at a lower current density. Reaction (38) will therefore predominate.

The work of Ihle\(^{112}\) on the Grove-Smee cell, corroborates the explanations made by Ellingham. Gradual dilution of the acid lowers the cell e.m.f. only slightly until a critical dilution is reached at which the e.m.f. decreases suddenly to a new and steady value.

C. Nature of the Surface of Aluminum

The wide use of aluminum and its alloys in chemical service is due to the protective coatings which form on the metal. The compound \( \text{Al}_2\text{O}_3 \) forms on aluminum under a wide variety of conditions. The coating thus formed is tightly adherent, transparent, and usually self-healing when exposed to oxidizing media. Champion\(^{113}\) furthermore ascribes the property of adaptability to the coating. He states that when the metal with the air formed film is exposed to a more corrosive environment the film is usually built up until the
protection adequate for the environment is attained.

The exact nature of the film has been the subject of much investigation. According to Tolley (114), six crystalline forms of alumina exist and all except $\alpha - Al_2O_3$ (corundum) may appear as corrosion products on aluminum. The film formed at ordinary temperature in air is believed to be amorphous or microcrystalline (115,116,117). When aluminum is made an anode in certain electrolytes, an additional coating of oxide begins to form on its surface. Edwards and Keller (118) classify the oxide formed as follows:

1. the electrolyte has no solvent action on the oxide. The oxide film is non-porous and non-absorptive. Growth of film stops.

2. the oxide is slightly soluble in the electrolyte. The coating is porous and absorptive and grows to great thicknesses.

3. the electrolyte dissolves the film as fast as it is formed. Anodic polishing or brightening takes place. At most a very thin film of oxide is formed.

All three types of action are known. It is the opinion of Edwards and Keller (119) that in all cases the oxide formed is not a hydrated form, but an anhydrous crystalline deposit which contains small percentages of mechanically entrapped liquid or electrolyte.

The mechanism of the growth of the anodic film seems to be quite complex. Lilianfeld, Appleton, and Smith (120) proposed that two films existed on anodized aluminum. A "dry" layer next to the
metal, and a "wet" layer atop the dry layer. The dry layer was postulated to be amorphous, anhydrous $\text{Al}_2\text{O}_3$ and the wet layer to be hydrate alumina plus entrapped electrolyte. Edwards and Keller (121) have named the inner layer the "barrier layer" and state that it is an impermeable film which has grown to a thickness just sufficient to prevent the transfer of ions sufficient to further growth. When a potential is applied, the migration of ions continues. A thick outer coating is formed which is porous. According to Tolley (122), these pores are 100 Angstrom units in diameter and $10^{11}$ per sq. cm. in number. At the base of such pores growth of the porous outer layer is propagated. Hoar and Price (123) assume (1) positive metal ions leave the metal and diffuse through the oxide and combine with oxygen at the interface of oxide and environment if electrons can also pass through, and (2) that electrons can pass through by thermionic emission into the conduction levels of the oxide or by the tunneling effect. Cabrera, Terrien, and Hamon (124) also believe this mechanism to be true for oxidation in air. Mott (125) concurs and believes the oxide film to be rich in metal in interstitial positions.

It is thought that the conditions of voltage and current influence the type of oxide deposit. The deposit will be more highly hydrated if voltage is low. Indeed it seems that a hard, anhydrous layer can be laid down in only a limited range of high voltage (126). Most layers will be thus porous and conducting in nature.

The oxide film on aluminum has another interesting feature.
When an anodized aluminum specimen is placed into an electrolyte as an anode, the oxide layer acts as a very high resistance. When the aluminum is made cathodic it allows free passage of current. It thus displays a "valving" or "rectifying" action. 

D. Experimental Techniques

1. Single Electrode Tests

In this type of experiment, the test specimen is coupled to another metal to form a galvanic cell, or the test specimen is coupled to an inert electrode, such as platinum and a source of external applied current completes the couple. The latter method is capable of better control and greater flexibility than is the former. It is common to use a tubulus in one form or another as a probe for measuring the potential of the test sample. Unless such a tubulus be unusually small, the gross potential of the test piece will be measured. This gross potential will be an average value of the potentials of the local anodes and cathodes on the surface of the metal. The gross potential is sufficient when the action of the test piece as a member of a galvanic couple is the property to be measured.

2. Tools for Potential Measurements

a. The Reference Electrode

The standard means of measuring an electrode potential is to measure the potential difference between the test electrode and some electrode of known and constant potential. The saturated calomel electrode is often used for reasons of convenience. It has a potential of 0.2415 volts at 25°C as compared to the standard.
hydrogen electrode\(^{134}\).

**b. The Potentiometer**

To measure the potential difference between standard electrode and test electrode, a balancing potentiometer is often used. This instrument opposes the current generated by the test couple with a back e.m.f. so that little current flows. Current flow would cause polarization shifts and obscure the potential readings, and in the case of the potentiometer only a small current flows through the galvanometer. Methods of zero current flow have been devised, notably by Pearson\(^{135}\).

**c. Interrupter Methods**

Because the polarization measurements taken while current is flowing include the I R drop of the electrolyte between the tubulus and the sample, methods have been devised for momentarily interrupting the current and measuring the potential at zero current flow\(^{136}\). Modern methods involve electronic interrupters for high speed operation to overcome the rapid polarization decay that occurs when current is interrupted\(^{137}\).
IV. EQUIPMENT

A. For Weight Loss Measurements

1. Single Metal Tests

   The test specimen is held in a glass cradle. The cradle is inserted into a wide-mouthed, 1000 ml. pyrex Erlenmeyer flask in such a manner that the specimen is in the vertical position. One hundred ml. of fuming nitric acid solution per square inch of area of specimen is poured into the flask, and the flask is put into a constant temperature bath. The mouth of the flask is closed with a loosely-fitting finger-type condenser.

2. Galvanic Couple Tests

   A schematic illustration of the galvanic couple used in these tests will be found in Figure 6. Electrical contact is completed from the aluminum test plate through the aluminum bolt, steel spring, and stainless steel bolt to the stainless steel test plate. The threaded Teflon tube protects the electrical contact from the acid, acts as a spacer to provide a fixed separation between the test plates, and insures that the test plates are parallel to each other. The couple is disassembled by unscrewing the two bolts, and the test plates are weighed.

B. For Corrosion Current Tests

   For the corrosion current tests the equipment shown in Figure 7 was used. Each test specimen was clamped to a horizontal support over the acid bath, and external electrical connection was made through a milliammeter.
0. **For Polarization**

1. **The Electrical System**

   A schematic illustration of the polarization testing equipment is shown in Figure 8. The Rubicon type B high precision potentiometer can be connected between either test specimen and its attendant reference electrode. The reference electrodes are saturated calomel cells. Currents up to 25 milliamperes can be impressed between the platinum electrode and either test electrode by means of a 6 volt lead-acid battery in series with a variable resistance. The two test electrodes can be short circuited through a milliammeter, the platinum electrode being on open circuit.

2. **The Fluid System**

   The fluid system is shown schematically in Figure 9. Placed closely adjacent to the test specimen is the potential probe. The probe consists of a pyrex tube with an asbestos fiber sealed into the end. This fiber allows passage of ions with only limited interchange of fuming nitric acid and bridge electrolyte. The potential probe is filled with 10% potassium nitrate solution. This salt was chosen as the salt bridge electrolyte since it has desirable characteristics for this use, i.e. the potassium ion and nitrate ions have high and nearly equal transference numbers. Potassium chloride, perhaps the most commonly used salt for bridge electrolytes, was judged unsuitable because the chloride ion is known to have a deleterious effect on the protective film on aluminum. The potential probe is connected to a cell containing the calomel electrode by means of a pyrex tube filled with a mixture of the 10% KNO₃ solution and
agar-agar gel. The mixture allows free passage of ions and prevents siphoning of solution.

The fuming nitric acid test solution is contained in a pyrex battery jar, 6 inches in diameter and 6 inches in height. The battery jar is fitted with a Teflon cover, pierced to allow ingress for potential probes and specimen holders. The battery jar is placed in a constant temperature bath in which the temperature can be controlled to within one degree Fahrenheit. The cell containing the calomel cell is not in the constant temperature bath but outside it and at room temperature.

3. The Specimen Holder

A schematic illustration of the sample holder is shown in Figure 27. The electrical connections are protected from the acid, and the test specimen is completely submerged so that no "water line" effects are involved. The glass tube of the specimen holder extends through the Teflon cover of the test cell and is rigidly clamped at the upper end as is the potential probe.

A photograph of the assembled equipment is shown in Figure 28.
V. MATERIALS AND PROCEDURES

A. Materials

Three commercial aluminum alloys were used. For the weight loss tests, 2S, 3S, and 61S rolled sheets were used as received. For the galvanic corrosion current tests 3S sheet was used. For the polarization tests 2S - 0 extruded rod was used.

Two A.I.S.I. Type 347 stainless steels were used. For the weight loss and galvanic current tests a commercial Type 347 stainless steel in sheet form was used. For the polarization tests the samples were machined out of a type 347 stainless steel casting which was made in the laboratory.

In table 1 are shown the compositions of these materials.

B. Procedures

1. The Weight Loss Tests

The stainless and aluminum specimens were cut from sheets, the bolt holes were drilled, the samples were abraded with a 120 grit paper until all the original surface was removed, and the dimensions of the samples were measured in order to compute their areas. The samples were washed in water, rinsed in acetone and dried in air. They were weighed and then mounted in the galvanic couples. They were inserted into the acid solutions for five 48-hour periods, being washed in water, rubbed with a rubber stopper, rinsed in acetone, and weighed after each 48-hour period. Fresh acid was used for each period. The weight loss in each period was noted and corrosion rates are reported as a five period average. The corrosion
rates are calculated in mils per year (M.P.Y.) according to the formula:

\[
\text{M.P.Y.} = \frac{527,000 \times W}{D \times t \times A}
\]

Where,

- \(W\) = the weight loss in grams,
- \(t\) = the test time in hours,
- \(D\) = the density in gms/cm\(^3\),
- \(A\) = the area of the specimen in square inches.

To test the effect of variation of anode and cathode areas upon the anode and cathode weight losses, test plates of various sizes were mounted in the galvanic couples.

To test the effect of separation distance upon anode and cathode weight losses, the Teflon spacer was lengthened.

The room temperature tests were not conducted in constant temperature baths. Constant temperature baths were used for the tests at 120°F and 160°F.

The specimen area, from which the corrosion rate was calculated, was the total area of the sample less the area covered by the bolt heads and less the area covered by the Teflon spacer.

2. Corrosion Current Tests

The samples were prepared as were the specimens in the above discussion. The bolt was inserted and screwed through the Teflon tube. Each of the couple members was clamped to a horizontal support, the electrical connections to the milliammeter were made, and the specimens were lowered simultaneously into the acid solution. For these tests the acid was contained in an open dish which had been
placed in a constant temperature bath. The galvanic current was read periodically and recorded when it appeared to have reached an equilibrium value.

For the effect of variation of cathode area upon galvanic current, one aluminum anode and several cathodes, in multiples of the anode area, were used. The anode and one cathode were tested, both were removed from the solution, the anode was resurfaced, and the anode, together with a new cathode, was inserted into the acid again. This procedure was reversed in determining the effect of varying the anode area upon the galvanic current, i.e. one cathode and several anodes were used.

To determine the effect of distance of separation upon the galvanic corrosion current, the clamps holding anode and cathode to the horizontal support were moved to measured positions along the horizontal support.

3. Polarization Tests

The polarization behaviors of aluminum and stainless steel were determined separately. The variation in potential of each metal with current was measured by impressing for current on the metal by means of an inert electrode. To determine the polarization of aluminum, the battery (see Figure 8) was connected between the aluminum and the platinum in such fashion that positive electricity flowed from the aluminum to the solution. The stainless steel electrode, having been previously removed, was not present in the test cell. In Figure 8 then, switches $S_1$ and $S_2$ are
closed and electrode B is not present. The amount of current flowing is regulated by the variable resistance R. The potential difference between the aluminum and the calomel reference electrode was read by closing switch $S_3$ to position B.

To determine the polarization behavior of the Type 347 stainless steel specimen, electrode C was removed from the test cell and electrode B was inserted. The battery was connected in such fashion that positive electricity flowed from the solution to the stainless steel. In effect the platinum acted as an anode and the stainless steel as the cathode. Switch $S_2$ was closed and switch $S_3$ was closed to position A.

To measure the behavior of the couple 2S - 0 aluminum - 347 stainless steel, electrodes B and C are inserted into the test cell. Switch $S_2$ is opened, switch $S_1$ is closed and switch $S_3$ is alternated between positions A and B to read the potentials of electrodes B and C respectively.

The operation of the equipment in the case of the stainless steel was quite simple. The electrode was prepared and inserted into the test cell. The impressed current was then set and held at some arbitrary value. Potential readings were taken periodically until a steady value was attained, and then the impressed current was set at a new value and so forth. With a stainless steel electrode it was possible to start at either end of the 0 - 25 milli-amperes impressed current range available. It was also possible to proceed freely up and down this range in either direction. The
only restriction was that if the stainless electrode were left very long at zero impressed current, previous potentials could not be reproduced. As long as some current was impressed, however, all potential readings between 1 and 25 milliamperes could be closely reproduced.

Such was not the case for aluminum. It was found that if the aluminum were initially run at some low value of impressed current, one could not further increase the current. The potential of the aluminum anode would become so cathodic as to be out of the range of the instruments, and the current would decrease to a steady value which could not be increased. So the aluminum was always operated at initially high impressed current. This initial rate was 25 milliamperes (25.4 M.A./in.²). The current was then decreased in successive steps, the potential being read at each step after equilibrium was attained, to zero. In the range 20–25 milliamps. the current could be increased or decreased. Below approximately 20 M.A., however, the current could be only decreased. An increase in current caused the high-potential and low-current condition described above. It was furthermore noted that a phenomenon of periodicity was encountered somewhere in this range of impressed currents. When the aluminum anode was tested in acid of nominally 100% concentration for example, the potential at a current setting of 15 milliamps. (15.2 M.A./in.²) varied periodically so rapidly that it could not be read. Furthermore the current varied accordingly. This periodicity occupied the range 12.5 to 16.5 milliamperes in the above example.
Below this range, the potential and current were again steady and could be read. In all acid concentrations tests, this periodicity was noted, and the location and extent of the periodicity range varied with the concentration of the acid.

When the stainless specimen and the aluminum specimen were short-circuited through the ammeter, it was found necessary to "season" the aluminum in the acid solution at 25 M.A. for a short time in order for the aluminum potential to assume the values determined for aluminum V.S. the platinum electrode. Hence the aluminum was so seasoned, the stainless cathode was then inserted, switch 2 was opened, and switch 1 was closed. The system was allowed to come to equilibrium, and current and potentials were read.

The equilibrium values spoken of in the above discussions are not true equilibria. The potential of the stainless steel does attain a steady value within a short time. The potential of the aluminum, however, continuously decreases for at least forty-eight hours. The potential of the aluminum varies rapidly for the first few minutes and then assumes a very slow rate of change. The potential at this point was recorded as the "equilibrium" potential. This procedure was made necessary by the nature of fuming nitric acid. The acid decomposes continuously. Gaseous compounds of nitrogen and oxygen, as well as elemental oxygen, escape from the liquid during the testing. Since this indicates that the composition of the solution is changing during the test, it is not unexpected
that the potential of a metal will change. Therefore the practice described above was adopted as a standard.

The preparation of the surface of the test specimens was found to be important. The potential of the aluminum test specimen is particularly sensitive to previous history of the surface. The most reproducible results were obtained by abrading the specimen on 400 grit paper, rinsing in alcohol, and immediate insertion into the test cell. This procedure was used for all test specimens.

New test solutions were made up for each test. The dilution of nitric acid was carried out by placing the water in the test cell and adding the acid. All solutions were heated for one hour at the testing temperature before the test specimens were inserted.
VI. DISCUSSION AND RESULTS

A. Weight Loss Data

1. General

The corrosion rates of 2S, 3S, and 61S aluminum have been determined in fuming nitric acid at room temperature, 122°F, and 160°F. As shown in Table 2, the corrosion rates of these materials are quite low. Type 347 stainless steel, however, displays much higher corrosion rates. When a galvanic couple is made of these metals, the corrosion rate of the aluminum is greatly increased, while the stainless steel is virtually protected from attack. It is apparent that the aluminum is acting as an anode and the stainless as a cathode. The attack upon the aluminum is uniform in appearance. The specimens were slightly discolored but possessed no visible film. The stainless specimens remain bright and unattacked.

2. The Effect of Relative Area.

The effect of changing the ratio of the area of the anode to the cathode in fuming nitric acid has been studied by means of weight loss measurements. The data obtained are so erratic as to prevent the construction of a smooth curve. The data does, however, indicate a general trend. As might be expected, the large is the cathode (Type 347 stainless steel) area relative to the anode area (2S, 3S, or 61S aluminum alloy), the greater is the corrosion rate of the anode, the corrosion of the cathode being essentially negligible in all cases. These data are shown in Table 3 for the 2S aluminum alloy which is typical.
Such behavior is well known. The effect of increasing the relative cathode area is to increase the current density upon the anode and correspondingly the corrosion rate. If the anode has the characteristic of polarizing appreciably, the increase in corrosion rate will be less than proportional to the increase in cathodic area. The results indicate such to be the case for the aluminum - stainless steel couple.

3. The Effect of Distance of Separation

The effect of distance of separation in fuming nitric acid has been studied by means of weight loss data. As is shown in Figure 10, the greater the distance of separation between an aluminum anode and a stainless steel cathode, the less is the corrosion rate of an aluminum anode and the greater is the corrosion rate of a stainless steel cathode. The data shown in Figure 10 are those for a 61-S aluminum anode and, as is always the case in this work, a Type 347 stainless steel cathode. The data for the 61-S anode are typical of all the aluminum anodes. The effect of distance of separation is presumed to be due to the effect of resistance to ionic transfer through the fuming nitric acid.

4. The Effect of Temperature

The effect of temperature on galvanic couples in fuming nitric acid has been studied by means of weight loss data. As shown in Figure 11, there is a sharp increase in anodic corrosion somewhere above 122°F. The exact cause for this effect is not known, but it is believed that the solubility of the anodic corrosion products might
be responsible. Some crude experiments were performed with carbon electrodes and fuming nitric acid which showed no marked increase in conductivity of the acid through the room temperature to 160°F temperature range. The corrosion reaction will undoubtedly proceed with greater vigor at the higher temperatures, but the difference in vigor with only an 80°F temperature increase seems too small to account for the observed effect and should furthermore be continuous. This is an aspect of the behavior of these galvanic couples which requires much more detailed investigation.

5. The Effect of Dilution of the Acid

The effect of dilution of fuming nitric acid with doubly distilled water on the corrosion rates of aluminum alloys and Type 347 stainless steel has been investigated by the weight-loss method. The results are shown in Figure 12. All corrosion rates are 5 period averages. The effect of added water on the corrosion of uncoupled 3S aluminum is to increase the corrosion rate sharply above 5.2% water. The effect on uncoupled Type 347 stainless steel is to decrease the corrosion rate markedly down to about 5.2% water and more gradually thereafter. At all dilutions tested, coupled 347 stainless steel was essentially unattacked. The effect of water on the corrosion rate of coupled 3S aluminum is most striking. There is a decided minimum in the corrosion rate at 5.2% water. The appearance of the test specimens as shown in Figure 13, indicates that the discontinuity in the corrosion rate is real. A pitting or localized attack takes place on the aluminum anode as opposed
to the more usual uniform attack which occurs at the other dilutions. Such anodes have the appearance of having had a thick, protective film which broke down in spots to give a pitting attack. On this assumption, samples of aluminum anodes corroded in 1.2, 4.2 and 11.2% water solutions of white fuming nitric acid were prepared and sent to Battelle Memorial Institute, Columbus, Ohio, for identification of the surface films. Although the three specimens were different in appearance, the 1.2% water specimen being discolored, the 5.2% as previously described, and the 11.2% having a bright, polished appearance, the laboratory report from Battelle Memorial Institute indicated no differences in surface film. Electron diffraction and x-ray diffraction analyses of the surface film indicated only the customary amorphous or microcrystalline film of aluminum oxide. A further discussion of the effect of water will be found in Section VI, C of this report.

Since water in the fuming nitric acid was found to be of considerable importance, analyses of the acids used in the work previously discussed were made, and an average value of 1.2% water in the white fuming nitric acid is assumed.

B. Corrosion Current Tests

Since weight loss measurements of corrosion are very time consuming, additional data was collected by means of measuring the current densities in galvanic couples. Although many of the same inaccuracies occur in current measurements that are found in weight loss tests, i.e. inhomogeneity of metal specimens, variations in acid composition, and non-
uniformity of surface conditions, much information can be collected by this method.

1. The Effect of Relative Area

The effect of varying the relative anode area on the anodic current density is shown in Figure 14. The effect of varying the relative cathode area on the anodic current density is shown in Figure 15. These data confirm the results found by weight loss methods, namely that the anodic attack is increased by increasing the relative cathode area. Preparation of the aluminum surface by concentrated hydrochloric acid is found to render the surface more active. The shape of the curves in Figures 14 and 15 is also informative. If the couple were under nearly ideal anodic control, the curve in Figure 14 would be near the abscissa and be nearly vertical. If the curve were under ideal cathodic control, the curve in Figure 15 would be a straight line passing through the origin. Since the increase in anodic current density is less than proportional to the increase in cathode area, the couple is not under ideal cathodic control. According to Figure 14, the couple is not under ideal anodic control. These results are considered as evidence that the 3S Al - 347 stainless steel is under mixed control. Since 2S, 3S, and 61S aluminum are so similar in their behavior as anodes in white fuming nitric acid, it is assumed that all of these alloys when coupled to type 347 stainless steels will operate under mixed control.

2. The Effect of Distance of Separation

The effect of distance of separation on galvanic corrosion
current is shown in Figure 16. The results confirm the observation made from weight loss data that the effect of the galvanic couple lessens with increased distance of separation. The shape of the current density curve is similar to the shape of the weight loss curve, but weight loss data cannot be correlated directly with corrosion current because Faraday's law cannot be applied. The amount of aluminum dissolved can no doubt be correlated to the amount of current used for that purpose, but part of the current passed is used in polarization effects. Attempts were made to apply Faraday's law in the case of 2S aluminum in white fuming nitric acid, but the amount of metal dissolved was found to be less than the theoretical by varying amounts.

3. The Effect of Temperature

The effect of temperature on the galvanic corrosion current of an 3S alumin - Type 347 stainless steel couple is shown in Figure 17. The effect was found to be approximately linear. The correlation between this data and the weight loss data is very poor. It is believed that the anomaly lies in the fact that the weight loss data were compiled from five 48-hour tests while the total time of measurement for the corrosion current data was about 3 hours. It is believed that if the galvanic couple whose current is being measured were held at each test temperature for several hours a curve similar in shape to that shown in Figure 11 would be obtained. If some solubility phenomenon were the prime factor in the temperature behavior of the test galvanic couple, such a phenomenon might well
be time dependent.

It should be pointed out that all the corrosion current data presented above do not represent the true corrosion currents. They are always less than the actual value by that amount of current necessary to the operation of the measuring milliammeter. The resistance of the meter, however, is small, and so the reported currents are quite close to the true currents.

C. Polarization Data

1. Polarization of Aluminum in 98.8% acid

The polarization of a 2S aluminum anode was tested by measuring its potential while current was impressed by means of an inert cathode. It was found that in white fuming nitric acid the electrode potential of aluminum is positive to the saturated calomel electrode at all tested values of impressed current. This observation agrees with the findings of Steiner and Kahlenberg\(^{140}\) who find the potential of aluminum is positive relative to the calomel electrode above 56% acid concentration and negative at lower concentrations. As discussed above under Procedures, Section V, it was also found that one could not impress initially low currents and subsequently increase the current. It was necessary to begin each test at initially high current and then decrease the current. The aluminum polarization curve in nominally anhydrous (actually containing 1.2% \(H_2O\)) white fuming nitric acid is shown in Figure 18. As the current is decreased a range of periodicity of potential and current is observed. This range of periodicity is represented by the dashed
portion of the curve in Figure 18 and extends from 10 to 15 applied milliamperes. In this range, potential and current fluctuate regularly and steadily up and down. The fluctuations are too rapid to allow the reading of potential and current values. This periodicity was observed in one test for a period of six hours with no diminution of the effect. Such a periodicity phenomenon of an aluminum anode in nitric acid has been observed before\(^\text{138}\). Hedges\(^\text{139}\) studied periodicity for aluminum anodes in nitric acid as well as other electrode-electrolyte systems, and he concluded that the necessary conditions for periodicity are: (1) a film must form over the anode, (2) this film must be soluble in the electrolyte when the circuit is broken; it follows that the electrode may exist in one of two possible states — with or without the film, and (3) the current density must be between two well-defined limits, which depend on the temperature, concentration, and composition of the solution. Hedges found that the periodicity effect for an aluminum anode existed at 50 milliamps. per cm.\(^2\) in 100% nitric acid at 30°C. The current value for periodicity was lowered by (1) raising the temperature and/or (2) lowering the concentration. Hedges did not find the basic cause of the mechanism but stated that the phenomenon occurred when the metal had about equal chances of remaining in an active or a passive state.

Below this periodicity range the potential of the aluminum anode and the impressed current remained steady and could be read.

An explanation of the basic mechanism of the anodic behavior of
2S aluminum can be developed. At high current densities, i.e. 15 to 25 milliamps impressed current, the anode dissolves rapidly and the rather low solubility limit of the acid for the aluminum ion is soon exceeded. Furthermore the nitrate ion is being supplied to the anode at a high rate due to the high impressed current. Therefore aluminum nitrate, presumably the hexahydrate, begins to precipitate heavily around and on the anode. This film changes the potential of the anode in a cathodic direction although the film is only semi-protective. This film is observed to form and to continuously spall off the anode. Gas evolution at the anode helps to keep this precipitate broken loose. The precipitate has been identified as aluminum nitrate. Dehydration experiments on the precipitate yielded somewhat anomalous results and the exact amount of water of hydration was therefore not experimentally proved. The analysis of the anode gas was found to be a prohibitively complex procedure, particularly since the total amount of gas evolved is small, and was not performed. The gas could be NO evolved by discharge of the nitrate ion at the anode.

At low current densities, i.e. zero to 9 milliamps impressed current, the solubility limit of the acid for aluminum nitrate is exceeded more slowly and the nitrate ion is also supplied much more slowly because of the lower impressed current. Nascent oxygen is present in nitric acid as a product of acid decomposition. The aluminum will therefore oxidize chemically as well as form the nitrate electrochemically. The rate of oxidation of the aluminum will not depend on the current density, because the oxygen is not present as
ions, and therefore the rate of oxidation of the aluminum anode ought to be constant over the range of impressed current. Furthermore the oxide produced will not adhere tightly to the anode at low current densities, but will do so at high current densities due to its previously discussed "valving" action. Therefore at low current densities the anode is not rapidly and extensively covered with aluminum nitrate, and the oxide film is not tightly adherent and may contain entrapped electrolyte or even be hydrated. The aluminum anode at low current densities would thus display a more anodic or active potential than at higher current densities. To summarize this explanation of anode behavior one can again start at the higher impressed currents. In portion A of Figure 18, aluminum is being rapidly dissolved and precipitated as nitrate salt and the oxide film is tightly adherent. As the current is gradually decreased the rate of dissolution of the aluminum diminishes as does the rate of precipitation of the nitrate. The potential becomes a little less cathodic. This process continues until region B is reached. Here periodicity ensues. The precipitate and the oxide are loosened and the potential becomes more anodic at the initial current decrease. This causes a fresh surge of current which again makes the potential more cathodic. This process then repeats itself. Such a mechanism satisfied Hedges' requirements for periodicity. The periodicity continues until region C is reached. In region C the rates of solution and precipitation are low, the oxide adheres still less tightly and a more active potential is observed. At zero current the potential suddenly becomes quite anodic as the valving action
becomes negligible and the rate of solution of the aluminum suffers a rapid decrease. There is a further consideration in this mechanism. Aluminum oxide was found to be slightly soluble in fuming nitric acid as is shown in Table 4. Furthermore there is a thermodynamic possibility that aluminum oxide is unstable in fuming nitric acid relative to aluminum nitrate. Consider the theoretical reaction.

\[
\text{Al}_2\text{O}_3 + 6\text{HNO}_3 + 9\text{H}_2\text{O} = 2\text{Al(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O}
\]

The free energy change of the reaction would be:

\[
\Delta F_{\text{reaction}} = [2\Delta F_{\text{fAl(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O}}] - [\Delta F_{\text{fAl}_2\text{O}_3} + 9\Delta F_{\text{fH}_2\text{O}} + 6\Delta F_{\text{fHNO}_3}]
\]

The necessary thermodynamic data has been found for 25°C.

\[
\begin{align*}
\Delta F_{\text{formation of Al(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O}} &= -526,230 \text{ cal/mole}^{(141)} \\
\Delta F_{\text{formation of H}_2\text{O}} &= -56,690 \text{ cal/mole}^{(142)} \\
\Delta F_{\text{formation of HNO}_3} &= -26,500 \text{ cal/mole}^{(143)} \\
\Delta F_{\text{formation of Al}_2\text{O}_3} &= -381,600 \text{ cal/mole}^{(144)}
\end{align*}
\]

Substituting these values in equation (2) we obtain

\[
\begin{align*}
\Delta F_{\text{reaction}} &= -1,052,000 + 1,050,835 \\
\Delta F_{\text{reaction}} &= -1,165 \text{ cal/mole at 25°C}
\end{align*}
\]

Thus it is possible that aluminum oxide may be slowly converted to aluminum nitrate. It may be assumed that this reaction will proceed more vigorously at the test temperature of 160°F. This reaction may explain, together with continual acid decomposition, the previously mentioned experimental observation that the potential of the aluminum anode does not reach equilibrium after 48 hours but decreases slightly and continuously.
Furthermore the necessity for the tests to be run at initially high currents can be explained. When the anode is first inserted into the test cell it is probably somewhat film free because of the method of surface preparation. After a period in the test cell, additional aluminum oxide was formed. An increase in current produces the valving action, the film becomes adherent, the potential becomes very cathodic, and the current subsequently decreases. The condition is one of high applied e.m.f. - that e.m.f. responsible for the impressed current - and high resistance producing a low current.

This proposed mechanism of the anodic behavior of 2S aluminum in white fuming nitric acid offers an explanation of the observed phenomena which is based on experimental results and supported by accepted theory.

2. Polarization of Aluminum in More Dilute Acid

Dilution of the white fuming nitric acid was found to have a marked effect on the anodic polarization of aluminum. Figures 19, 20, 21, 22, and 23 illustrate the polarization curves for an aluminum anode in the tested concentration of acid. The mechanism of the polarization of aluminum in white fuming nitric acid as proposed above can be expanded to explain the effect of dilution.

The effect of water in such a system is threefold: (1) water has an effect on the solubility limit of the aluminum ion; (2) water must be present for the precipitation of the hydrated nitrates of aluminum; no anhydrous nitrates of aluminum are known; and (3) water, in amounts less than 5% by weight, has an anticatalytic effect
towards the decomposition of nitric acid, i.e. it opposes the formation of further water, above 5% water the anticatalytic action is less effective.

The effect on the polarization of aluminum of 2% water added to the acid to give an acid of actually 3.2% water is shown in Figure 19. The polarization curve in this media closely resembles the polarization curve of aluminum in the acid of 1.2% water content. It is apparently safe to assume that the same conditions and reactions are operative in acid of this strength as those which are found in the acid of only 1.2% water content.

When the acid is diluted with 10% by weight of water to make a solution of 11.2% water content, the polarization of an aluminum anode is markedly affected. Such a polarization curve is shown in Figure 23. No region corresponding to "A" in the previous curves was found. The periodicity range, Region B, extends over the range of current from 10 to 25 milliamps. Region C is more anodic in acid of this dilution than in the more concentrated acid solutions. Assuming that the \( \text{Al}^{+++} \) ion is more soluble in this acid than in more concentrated acids, this polarization curve confirms the previously suggested mechanism for the anodic behavior of aluminum. It is proposed that region A is not found because the solubility is large enough that no massive accumulation of precipitated \( \text{Al(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \) can build up on the anode. Instead the conditions of Region B prevail. That is, the nitrate forms on the surface depleting the water content in the vicinity of the anode, water returns by diffusion and dissolves
the nitrate, thus suddenly and autocatalytically permitting the resolution of the rest of the precipitate. The current again builds up a concentration of nitrate and aluminum ions locally around the anode and the process repeats giving rise to the periodicity. Region C corresponds to the same region of the previous curve and is a region where dissolution of aluminum and anodic discharge of nitrate ions are slower processes and do not proceed rapidly enough to cause local saturation.

The polarization curve of an aluminum anode in a solution of 9.2% water content is very similar to the polarization curve obtained in the 11.2% water content solution discussed above. It is shown in Figure 22. The same conditions are operative and it is assumed that the aluminum potentials are a little more cathodic due to a slightly decreased solubility of the Al^{+++} ion.

Two types of polarization behavior have thus far been discussed. One type, that observed in "concentrated" acid, is comprised of regions A, B, and C. The other type, that observed in "dilute" acid, is comprised of regions A and B only. The curves for the polarization of aluminum in the "transition" range between the two types of polarization behavior are shown in Figures 20 and 21. They were obtained in acids of 5.2% and 7.2% water content respectively. In this region a third type of anodic polarization behavior for aluminum in nitric acid is noted. Region A is large in extent and persists down to very low current densities. Region B is very limited in extent and occurs at a low current density value. Region C is likewise
limited in extent and is found at a low value of current density. The explanation of the behavior of aluminum anodes in acids of this concentration range depends on the assumption that this is a condition in which the processes of precipitation of the nitrate and of solution of the nitrate have nearly equal rates. Furthermore this is the range of water contents where the anticatalytic effect of water towards the production of further water is on the verge of transition to a region where the anticatalytic action diminishes in importance. Thus the 5 - 7% water content solutions are in a range of transition from one type of anodic behavior to another. The appearance of an anode which has been tested in solutions of this water content indicates that both types of anode behavior are operative. As shown in Figure 25, the specimen has areas typical of the appearance of anodes tested in concentrated acid solutions and areas typical of the appearance of anodes tested in dilute acid solutions. These areas appear very early in the test and remain unchanged down to very low current densities. The potential exhibited by these specimens is thus an average of the potentials of the different areas. Correspondingly the potential is between the potentials of anodes in concentrated acid solutions and of anodes in dilute acid solutions. This gross potential will persist to low current densities because perhaps more of the current is carried by the "high concentration behavior" areas and therefore the current on these areas may be nearly that at breakdown of anodes corroded in concentrated solutions.
The three types of aluminum anode behavior may thus be summarized as follows:

**Case I. Low Water Content (1.2 - 3.2%).** The anodic polarization curve has three well-defined portions A, B, and C. Portion A is caused by thick precipitation of \( \text{Al(NO}_3\text{)}_3.6\text{H}_2\text{O} \) on the anode. The solubility of the acid for the nitrate is low. Portion B is a region of periodicity and breakdown of the nitrate film formed in portion A. Portion C is the potential due largely to an oxide film on the anode which loses its adherence at low impressed current values. See Figure 24.

**Case II. High Water Content (9.2 - 11.2%).** The anodic polarization curve is comprised of portions A and B only. The solubility of the solution for the Al\(^{+++}\) ion (and consequently the hexahydrate of aluminum nitrate) is high so that no precipitation of the nitrate occurs within the time of testing. Portions A and B are the same as in Case I.

**Case III. Intermediate Water Content (5.2 - 7.2%).** The anodic polarization curve is largely comprised of portion A' with B and C being present only in a very limited range. This case represents the transition between Cases I and II. Portion A' is stable over a wide range of impressed currents and is an average of portions A and C. Portion B is shortened by the sudden breakdown of the nitrate film. Portion C probably exists over a wider range than appears to be the case but the effect is obscured by the potential of the nitrate layer.
The proposed hypothesis is based on the assumption that the solubility of aluminum nitrate increases with water content of the acid. Furthermore it is assumed that the nitrate in question is the hexahydrate. This latter assumption is made on the basis of the work of Seligman and Williams which was discussed in the literature survey\(^{(149)}\). Experimental attempts to determine the water content of the nitrate yielded anomalous results. It was also impossible to determine directly the effect of dilution on the solubility limit of white fuming nitric acid for the hexahydrate nitrate. This nitrate is apparently not stable unless present in concentrated nitric acid. The white fuming nitric acid used in these tests was shipped in aluminum drums. The drums contained a considerable amount of sediment, similar in appearance to the precipitate observed in the test cell, which was identified as aluminum nitrate. An experiment was performed in which measured amounts of water were added to a measured sample of acid containing the sediment. The sediment appeared to remain stable until approximately 5% of water had been added at which point the sediment appeared to dissolve rather suddenly. Attempts were made to determine the solubility of the enneahydrate \(\text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}\) in acids of various water content but the results were inconclusive. Therefore the assumptions that the solubility of the hexahydrate is greater in dilute acid than in concentrated acid and that 5 – 7% dilution is a critical range for this solubility have not been proved true. Some experimental and indirect support has been obtained.
The proposed solubility phenomena is similar to the proven example of anodic oxidation of aluminum. As discussed in the literature survey, the aluminum has a polished, bright appearance when made the anode in a solution in which the oxide is readily soluble. The anode has a coated, dull appearance when anodized in a solution in which the oxide is slightly soluble. Thus it appears that the familiar anodizing process and the process of aluminum nitrate precipitation of this investigation may be highly similar.

It should be emphasized that the polarization tests are of rather short duration. Each polarization curve was completed in eight hours. The results of these tests may not apply to long-term corrosion tests. It is conceivable that in curves of Type II, for instance, the solubility limit of the dilute acid may be exceeded and the potential thereby be affected. This fact does not, however, negate the value of these curves as tools for studying the prevention of galvanic corrosion in the couple under discussion.

3. Polarization of Type 347 Stainless Steel in Acid Solutions

The cathodic polarization curves for Type 347 stainless steel in various concentrations of acid solution are shown in Figures 18, 19, 20, 21, 22, 23, 24 and on an expanded scale in Figure 26. The stainless steel was found to be essentially non-polarizing in all concentrations tested. The addition of water to the acid altered the potential very slightly in an anodic direction. No evolution of gas was observed. It is believed that the cathodic reaction
is the reduction of nitric acid to nitrous acid as suggested by the work of Ellingham which was discussed in Section II B.3. Accordingly, no great change in cathodic potential should be expected until a dilution is reached where the cathodic reaction can become the evolution of hydrogen. This causes a sudden and large decrease in potential such as is evidenced in the previously discussed case of dilution of the Grove-Smee cell.

4. **Polarization of the Galvanic Couple**

Some experimental attempts were made to determine the galvanic current generated by a 2S aluminum anode which had previously been corroded at 25.4 milliamps. per in.² for one hour and a type 347 stainless steel cathode. The results for acids of each concentration are shown in Figures 18, 19, 22 and 23. It was not possible to obtain this data in what has been termed the "intermediate" range of acid concentration, i.e. the acids of 5.2% and 7.2% water content. The short time consumed in switching from the platinum cathode and impressed current used in preparing the anode to the stainless steel cathode apparently was sufficient to disturb the equilibrium existing at the anode. Consequently at the measured galvanic current the potential of anode and cathode were not those previously determined for that current. Good agreement was obtained in the "concentrated" and "dilute" ranges of acid concentration.

The galvanic current of 6 milliampères observed in the acid of 1.2% water content would cause a corrosion rate of approximately 1300 mils per year according to Faraday's Law. This is about three
times greater than the corrosion rate observed in the weight loss tests. This result is not unexpected. The aluminum anodes in the weight loss tests were initially covered with an air-formed oxide film which must be rendered ineffective before large currents can pass. This oxide film has been shown to be slightly soluble in fuming nitric acid. The determined solubilities are shown in Table 4. Another factor which may aid in activating the aluminum surface is the previously discussed possibility that nitric acid possibly may convert aluminum oxide to aluminum nitrate. The activation process is probably quite slow because of the competing passivation process of direct oxidation of the aluminum by the oxygen present in the acid. The factors causing the discrepancy between observed galvanic current and observed anode weight loss can be summarized as follows:

1. The anodes used in weight loss tests are covered with a passive film of $\text{Al}_2\text{O}_3$.
2. This film dissolves slowly in nitric acid.
3. The negative free energy change which may cause the conversion of the oxide to the nitrate is small.
4. Free oxygen in the acid tends to re-passivate the aluminum.
5. The overall activation process is therefore probably slow because factors 2 and 3 are probably slow and are furthermore opposed by factor 4.
6. Additional experiments using variable impressed currents have shown that Faraday's Law is not directly applicable; the actual weight loss is less than the theoretical weight loss.
D. Correlation of Tests

The correlation between weight loss and corrosion current tests has been previously discussed. It was shown that good qualitative agreement was not strictly obtained because of the inapplicability of Faraday's Law. The correlation of the polarization data with the other data is interesting. The potential difference between the metals is not an indication of the galvanic corrosion which will ensue when the metals are coupled but rather a measure of their tendency to corrode. For instance an aluminum anode which is in the range of portion A of the polarization curve has a quite cathodic potential but still corrodes at a rapid rate. The effect of water on the polarization of aluminum in fuming nitric acid is a good reflection of the effects of water on the galvanic corrosion of the test couple in fuming nitric acid. The equipotential points in the various polarization curves represent the limiting current for the galvanic couples. In accordance with the weight loss results, the equipotential points indicate that the galvanic corrosion in 1.2% and 3.2% water should be about equal, that the region around 5% water should exhibit a low corrosion rate, at least initially, and that the galvanic corrosion in 9.2% and 11.2% water content should be nearly equal and higher than in the other test solutions. The values obtained for actual galvanic corrosion current, those values designated at I_g, also show the relationship. Thus the polarization data can apparently be used to make approximate predictions of corrosion behavior.
E. Significance of Results

This investigation has revealed much knowledge of the behavior of the tested galvanic couple in fuming nitric acid. The applicability of polarization testing to the studied galvanic system has been proved. The nature of the polarization curves has shown the futility of using cathodic protection through impressed current to prevent this galvanic corrosion, for the stainless steel cathode does not readily polarize and a prohibitively large impressed current would be necessary to polarize the cathode to the open circuit potential of the anode. The use of cathodic inhibitors has been indicated to be a logical method of galvanic corrosion mitigation. An inhibitor which will cause cathodic polarization, that is increase the slope of the polarization curve for stainless steel, is shown to be desirable. The inhibitive effect of water is shown to be that of an anodic inhibitor. Theoretically this type of inhibition is unsafe and practically this investigation has shown that when the anodic inhibition at 5.2\% water is operative, the general anodic attack is eliminated but is replaced by a pitting attack. The pitting takes place at faults in the nitrate film and is of such magnitude that the usefulness of this inhibition is nil. The pitting can be seen in the aluminum anode labelled 4\% water in Figure 13.

The investigational methods developed, as well as the standard methods applied, have been proved valuable in the study of galvanic
corrosion in fuming nitric acid. These methods are capable of much more information such as screening tests for selection of metals for use in this acid.
VII. Suggestions for Future Work

Further work which can be performed with the test apparatus can be classified into four divisions:

1. Investigation of the fundamental effect of temperature on the corrosion behavior of the aluminum-stainless galvanic couple in fuming nitric acid.

2. Investigation of other galvanic couples with a view to selection of materials for service in the acid.

3. Investigation and selection of inhibitor for any galvanic couple of interest.

4. Continued fundamental investigation of the properties on behavior of the nitrate film, not only on aluminum, but on other possible anodes. It is suspected that the nitrate film may have a valving action similar to that of the oxide film.
VIII. BIBLIOGRAPHY


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133. See Reference 9.


143. See Reference 142.

144. See Reference 142.


146. See Reference 27, p.486.
147. See Reference 29, p. 531.


149. See Reference 104.
<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>2S - 0 Rod</td>
<td>99.0% Al</td>
</tr>
<tr>
<td></td>
<td>1.00% Max. Si Fe</td>
</tr>
<tr>
<td></td>
<td>0.20% Max. Cu</td>
</tr>
<tr>
<td></td>
<td>0.05% Max. Mn</td>
</tr>
<tr>
<td></td>
<td>0.10% Max. Zn</td>
</tr>
<tr>
<td>2S Sheet</td>
<td>99.0% Al</td>
</tr>
<tr>
<td></td>
<td>1.0% others</td>
</tr>
<tr>
<td>3S Sheet</td>
<td>1.0 - 1.50% Mn</td>
</tr>
<tr>
<td></td>
<td>Balance Al</td>
</tr>
<tr>
<td>61S Sheet</td>
<td>1.0% Mg</td>
</tr>
<tr>
<td></td>
<td>0.5% Si</td>
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<tr>
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<td>0.25% Cu</td>
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<tr>
<td></td>
<td>0.25% Cr</td>
</tr>
<tr>
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<tr>
<td>Type 347 Stainless Sheet</td>
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<tr>
<td></td>
<td>1.48% Mn</td>
</tr>
<tr>
<td></td>
<td>0.018% P</td>
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<tr>
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</tr>
<tr>
<td></td>
<td>0.61% Si</td>
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<tr>
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<td>10.36% Ni</td>
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<td>17.15% Cr</td>
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<tr>
<td></td>
<td>0.97% Cb</td>
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<tr>
<td>Type 347 Stainless Rod</td>
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<td>19.88% Cr</td>
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</tr>
<tr>
<td>347 Stainless</td>
<td>1.0</td>
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</table>

* All rates are 5 period averages.
**TABLE 3**

Effect of Relative Anode Area on the Corrosion Rate of 2S Aluminum Alloy in Fuming Nitric Acid at 160°F

Distance of Separation = 1 inch
All Rates are 5 - pd. Averages

<table>
<thead>
<tr>
<th>Area of 2S/Area Stainless</th>
<th>Corrosion Rate (M.P.Y.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2S Aluminum</td>
</tr>
<tr>
<td>1:3</td>
<td>766</td>
</tr>
<tr>
<td>2:3</td>
<td>570</td>
</tr>
<tr>
<td>1:1</td>
<td>508</td>
</tr>
<tr>
<td>3:2</td>
<td>443</td>
</tr>
<tr>
<td>3:1</td>
<td>374</td>
</tr>
<tr>
<td>Time (Hrs.)</td>
<td>Gms./20 c.c. acid</td>
</tr>
<tr>
<td>------------</td>
<td>------------------</td>
</tr>
<tr>
<td>2</td>
<td>0.0023</td>
</tr>
<tr>
<td>3-1/2</td>
<td>0.0026</td>
</tr>
<tr>
<td>5</td>
<td>0.0032</td>
</tr>
<tr>
<td>6</td>
<td>0.0039</td>
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<td>9</td>
<td>0.0038</td>
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<tr>
<td>11</td>
<td>0.0041</td>
</tr>
<tr>
<td>12-1/2</td>
<td>0.0044</td>
</tr>
</tbody>
</table>

**TABLE 4**

Solubility of Aluminum Oxide in White Fuming Nitric Acid at 160°F
Fig. 1

Illustration of Pourdaix or Continental type of polarization diagram.

$E_a$ = Gross Potential

$I_o$ = Local Current

Potential

Current

$-I_o$  $O$  $+I_o$
Comparison of local cell polarization characteristics and polarization characteristics of electrodes when a current from an external source is applied (145).

Fig. 2
Illustration of types of polarization control in Galvanic Cells (146)

Fig. 3
Note: For cathodic protection, $E_C$ must be polarized to potential $E_a$. The impressed current necessary to do this is measured along $X$ to the point of intersection of $X$ and $E_C$. Obviously a prohibitively large current is needed.

Illustration of a case of difficult cathodic protection (147)

Fig. 4
Illustration of current flow in galvanic couple (148)

Fig. 5
CONSTRUCTION OF GALVANIC CORROSION COUPLE

FIGURE 6
Schematic illustration of device for measuring corrosion current

Fig. 7
SCHEMATIC ILLUSTRATION OF DEVICE FOR MEASURING ELECTRODE POTENTIALS

Fig. 8

A - Pt electrode
B - 347 stainless electrode
C - 3S Al electrode
DETAIL OF SALT BRIDGE CONSTRUCTION

Fig. 9
The effect of distance of separation of Anode and Cathode in fuming nitric acid at 1600°F.
Temperature Effect on Galvanic Couples in Fuming Nitric Acid

Area Ratio = 1:1

Fig. II  Corrosion Rate of Al M.P.Y.

Temperature °C

- 2S VS. 347
- 61S VS. 347
CORROSION OF 3S ALUMINUM & 347 STAINLESS IN AQUEOUS W.F.N.A. AT 160°F

FIGURE 12
Figure 13. Appearance of Galvanic Test Plates.
EFFECT OF INCREASING ANODE AREA ON GALVANIC CORROSION CURRENT PER UNIT ANODE AREA

3S AI - 347 STAINLESS, 6" SEPARATION W.F.N.A. FROM AI DRUM AT 156 °F.

- Sample abraded on 120 grit paper, rinsed in conc. HCl for 15 sec., rinsed in acetone and dried.
- Sample abraded on 120 grit paper, rinsed in acetone and dried.
EFFECT OF INCREASING CATHODE AREA ON GALVANIC CORROSION CURRENT PER UNIT ANODE AREA

3S Al - 347 STAINLESS, 6" SEPARATION W.F.N.A. FROM AI DRUM AT 156°F.

- Samples abraded on 120 grit paper, rinsed in acetone and dried.
- Samples abraded on 120 grit paper, dipped in conc. HCl for 15 sec., rinsed in acetone and dried.

Figure 15

Anodic Current Density M.A./in.²

Cathode Area (in.²)
EFFECT OF SEPARATION ON CORROSION CURRENT

3S AL-347 STAINLESS COUPLE, III AREA RATIO,
W.F.N.A. FROM AL DRUM AT 182º F

FIGURE 16
EFFECT OF TEMPERATURE
ON
GALVANIC CORROSION CURRENT

35 AL-347 STAINLESS COUPLE, 1:1 AREA RATIO, 3" SEPARATION, W.F.N.A. FROM AL DRUM

- HEATING DATA
X COOLING DATA

FIGURE 17
Polarization of 2S aluminum and type 347 stainless steel in 98.8% white fuming nitric acid at 160°F

Distance of separation = 3 in.
Area ratio = 1:1

- = 2S aluminum
○ = Type 347 stainless steel

Current density = current/0.98 in.²

Figure 18
POLARIZATION OF 2S ALUMINUM AND TYPE 347 STAINLESS STEEL IN 96.8% WHITE FUMING NITRIC ACID AT 160 °F

DISTANCE OF SEPARATION = 3 IN.
AREA RATIO = 1:1

• = 2S ALUMINUM
○ = TYPE 347 STAINLESS STEEL

CURRENT DENSITY = CURRENT / 0.98 IN.²

FIGURE 19
POLARIZATION OF 2S ALUMINUM AND TYPE 347 STAINLESS STEEL IN 94.8% WHITE FUMING NITRIC ACID AT 160 °F

DISTANCE OF SEPARATION = 3 IN.
AREA RATIO = 1:1

● = 2S ALUMINUM
○ = TYPE 347 STAINLESS STEEL

CURRENT DENSITY = CURRENT / 0.98 IN.²

FIGURE 20
POLARIZATION OF 2S ALUMINUM AND TYPE 347 STAINLESS STEEL IN 92.8% WHITE FUMING NITRIC ACID AT 160 °F

DISTANCE OF SEPARATION = 3 IN.
AREA RATIO = 1:1

- = 2S ALUMINUM
O = TYPE 347 STAINLESS STEEL

CURRENT DENSITY = CURRENT / 0.98 IN.²

FIGURE 21
POLARIZATION OF 2S ALUMINUM AND TYPE 347 STAINLESS STEEL IN 90.8% WHITE FUMING NITRIC ACID AT 160 °F

DISTANCE OF SEPARATION = 3 IN.
AREA RATIO = 1:1

○ = 2S ALUMINUM
● = TYPE 347 STAINLESS STEEL

CURRENT DENSITY = CURRENT / 0.98 IN.²
Polarization of 2S Aluminum and Type 347 Stainless Steel in 88.8% White Fuming Nitric Acid at 160 °F

Distance of separation = 3 in.
Area ratio = 1:1

- = 2S Aluminum
○ = Type 347 Stainless Steel

Current density = Current / 0.98 in.²

Impressed current, m.a. →

Figure 23
Polarization of 2% aluminum in aqueous solutions of white fuming nitric acid at 160° F.

- ○ = 1.2% water
- ■ = 3.2% water
- × = 5.2% water
- ○ = 7.2% water
- ● = 9.2% water
- ○ = 11.2% water

Current density = current / 0.98 in.$^2$

**Figure 24**
Figure 25. 2S Aluminum Anode Tested in 94.8% White Fuming Nitric Acid
POLARIZATION OF TYPE 347 STAINLESS STEEL IN AQUEOUS SOLUTIONS OF WHITE FUMING NITRIC ACID AT 160°F.

CURRENT DENSITY = CURRENT / 0.98 IN.²

- ⊗ = 1.2% WATER
- • = 3.2% WATER
- ◇ = 5.2% WATER
- ◆ = 7.2% WATER
- ★ = 9.2% WATER
- ♦ = 11.2% WATER

NOTE EXPANDED SCALE FROM .8V - 1.1V

IMPRESSED CURRENT, M.A.

FIGURE 26
DETAIL OF SAMPLE HOLDER

FIGURE 27
Figure 28. Photograph of Polarization Testing Equipment.
AUTOBIOGRAPHY

I, James F. Willging, was born in O'Neill, Nebraska, October 11, 1924. I received my pre-collegiate schooling in the St. Patrick's Parochial School and the Lead High School, both in Lead, South Dakota. My undergraduate training was received at the South Dakota State School of Mines and Technology and the University of Minnesota, from which latter institution I received the degree Bachelor of Science in Naval Technology in 1945. After a period in the United States Naval Reserve I returned to the South Dakota State School of Mines and Technology and received the degree Bachelor of Science in Metallurgical Engineering in 1947. In 1951 I received the degree Master of Science from the South Dakota State School of Mines and Technology. In January 1951 I received an appointment to a Research Fellowship at the Ohio State University which I held until June of 1951 when I was appointed Research Associate. I held this position for 18 months while completing the requirements for the degree Doctor of Philosophy.