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1955
THE POLARIZATION CHARACTERISTICS OF ALUMINUM AND STAINLESS STEEL IN FUMING NITRIC ACID AND THEIR APPLICATION TO CORROSION, ANODIC PASSIVATION AND CATHODIC PROTECTION

DISSERTATION

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

By

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Approved by:

[Signature]

Adviser
Dedicated to Phyllis, Laney, and Martin
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The University assumes no responsibility for the accuracy or the correctness of any of the statements or opinions advanced in this thesis.
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I. INTRODUCTION

As greater and greater demands are made on the propulsion systems of aircraft, attention becomes directed toward the utilization of fuels and propellants which possess those unusual properties that will fulfill these very stringent requirements. Recourse is thus made to powerful oxidizing agents for use in rocket propellant systems which will provide the thrust that modern aircraft of today must possess. One of these oxidizing agents is Fuming Nitric Acid.

One of the fundamental problems presented by this acid is its extreme corrosiveness. The proper handling and storage of it requires special materials and techniques which make for added and almost, at times, prohibitive expense and labor. Two of the materials considered for these functions are AISI Type 347 stainless steel and 2S aluminum. The purpose of this investigation was to secure polarization characteristics from the electrochemical roles which these two metals display in Fuming Nitric Acid as an aid in understanding their behavior in subject corrosion environment and to gauge this behavior in terms of solving the problem.

The phases which were singled out for study included the following:

a. Measurement of potentials of each metal to determine their polarization characteristics under a number of conditions. This included the variables of temperature, nitrogen dioxide, water, and acid content, as well as the effects of static versus agitated or stirred solutions.
b. The attempt to correlate predicted corrosion rates calculated from polarization data, secured under a variety of conditions, with those rates obtained from experimental measurements in the same circumstances.

c. Study of the phenomenon of anodic passivity of 2S aluminum in subject environment and development of an explanation of it.

d. Development of appropriate apparatus for and the study of the feasibility of cathodic protection of AISI Type 347 stainless steel.
II. SUMMARY AND CONCLUSIONS

As a result of polarization tests, supplementing experiments, research into anodic passivity and cathodic protection reviews, the following conclusions were drawn:

1. The metal 2S aluminum corrodes sacrificially to AISI Type 347 stainless steel in white fuming nitric acid. This takes place at temperatures from room to 160°F, in agitated and non-agitated solutions.

2. Subject couple behaves similarly in red fuming nitric acid at 122°F and 130°F.

3. Increasing the temperature and current density increases the anodic polarization of 2S aluminum, making it less noble. This promotes dissolution of the metal according to Faraday's law, in both white and red fuming nitric acids.

4. The cathodic polarization of 2S aluminum is unaffected by increase in temperature and current density in both WFNA and RFNA. No corrosion occurs.

5. Increasing the temperature and current density do not affect the anodic polarization of stainless steel. It continues to dissolve rapidly according to Faraday's law in both WFNA and RFNA.

6. The stainless steel as a cathode polarizes only slightly, is unaffected by changes in temperature and current density in WFNA and RFNA, and does not corrode.

7. Stirring of the electrolyte does not significantly affect the polarizing characteristics of 2S aluminum or 347 stainless steel.
8. The use of the Evans type polarization curves provides equipotential points for subject couple. These data, when used in Faraday's law, provide good correlation with corrosion rates obtained from experimentally measured weight losses.

9. At about 140°F, in addition to the hexahydrate of aluminum nitrate, another nitrate of aluminum is formed in the active range, and is probably Al(NO₃)₃ · 1½ H₂O.

10. Anodic passivity of 2S aluminum is manifested at certain current densities and potentials. A marked change involving the formation of aluminum oxide occurs at all seven conditions of test.

11. The aluminum oxide film which causes passivity is insoluble, highly resistant, transparent, non-porous, and tightly adhering. It is considered to be Al₂O₃ or Al₂O₃ · H₂O.

12. Corrosion of aluminum practically ceases when aluminum becomes passive, and alternately using cathodic treatments will not reproduce the active state.

13. Cathodic protection, per se, may be readily achieved for stainless steel in WFNA or RFNA. The protective current densities were found to be 2 ma./in.² for WFNA at 122°F, 7 ma./in.² for WFNA at 140°F, 10 ma./in.² for WFNA at 160°F, 1.5 ma./in.² for RFNA at 122°F, and 1.5 ma./in.² for RFNA at 130°F.
III. LITERATURE SURVEY

A. General Theory of Electrochemical Corrosion

1. Basic Concepts

Among the early proposals that the corrosion of metals is an electrochemical process was one by Whitney.


He stated that in the oxidation or rusting of iron, it always passes through or into a state of solution in the form of ions, is affected by the potential difference between iron and its surroundings, and that therefore the whole subject of the corrosion of iron was an electrochemical one, the rate of corrosion being simply a function of electromotive force and resistance of the circuit. As long as the corrosion products which were formed were soluble, corrosion would proceed; insoluble products could stop the attack. He further postulated that hydrogen gas formed which could not be seen because it dissolved in solution. Evans, Bannister, and Britton


reaffirmed the view that the wet corrosion of metals is usually an electrochemical process, accompanied by the flow of electric currents over measurable distances. In cases where electrochemical attack leads to insoluble products, they maintain that attack would not cease.
if sparingly soluble products were precipitated at a sensible distance from the metal. The electric currents involved in the corrosion process may be set up by differences in a metallic object (such as on a "bimetallic" specimen where one metal serves as a cathode and the other as an anode) or on iron partly covered with mill-scale which serves as the cathode, the exposed metal acting as anode. The metal would act as part of the circuit. Cathodes and anodes are further created by differences in the liquid, notably in oxygen concentration, causing the "aerated" part of the metal to be cathodic and the "unaerated" to be anodic. In the case of two separate metals, one would be the anode, the other the cathode, and the circuit could be completed by an external conductor. These writers established experimentally that the corrosion produced corresponded closely to the current actually tapped (using Faraday's law). Corrosion current correlations were determined not only in cases where the anodic and cathodic areas consisted of different metals but also where the whole specimen consisted of one metal, the anode and cathode areas being determined by differences in oxygen concentration. Further experiments by Evans and Hoar


confirmed these earlier ideas by carrying out tests on vertical specimens of iron and steel immersed in a number of solutions showing that corrosion is connected with differential aeration currents set up between a cathodic area along the water line and an anodic area along the bottoms and
sides of the specimens. Müller


has based corrosion on the local surface cell theory, supported by experiments on passivity and the corrosion of metals. He states that the electrical behavior of an ordinary galvanic cell may be represented by:

$$E_C - E_A = i (R_i + R_x)$$  \hspace{1cm} (1)

where $E_C$ and $E_A$ are the cathode and anode potentials respectively, $i$ the current, and $R_i$ and $R_x$ the internal and external resistances of the cell. He then considers a single specimen whereby the external resistance becomes zero and only the internal resistance of the local cells being present, yields:

$$E_C - E_A = i_L \cdot R_L$$  \hspace{1cm} (2)

Designating the potential of the metal at the base of the pores as $E_A$ for anodes and that of the surrounding metal cathodes as $E_C$, the resistance of the pore material of the film as $R_p$ and that of the solution in the pores of the film as $R_s$, we obtain according to Kirchoff's law:

$$E_A + (i_L \cdot R_p) + (i_L \cdot R_s) - E_C = 0$$  \hspace{1cm} (3)

In measuring the single potential of a metal, it includes the potential drop through the porous film corresponding to the product
of the current and resistance of the solution in the pores:

\[ e' = E_A + i_L \cdot R_P \]  

(4)

From (3) we obtain:

\[ i_L = \frac{E_c - E_A}{R_P + R_S} \]  

(5)

\[ e' = E_A + (E_c - E_A) \frac{R_P}{R_P + R_S} \]  

(6)

Thus it can be seen that for corrosion to occur, the potential of the cathodic points in the surface of the metal must be more noble than the potential of the anodic points.

The above hypothesis has been experimentally confirmed many times. After the study of Evans and Hoar


which included work on only one metal (iron) and one type of solution (potassium chloride) Brown and Mears


actually measured the current generated by the local anodes and cathodes of aluminum specimens which had been first coated with aluminum oxide by coating with wax. The current which was generated was substituted into Faraday's law,

\[ W = \frac{(MW)(I)(t)}{n F} \]  

(7)
where \( W \) = weight of metal dissolved in time \( t \)

\[ I = \text{current} \]

\[ MW = \text{molecular weight of metal} \]

\[ n = \text{equivalents} \]

\[ \mathcal{F} = \text{Faraday, 96,500 coulombs}. \]

The calculated weight loss compared very well to the weight loss experimentally measured.

Thus we see that corrosion proceeds because of the existence of anodes and cathodes the difference in potential of which provides the driving force for metal dissolution. These anodes and cathodes can be local, on a single specimen, and can form due to heterogenity of the surface, inclusions, stressed areas, cracks, etc. In a couple system, one specimen would generally be the anode while the other specimen would be the cathode. In both cases, the anodes corrode in preference to the cathodes. However, measurement of potentials of local cells pose far greater problems than measurements of potentials of single specimens, whether anodes or cathodes. This aspect is discussed later.

2. Thermodynamic Considerations

Glasstone


discusses electrode potentials in terms of reversible reactions. A voltaic cell or element consists essentially of two electrodes immersed in an aqueous solution, connected by a conducting material, such that a potential difference is set up between them. This potential difference is equal to the algebraic sum of the single
electrode potentials. In turn, the single electrode potentials are those existing between the individual electrodes and the solution. If a metal is inserted in a solution of its own ions, there exists a tendency for the metal to pass into solution as ions as well as for the ions from the solution to discharge on to the metal. When equilibrium is reached, the reversible potential of the electrode is established, and the two reactions take place at equal speeds. If the discharge of ions is more rapid than the reverse reaction, free electrons will be left on the metal and positive ions will accumulate on the solution side of the electrode. Thus an electrical double layer is formed. The potential difference across this double layer is called the single electrode potential. This theory differs from that of Nernst


who considered all substances in aqueous solution as having a particular tendency to pass into solution. Thus it would have a pressure similar to vapor pressure, while in the solution itself, the ions exert osmotic pressure, or plating-out force. Basically the two processes then are very comparable, as far as measurements of potentials are concerned. When all of the substances taking part in a reaction in a reversible cell are in their standard states (at unit activity) the potential is the standard potential, E°. If n Faradays are involved in the reaction, the standard free energy change then is equal to

\[ \Delta F^\circ = -nF E^\circ = -RT \ln K \] (8)
where $\mathcal{F} = 96,500$ coulombs

$K = \text{equilibrium constant}$

$R = \text{gas constant}$

$T = \text{absolute temperature}$

If the reactants and products are not at unit activities, the potential is $E$ and

$$\Delta F = -n \overline{\mathcal{F}}E$$

for the reaction

$$aA + bB + \ldots = lL + mM + \ldots$$

involving the passage of $n$ Faradays

$$-\Delta F = RT \ln K - RT \ln \frac{a_l^a a_m^b}{a_A^a a_B^b}$$

and hence

$$n \overline{\mathcal{F}}E = n \overline{\mathcal{F}}E^o - RT \ln \frac{a_l^a a_m^b}{a_A^a a_B^b}$$

and

$$E = E^o - \frac{RT}{n \overline{\mathcal{F}}} \ln \frac{a_l^a a_m^b}{a_A^a a_B^b}$$

The $E$ value would be the potential as measured in an actual cell, being the algebraic sum of the single electrode potentials. In the case where activities would be extremely difficult to measure, as is true in this investigation, potentials are measured for use in the above equations so that free energy changes can be readily calculated. These potentials were actually measured by using a saturated calomel half-cell as discussed under Procedures and Equipment.
3. The Galvanic Couple

The conventional Electromotive Force series consists of a listing of the metals arranged according to their potentials compared with the reference hydrogen electrode which is given a zero value, as measured by Latimer.


In this reference electrode, hydrogen gas at unit fugacity is bubbled into a solution of hydrogen, H\(^+\), ions at unit activity using Platinum as an electrode. The other portion of the cell contains the metal immersed in a solution of its own ions, at a fugacity of 1 atmosphere and a 1 molal, i.e., 1 mole per 1000 grams of water, concentration, all at 25°C. This series is of good theoretical value but it cannot be relied upon to predict the potential differences between metals immersed in solutions under conditions which depart considerably from the standards.


Further, it does not take into account the problem of acceleration as opposed to equilibrium conditions. It predicts that the further apart in the series the two metals are, the greater the galvanic force created between them and consequently the greater corrosion by the more anodic or less noble metal. Thus, the lower metals like gold, platinum, etc. will be cathodic or more noble than those above hydrogen such as aluminum, zinc, and magnesium.
The subject of this investigation is the galvanic couple formed when AISI Type 317 Stainless Steel and 2S Aluminum are immersed in FNA, setting up a cell as described above. Since, under these conditions, the aluminum corrodes sacrificially to the steel, the following mechanism is evident at the anode:

$$\text{Al}^0 \rightarrow \text{Al}^{+++} + 3\text{e}^-$$  \hspace{1cm} (13)

Here it is seen that the reaction taking place at the anode is oxidation. For current to flow, a reduction reaction must take place at the cathode where electrons equal in number to those emitted at the anode must be received. Willging


has determined for the subject couple that the aluminum is anodic to the steel in the range of concentrations tested, and above room temperature to and including 160°F. At room temperature, neither metal corrodes preferentially to the other.

An example of the electrolytic action occurring during the corrosion of a single specimen is seen in (a) of Figure 1. Currents flow from anodes to cathodes resulting in the destruction of the anodes. In the same manner for a couple, galvanic action is depicted in (b) of Figure 1,


where current flowing from the anode to the cathode results in the corrosion
of the anode. A source of current can be inserted in the external circuit of (b) so that impressed currents could be utilized. The basic principle illustrated remains the same.

When a natural galvanic couple is modified by using impressed currents the equilibrium potential $E^0$ may shift in appreciable amounts. This effect is termed polarization and the changes thus created provide the basis for the results produced by this research.

B. Polarization

1. Fundamentals: Equipotential Point

The field embraced under the heading of polarization covers a great variety and complexity of situations. Uhlig


simply defines it as the creation of a counter-emf, by the products formed or by the concentration changes resulting from current flow through an electrolytic cell. Glasstone.


maintains that polarization results because the equilibrium condition of the electrode is disturbed due to the slowness of one or more of the processes occurring at the electrode during the discharge or production of an ion. Polarized electrodes behave irreversibly; this irreversibility comes from the fact that one or other stage in the electrode process requires an activation energy. Evans

states that the external EMF raises the potential of one electrode, lowers it at the other. In the case of two silver electrodes, for example, placed in silver nitrate solution of normal ionic activity, the external EMF maintains transfer of silver from one electrode to the other. The solution becomes so enriched in ions around the anode and so impoverished around the cathode that even the equilibrium potentials are shifted to oppose this passage of current. This is called concentration polarization and will produce a back EMF if the external current is stopped. Pourbaix


has indicated several types of polarization curves as illustrated in Fig. 2. Evans


has presented similar data in another way as shown in Fig. 3. From the Pourbaix type curve, when applied to both the anodic and cathodic members of a galvanic couple, information can be secured for both the oxidation and reduction reactions of both electrodes. He relates that all the oxidation reactions will be represented on the right side of the 0 ordinate while those involving reduction will be represented on the left side of the 0 ordinate. Positive current accompanies oxidation; negative current accompanies.
reduction. The series of U curves represent different types of polarization which varies according to the degree of irreversibility of the reactions. Evans (Fig. 3) has taken the cathodic (-) curve obtained for the cathode of a galvanic cell and placed it in the oxidation region (+). Thus it will be seen that the maximum galvanic current which can flow in a given couple is obtained from the intersection of these polarization curves. This analysis follows from the following equation:

\[ E_C - E_A = I R_e + I R_m \]  

where \( R_e \) = resistance of the electrolytic portion of the galvanic circuit

\( R_m \) = resistance of the conductor

\( E_C \) = effective (polarized) potential of the cathodic member of the couple

\( E_A \) = effective (polarized) potential of the anodic member of the couple

The term, open circuit potential, is that value of the potential at the zero ordinate for a member of a couple. The open circuit potentials can be measured when the circuit is completed naturally or by using impressed currents and maintaining zero current. They should compare favorably.

Thus, for the analysis begun above for Fig. 3, when \( R \) is infinite, no current flows and \( E_C - E_A \) at the ordinate is the open circuit value of the cell potential. As \( R \) is made smaller, \( I \) increases and \( E_C - E_A \) decreases because of polarization. Finally \( I \) reaches its maximum value
(limiting galvanic current) at $R = 0$ and $E_C = E_A$. Thus it can be seen that the maximum possible corrosion for a galvanic couple occurs at this point, termed the equipotential point.


Obviously in practice this cannot occur because the electrolyte does impose a resistance as does the electronic conductor. From an analysis of these polarization curves, a prediction of the maximum corrosion possible for a couple can be made for correlation with experimental data. This correlation is one of the objects of this investigation.

2. Overvoltage

According to Glasstone,


although the decomposition voltage of an aqueous solution of an acid or base is about 1.7 volts when using smooth platinum electrodes, this potential varies if other metals are used as electrodes. The difference between the potential of the electrode when gas evolution occurs under the latter condition and the theoretical reversible value for the same solution was called "Überspannung" or overvoltage by Caspari.

states that the overvoltage of an electrochemical reaction is equal in magnitude and sign to the difference between the reaction potential and the equilibrium potential of the reaction such that the "affinity of an electrochemical reaction can be measured in magnitude and sign by the value of its overvoltage." It thus provides a measure of the irreversibility of the reaction, and is a generalization of the more usual concept of overpotential. He then ascribes the connotations of oxidation to the reaction if the overvoltage is positive and reduction to the reaction if the overvoltage is negative. Glasstone has suggested that overvoltage may relate to the possibility of the evolution of hydrogen as an alternative occurrence in electrolytic reduction and metal deposition. These measurements are not easy to control because of such factors as variation in electrode surfaces as well as the existence of some impurities in the solutions.

The minimum overvoltage is that potential where bubbling of hydrogen gas commences at a definite current density. Overvoltage can play a very important role and serve to shed light on some otherwise puzzling circumstances. For instance, as presented by Glasstone...
where it would be expected that lead (which has an approximate potential of 0.12 volts) ought to dissolve in hydrochloric acid accompanied by hydrogen discharge (which has a potential of approximately 0.0 volts), hydrogen evolution does not occur. This is because the overvoltage of lead is about 0.6 volt and \(-E_h=\) (overvoltage of lead) \(-0.6 \text{ volt.} \) Therefore, the hydrogen ion concentration would have to be increased, the hydrogen dissolution potential will drop and the driving force would not have to be so great in order to dissolve the lead. This reasoning actually is substantiated in practice.

3. The Effects of Agitating the Electrolyte

A number of investigations have been made on galvanic couples to secure polarization data while the electrolyte was in motion. Bomberger conducted tests on several galvanic couples and concluded that the effect of increasing the velocity of flow of the electrolyte was to decrease concentration polarization and cause film erosion. In solutions containing dissolved oxygen, the electrode potential becomes more noble. More efficient distribution and use of oxidizing agents for cathodic depolarization causes more noble values of gross potentials. With copper in air-saturated sodium chloride solutions, higher solution velocities than 150 feet per minute caused excessive turbulence and non-uniform corrosion. Newbery and Smith
studied the potential changes caused by electrolyte motion and named them "motor-electrolytic potentials" (M.E.P.). No direct proportion was found between M.E.P. and potential drift because of complex secondary reactions. It was suggested that mechanical agitation raises the electrode potential if the environment is a reducing agent and lowers it if the environment is an oxidizing agent. By removing the thin layer of electrolyte surrounding an electrode, equilibrium is upset, ions cannot be supplied at an adequate rate, and hence the potential is adversely affected.

LaQue and Cox


obtained data on potentials of metals and alloys in sea water flowing at 70 gallons per minute (15 ft. per minute). In cold sea water the film on lead made it relatively noble; it decreased as the temperature of the water rose. A surprising degree of nobility was noted for types 304 and 316 stainless steel specimens.

In his investigation of copper and copper alloys in stagnant and stirred solutions, Evans


attests that abnormal currents produced in cells through which oxygen is bubbled is caused by the stirring motion
and not by the effect of the aeration. If iron, zinc, cadmium, or lead electrodes are placed in divided cells in sodium chloride while air, free from carbon dioxide is bubbled through one cell, it becomes the positive pole. Copper electrodes reverse this polarity. Practically, flowing streams remove ions from the surfaces of electrodes which affects the corrosion rather than the presence of the oxidizing agents.

Hedges


states that Veley had noted that a rolling sphere of copper dissolved more slowly in nitric acid than a stationary one because nitrous acid, acting as an autocatalyst, was being removed from the metal surface. He used nitric acid which was freed of nitrous acid. Corrosion was considerably retarded when a sample of copper was rotated as high as 450 rpm in the acid. The cause was suggested as the removal of a product of reaction that normally accumulated at the surface and acted as a catalyst. The catalyst was presumed to be nitrous acid and it was added in the form of sodium nitrate. The suppositions were confirmed. Addition of copper nitrate had little effect. Nitrous acid is here considered an activator by removing a protective, passivating oxide film.

Uhlig

maintains that at velocities up to about 20 ft. per second, aluminum as such is little affected by solution movement. When movement provides greater homogeneity of environment, attack may even be retarded. The variation in pH by such motion is usually within the allowable limits for the corrosion of aluminum. Hirth


postulates that in the range of acid concentration investigated, stainless steel corrosion rates decrease while those for aluminum alloys increase with increasing velocity of solution. He further concludes that in an aluminum-stainless steel galvanic couple, the effect of velocity is negligible compared to the effects of temperature and acid (water) concentration.

iv. Anodic Passivation

A very practical but true definition of passivity as applied to corrosion in general would be that a metal or alloy stopped corroding when it should have either continued corroding steadily or even perhaps have increased in velocity. It is a fundamental manifestation which has been the object of much controversy both as to mechanism and control.

Even Whitney

as early as 1903 stated that certain corrosion products could hinder any further corrosion. In its broadest sense, this is akin to passivity in that it is a change that comes over a corroding specimen that causes it to cease corroding.

Müller


describes a metal as passive if it is hardly attacked when it acts as an anode in an electric circuit or when exposed to chemicals. It is active if under the same conditions it is attacked appreciably. It causes much speculation when a metal can be either active or passive. He cites the fact that this phenomenon was demonstrated at the end of the eighteenth century but with no more than mild reception. First major publications assumed an oxide layer was responsible for this state. Then the explanation was offered that kinetics entered the picture such that the time aspect became a factor whereby it was necessary to build up certain resistant layers of materials on the specimens. Müller then began experiments on passivity which involved impressed currents and characterized passivation by a specific upper limit of current density which he designated "passivating current density." Through theoretical considerations the following formula was derived:

\[ t = C + A \left( \frac{I}{I_0 + I} + \frac{2.3}{I_0} \log \frac{I_0 + I}{I} \right) \]  

where \( t = \text{time} \)
\( C = \text{a constant} \)
\( A = \text{a constant} \)
\( I = \text{current} \)
This relationship held under certain conditions for iron, nickel, zinc, and copper. The electrode thus becomes nobler than the covered metal and this type of polarization was termed "layer polarization." Aluminum was considered to be spontaneously passive by virtue of the air-formed oxide layer.

Hedges


refers to the work of Müller and reiterated his views that passivity was due to the presence of a protective film but not necessarily that of the oxide. The existence of air-formed oxide films was presumed to be definitely established for copper, aluminum, and iron, thereby interfering with the reactivity of the underlying metal. He maintained that concentrated nitric acid very definitely affected iron in such a manner. Temperature was also a factor. Earlier, Randolph


asserted that two modes of anodic action were possible, one, dissolution of the metal and, two, oxidation or passivation. This inactive state was produced either through a film of free oxygen or metal oxide covering. Through ion interchange, activation could be restored when the current density was once again lowered. White

briefly the known data up to his time and returned to the first explanation of passivity, going through velocity of reaction between metal and oxygen, to the oxide film theory. He further stated that the passivity of iron in concentrated nitric acid was overcome by magnetism.

Uhlig


discusses the Electron Configuration Theory. It is confined to those metals mostly in the transition groups of the Periodic Table whose atoms are characterized by incomplete inner shell (d electron) energy levels and by unfilled d energy bands in the metallic state. It is postulated that the unfilled energy levels are prone to become saturated with electrons just as the closed shells of atoms tend to become saturated in chemical combination. Thus passivity involves having unfilled d bands in the specimen while the active state presumes that the d band is filled with electrons. Optimum passivation is associated with adsorbed oxygen or oxidizing substances since they absorb electrons and at the same time are not prone to transmit electrons to atoms of the metal surface. Hydrogen produces an opposite effect. Evans


is a proponent of the film formation theory on the surface of metals and believes that the "oxygen charge theory" promotes passivity only
in the limited sense that it causes a delay in the reduction of an oxide film at high current densities, when using impressed currents through the application of an external EMF. He questions that passivity is induced by a film of free oxygen, such as produced by potassium chromate because of the improbability of its decomposition furnishing oxygen as such. He disparages the theory of the single atomic layer of chemi-adsorbed oxygen on the grounds that the metal probably would have to possess stress to accrue such passivity inasmuch as the films existing on ordinary passive iron are known to be a three-dimensional oxide of measurable thickness.

Uhlig


presents a special type of passivity brought about by inhibitors. An inhibitor is any substance which when added in small amounts to the corrosive environment of a metal or alloy appreciably restricts corrosion. This is explained on the basis of energy reduction during corrosion being equal to the total of the energies dissipated throughout the electrochemical system. Beck and Fontana


proposed "that the passivity of 18-8S stainless steel as a result of the sulphuric acid-air treatment is due to a physically adsorbed gas, an hydrous oxide film, or a combination of these two."

Glasstone
as well as a number of other writers, in discussing particularly an aspect of anode potentials of electrolytic cells utilizing impressed currents, employs the term "electrochemical passivity." As the current density is raised the potential of the anode increases approximately linearly and dissolution of the metal proceeds quantitatively by Faraday's law. Increase of the current density, however, no longer continues in an approximately linear fashion once a certain point is reached. In fact, at this point, the anode potential increases very rapidly accompanied by a decrease in current density during which period anode dissolution is arrested. Electrochemical, or anodic passivity has set in and the course of it is depicted in Figure 4. The line AB shows the change of anode potential with current density while the electrode is in the active state during dissolution. At B, passivity is induced and the current and potential arrive at C values rapidly, and only a substantial increase in potential will increase the current. He suggests that a reduction in potential then from point E will cause the return to points G and H where dissolution of the anode will once more be quantitatively expressed. Further, activation can also be regained quickly either by making the anode the cathode, or by touching it with a less noble metal, or fracturing the surface while still immersed in the electrolyte. Oxide films are primarily represented as the responsible passivators. Evans

discusses the work of several authors on isolation of oxide films from aluminum, such as heating in a current of dry hydrogen chloride gas, which by carrying off the aluminum as a vaporous chloride, will leave the oxide film intact. Fusion methods and other dissolution methods are also proposed, as well as stripping and the application of electron diffraction and X-ray studies.

Landau and Oldach


after having tested a number of alloys (not including aluminum) refer to passivity as a "slow rate of corrosion despite a thermodynamic tendency to react." They discuss passivity of alloys as caused by an invisible protecting film and the change in alloy composition that precludes passivation. Passivity appears to be most pronounced by chromium, molybdenum and tungsten. Landau


states that the limit of passivity is dependent on the stability of the film on the alloy and not wholly on electrochemical behavior. An oxide film, for example of aluminum, might be a potent passivator if highly stable in a particular environment.

C. Cathodic Protection

A metal or alloy which normally corrodes in a particular environment can be protected from such attack by being made the cathode of
a couple in which the anode corrodes sacrificially while the cathode remains unscathed. Thus a galvanic couple would be formed, the flow of current being through the electrolyte to the cathode and through an external, or an insulated internal conductor, from the cathode to the anode. As long as the anode lasted, the cathode would be virtually intact. Now if the anode were made of an inert material and a suitable current were impressed in the same direction as that of the generated current in the "natural" couple, the same end could be attained. Both methods comprise "cathodic protection."

Sir Humphrey Davy

Sir Humphrey Davy, "On the Corrosion of Copper Sheet by Sea Water, and on Methods of Preventing this Effect; and on Their Application to Ships of War and Other Ships," Phil. Trans. Royal Society of London Part I, (1824) p. 151.

found that if copper was attached to zinc, iron, or tin in sea water, the copper was unattacked. He called this condition of copper "defended." It is analogous to the present term "cathodically protected."

Mears and Brown


demonstrated that if the corrosion is wholly electrochemical, complete cathodic protection can be secured by polarizing the cathodes of the cell to the open circuit potential of the anodes. Basically, the current must flow from the solution to the metal -- the antithesis of dissolution. The theory proposed is thus explained with reference to Figure 5. Here curve 1 represents the
manner in which the less electronegative areas (cathodes) of most of the common metals polarize in chloride solutions. Most of the anodes therein polarize as shown in curve 2. At the equipotential point, D, (discussed earlier) maximum current is generated causing maximum corrosion. By using an external EMF, the cathode areas can be polarized to this equipotential value at D. Since under these circumstances the potential of the anodic points on the specimen would still be anodic to point D, some current could still flow from them to the cathodic areas. This current flow could be equal to EF on the current ordinate. Then by increasing the potential of the cathode to point B, the entire surface is made equipotential and no driving force would exist. Protection would be complete if no corrosion resulted from electrolysis products. Verifying experiments substantiated this theory.

Mears


added that in the special case where oxygen diffusing completely controlled the corrosion, the quantity of current required would be equal to that which produced free corrosion. Brown and Mears


further extended the theory of local cathode and anode polarization curves as criteria for cathodic protection to dissimilar metals, using the same principles enumerated above.

Pourbaix

illustrates a similar idea as shown in Fig. 6. Depressing the polarization curve of the cathode to the open circuit potential of the anode reduces corrosion to zero.

Mears and Fahrney


contend that in the usual situation, protective currents may surpass the current generated by self-corrosion by a factor of several hundred per cent. In the case of aluminum, excess cathodic current in aqueous alkali can cause concentration changes in the vicinity of the electrode so that the metal is attacked. Hence, zinc, used sacrificially is more normally employed, in order to avoid "cathodic corrosion." Although zinc is higher in the EMF series than aluminum, it was earlier pointed out that this series includes a special situation.

Hoar


discusses the fact that in order to minimize tin-plate corrosion, inhibitors of cathodic reactions at the iron surface should be sought. This is a special case of cathodic protection, for dilute acids in which the subject couple is considered.

Various methods of determining the minimum current densities required for cathodic protection are presented by Kehn and Wilhelm.
They compared their colorimetric analyses during corrosion tests with those made by the Britton curve method. Their colorimetric analyses involved determining the amount of rust formed by dissolving it and comparing the resulting solutions with standards for the amount of corrosion products. The Britton-curve method incorporated measurement of potentials of the subject electrode and the plotting of potentials against current densities which thereby required a half-cell reference electrode and potentiometer. Indications were that the potentiometric method was only approximate compared to the colorimetric one.

In this investigation of cathodic protection, the method of weight loss measurements was used and required a unique set-up because of the extreme conditions of environment. Proper current distribution was assured by the use of platinum wire coils surrounding the cathode (Type 347 Stainless Steel).

D. Some Chemistry Considerations

1. Chemical Properties of Nitric Acid

Nitric acid is one of the most powerful of the monobasic acids, and usually behaves as an oxidizing agent, and is itself reduced.

Mellor

states that the nature of the reduction products depends on the conditions. There may be produced: nitrous acid, nitrogen peroxide, nitric oxide, nitrous oxide, nitrogen, ammonia, hyponitrous acid, hydroxylamine. This is presumed to apply to the entire range of concentrations of nitric acid. With non-dilute solutions, the following reaction can occur endothermally when exposed to light:

\[ 4\text{HNO}_3 = 2\text{N}_2\text{O}_5 + 2\text{H}_2\text{O} + \text{O}_2 \] (15)

One hundred per cent HNO\textsubscript{3}, sealed, even in darkness assumed a bright yellow color in 12 months and had developed an oxygen pressure of 9.7 atm. Evans

states that at low concentrations, the acid properties are pronounced; at high concentrations the oxidizing properties prevail.

2. The action by Nitric Acid on Iron and Steel

Iron is attacked with considerable velocity in dilute nitric acid, which increases with concentration.

Above 12N the attack decreases, and is presumed due to an oxide film. In the cell

Iron / Nitric Acid / Platinum

where iron is the anode, passivity is induced. This resulting oxide film was studied by Tronstad and Borgman.
They have optically studied this surface film by mirrors which were immersed in the solutions during the analyses. They found that the protective films on austenitic "stainless steels" in concentrated nitric acid were almost of the same thickness as when formed on iron in dry air.

Mellor


reports that during the attack by nitric acid on metals, oxygen is transferred to the metal with the evolution of heat, reaching incandescence if concentrated acid is poured on heated iron filings. It was noticed that attack occurred only when a trace of free nitrous acid was present; this has been confirmed by other authors. Veley


observed that

"(1) The primary change is that between the metals and nitrous acid.

"(2) No gas is evolved at first from the surface of the metal.

"(3) The amount of nitrous acid increases up to a constant acid maximum proportion.

"(4) Those conditions which increase the amount of metal dissolved per unit time are equally those conditions which increase this constant proportion of nitrous acid."
Thus it is explained that:

"(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.

"(3) The nitric oxide formed in (1) is not evolved as such but reduces the nitric acid or the nitrate to produce a further quantity of nitrous acid."

This is opposed by the hydrogen theory which postulates:

\[ M + 2\text{HNO}_3 = M\left(\text{NO}_3\right)_2 + 2\text{H} \quad (16) \]

The hydrogen is then supposed to act on the free acid or the formed metal nitrate, reducing it to nitrous acid, hyponitrous acid, hydroxylamine and ammonia; secondary reactions are formation of nitrogen peroxide, nitric oxide, nitrous oxide, and nitrogen. Thus the processes of reduction, hydrogenation, dehydration and hydration occur.

Uhlig


reports that the attack by non-oxidizing acids takes place rapidly even in the absence of oxygen where hydrogen is reduced and escapes as the gas. In the attack by oxidizing acids, the cathodic reaction consists of the reduction of the oxidizing agent and may even be autocatalytic.

The work of Ellingham on the cathodic reduction of nitric acid is reported by Evans.
At high current densities free hydrogen was obtained; at low current densities the autocatalytic reduction of nitric acid to nitrous acid and oxides of nitrogen was noted. According to Divers and Bancroft


metals can be divided into two classes, one being highly reactive metals like magnesium, zinc, and cadmium which could evolve hydrogen from non-oxidizing acids. Noble metals such as silver, mercury, and copper cannot liberate hydrogen continuously and the cathodic reaction consists of reducing nitric acid:

\[
\begin{align*}
\text{HNO}_3 + \text{H}^+ + e^- & \rightarrow \text{NO}_2 + \text{H}_2\text{O} \\
\text{NO}_2 + \text{H}^+ + e^- & \rightarrow \text{HNO}_2 \\
\text{HNO}_2 + \text{H}^+ + e^- & \rightarrow \text{NO} + \text{H}_2\text{O}
\end{align*}
\]\n
(17)  (18)  (19)

Ionic reduction would proceed as:

\[
\begin{align*}
\text{NO}_3^- + 2\text{H}^+ + e^- & \rightarrow \text{NO}_2 + \text{H}_2\text{O} \\
\text{NO}_2^- + e^- & \rightarrow \text{NO}_2 \\
\text{NO}_2^- + 2\text{H}^+ + e^- & \rightarrow \text{NO} + \text{H}_2\text{O}
\end{align*}
\]\n
(20)  (21)  (22)

Equation (21) is postulated to be controlling and from:

\[
\text{HNO}_2 + \text{HNO}_3 = 2\text{NO}_2 + \text{H}_2\text{O}
\]\n
(23)

the corrosion increases until the loss of nitrous acid by thermal decomposition or cathodic reduction to NO balances the increase. Thus autocatalytic action is explained as well as the reason for the intensity of attack.
at areas where the products adhere to the metal surface.

3. The Action of Nitric Acid on Aluminum

(a) General

It appears to be anomalous to state that aluminum is highly resistant to corrosion because it is so reactive. The fortunate aspect is that this high reactivity produces a film which is so adherent and non-reactive that it serves as an excellent protector of the underlying metal. Seligman and Williams


performed a series of tests on the effect of nitric acid upon aluminum and reported that in nitric acid, the reaction with aluminum will produce the enneate hydrate of aluminum at low concentrations of the acid. At the higher (over 80%) concentrations of nitric acid, the hexahydrate of aluminum is formed. These tests were conducted at approximately room temperature. Evans


reports that the attack of nitric acid on aluminum increases with increase in concentration to about 30% and then falls. He cites Inglis who states that aluminum of 99.5% purity becomes industrially useful for acid above about 92% concentration and that the thermal history of both are important. For transport purposes, chlorides must not be present and the purer the aluminum the slower the attack. Uhlig

confirms this data, stating that 80% to 99% nitric acid is a safe range.

The fact that many metals are impervious to the concentrated but not the dilute form of nitric acid is also mentioned by Mellor


who cites Boyle.

R. Boyle, "Considerations Touching the Usefulness of Experimental Natural Philosophy," Oxford, 1663.

Mellor


states that the hexahydrate of aluminum nitrate is stable in nitric acid of specific gravity of 1.5 or greater than 81% concentration, but at 1.42 specific gravity soon changes to the enneahydrate. Two other hydrates at intermediate and lower concentrations have been reported -- a dihydrate and an octahydrate. Pascal


includes by diagram, similar data, by presenting the thermal analysis of the binary system of various aluminum nitrates in water as a function of temperature. It shows that above about 68% nitrate and 32% water, only the hexahydrate prevails, at all the temperatures considered.
(b) Oxides Formed by the Action of Nitric Acid upon Aluminum

The most common form of aluminum oxide is widely known as bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. Gandrud and DeVaney


report that bauxite dates back to 1821 when it was found that it was not clay but mainly oxides of aluminum and iron. They state that the above composition is not a main source of aluminum in bauxite.

Since then many authors have formed oxides of aluminum in various ways and have conclusively proved its existence. (See literature survey section on anodic passivity for further details on this oxide.)

Rossini, Wagman, Evans, Levine, and Jaffee


have published data on the free energies, enthalpies, and entropies of aluminum oxides and nitrates which are very useful in calculations involving thermodynamic relationships. Latimer


refers to these for use in deriving electrochemical data. Four aluminum oxides are listed: $\text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. 

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E. Experimental Techniques

1. Natural Galvanic Tests

As shown in Figure 7, a natural galvanic couple can be utilized that is simple but which adequately fulfills the requirements of a cell. Willging


performed a number of experiments with this couple and found that the 2S aluminum is anodic to the stainless steel at all temperatures above room temperature through the 160°F range.

2. Single Electrode Tests

By coupling the desired electrode to an inert metal such as platinum, galvanic couples can be formed which readily lend themselves to potential measurements of either electrode.


Easy facility is had through the use of impressed currents as shown by Gilbert.


A probe (see Figure 11) from a calomel half-cell may be used to measure such potentials, which are considered to be the gross potentials of the electrode,
i.e., the sum of the values of the local anodes and cathodes of the electrode. The resistances of the surface of the metal are thus neglected and if small enough do not at all affect the overall interpretation of the results.

3. Equipment for Measurement of Potentials

(a) The Reference Electrode

The single electrode potentials can be measured by reference to various half-cells. The most convenient one is the calomel half-cell.

Hamer


found that the potential of the saturated calomel half-cell at about 25°C is $0.2415 + 0.00076(t-25)$ when compared to the zero potential of the reference hydrogen electrode.

(b) Potentiometers

A convenient method of measuring potentials can be had through the use of potentiometers.


They are used extensively because only the galvanometer current is drawn. The only obstacle would be the resistance between the probe and electrode and this can be largely overcome by placing the probe quite close to the electrode as stated by Müller.
IV. EQUIPMENT

A. Equipment for Obtaining Corrosion Rates from Weight-Loss Data

1. Controls (Single Specimens)

Controls, or single specimens, were prepared for test by being placed in glass cradles which in turn were inserted into wide-mouthed, 1000 ml. pyrex Erlenmeyer flasks fitted with finger type condensers. These specimens were generally about 1 inch square by 1/16 inch thick. Fuming nitric acid, at a ratio of one hundred ml. per square inch of area of specimen was poured into each flask. The flasks were maintained at desired temperatures in constant-temperature baths.

2. Galvanic Couples (Natural, not using Impressed Currents)

The natural galvanic couple tested herein is one which consists of two plates of dissimilar metals so connected as to form a couple, the connector being insulated from the electrolyte, so that the entire assembly can be immersed. The plates or specimens are usually 1" x 1" x 1/16" and are in electrical contact by means of bolts (made of the same materials as the respective plates) and a spring. This equipment can be seen in Figure 7. The threaded Teflon tube serves to protect the electrical contact from the acid, insures that the test specimens are parallel to each other, and maintains a given distance between them. The assembly is placed on edge for test.

Natural galvanic couples and control specimens were tested in both static and agitated acid environments. In static solutions, placing the specimens on the bottoms of the flasks was sufficient. In the agitation tests, a stirrer was provided. It consisted of a glass rod to which a glass propeller was attached. Rotation of the stirrer was accomplished by means of an air or electric motor. A
special type of finger condenser was thereby required which incorporated an opening through the center to accommodate the stirrer. In this way the standard 1000 ml. Erlenmeyer flask could still be utilized. This special equipment is shown in Figure 8 which depicts a condenser extending about 2 inches above the mouth of the flask. The speed of rotation of the stirrer was approximately 500 rpm. When tests were conducted below 140°F, the special condenser used was of the same height as the conventional one, not extending above the flask at all.

B. Polarization Apparatus

The equipment used for polarization studies was in essence that used by Willging,


and fashioned after that of Brown and Mears,


with a number of modifications. A schematic sketch of the setup is presented in Figure 9 and a photograph of the actual installation is presented in Figure 10. By proper manipulation of the switches in Figure 9 it is possible to measure the potential of any one of the electrodes indicated. Current was supplied by a 6-volt storage battery in series with a variable resistance. One of the modifications included the construction of a new circuit for the potentiometer, shown in Figure 10, in order to be able to read potentials as high as 2.2 volts.
Details of the salt bridge are shown in Figure 11. One end of an agar-agar gel bridge containing 10% KNO₃ was inserted into a tube filled with a 10% KNO₃ solution and equipped with an asbestos fiber. This probe was placed in close proximity to the specimen whose potential was being measured. The other end of the bridge was immersed in a 10% KNO₃ solution into which a saturated calomel reference electrode was placed. Thus a complete circuit was formed. Here another innovation was introduced in that the half of the bridge used in the probe was emptied of agar-agar gel and replaced by liquid 10% KNO₃. This produced much greater sensitivity in the reading of the galvanometer by considerably reducing the bridge resistance. A special technique was developed for the assembly of the bridge into the probe so that a continuous circuit could be assured. As discussed previously by Willging,


the KNO₃ solution was used because both the potassium ions and nitrate ions have high and nearly equal transference numbers.

The details of the electrode are shown in Figure 12. As will be noted, the electrical connections are well protected from the acid, permitting the use of stainless steel rods for the aluminum electrodes as well as for any other electrode material. These test electrodes were approximately 1.4 cm. long by 1.2 cm. diameter, exposing about one square inch of open surface.
A battery jar was used to contain the FNA. The water bath temperature was accurately controlled by a merc-to-merc thermoregulator.

The above equipment was altered slightly to promote agitation of the electrolyte. As shown in Figure 13, an additional motor with a glass stirring rod was added to the basic equipment to effect turbulence. This caused additional fumes to be given off by the acid and additional precautions such as glyptal covering of all exposed parts was required. All wiring was protected from the fumes by the use of Tygon tubing for covering.

C. Cathodic Protection Equipment

This setup was devised to ascertain the feasibility of cathodically protecting stainless steel. The apparatus was set up as shown in Figure 14. Four Type 347 stainless steel and platinum couples were assembled in acid baths in series. A fifth specimen of approximately two square inches in area was used for a control. These solutions were maintained at constant temperatures by means of water baths as indicated in the photograph. By means of a selenium rectifier, a constant source of direct current was made available for impressment across the battery of electrodes. Potentials up to 24 volts could thus be precisely used to impress a range of currents through the installation. This source and the attendant controls are presented in Figure 15. The couples, of which details can be seen in Figure 16, were introduced into the Erlenmeyer flasks through modified finger type condensers equipped with central openings. As shown, the four Type 347 stainless steel electrodes were cylindrical in shape and had exposed
surface areas of approximately one, two, three, and four square inches respectively. They were provided with holes drilled and tapped with 5-40 threads to accommodate the threaded stainless steel rods. The Teflon tubing both supported and insulated the specimens. Platinum wire coils acted as anodes and were carefully coiled about the specimen to insure uniform current distribution without touching the steel. The end of the platinum wire was located beneath the steel electrode.
V. MATERIALS AND PROCEDURE

A. Materials

The environments used in this study consisted solely of White Fuming Nitric Acid (WFNA) and Red Fuming Nitric Acid (RFNA) possessing the range of compositions shown in Table 1. These acids had been shipped and stored in aluminum drums.

The materials herein investigated comprised AISI Type 347 Stainless Steel and 2S Aluminum of which the compositions are presented in Table 2.

B. Procedures

1. Corrosion Rates from Weight Losses

To prepare either controls or galvanic couples for test, specimens were final polished on grit No. 120 emery cloth, exact areas ascertained, and then degreased in alcohol before insertion into the acid. They were then tested for 5½ hour periods. At the end of each ½-hour period, they were removed from the acid, washed with water, rubbed with a rubber stopper, rinsed in acetone and weighed. This procedure applied to controls as well as to elements of a couple. Corrosion rates in terms of mils per year were determined for each of the five periods and averaged. The following formula was used:

\[ \text{M.P.Y.} = \frac{(527)(W)}{\left(\frac{\rho}{(A)}(t)\right)} \]

where \( W \) = weight loss in milligrams
\( \rho \) = density of the metal, gm./cm.²
\( A \) = area of exposed surface, in.²
\( t \) = time of test for \( W \) weight loss, hours
The exposed surface area was considered to be the total plate area minus the area of the bolt head and that covered by the Teflon tube (only in the case of natural galvanic couples).

Natural galvanic couples were tested in both static and agitated acid environments. Identical procedures were used in the two conditions with the exception being that the special stirring apparatus described under Equipment was used for creating turbulence during the entire 240 hours of test.

2. Polarization Studies

Prior to immersion of the aluminum and/or the stainless steel cylindrical electrodes, they were abraded on 400 grit paper, washed, weighed and measured, and rinsed in alcohol. At the end of each run, weights were once more secured. From these measurements, accurate current densities could be assured and from the weight determinations, a qualitative interpretation could be derived for correlation with the corrosion behavior of the specimens. Steady state temperatures of the acid environment were obtained before immersing the specimens.

Polarization runs consisted of coupling a 2S aluminum electrode anodically or cathodically to platinum and then measuring its potentials at various impressed currents. The Type 317 stainless steel electrode was similarly treated. In each case, the inert platinum electrode was always used as one of the electrodes. The setup was such that if the aluminum was to be the cathode, the battery was so connected in the circuit that positive current flowed from the platinum into the acid. The magnitude of the current was controlled by varying the resistances which were connected in series with the battery and the
couple. The potentials thus recorded were measured against the saturated calomel half-cell. The voltage which was read was actually that at the junctions of the potentiometer.

Anodic potentials were determined by connecting the battery so that positive current flowed from the electrode in question to the acid. In the case of anodic aluminum, it was always necessary to start initially at fairly high current densities (the magnitudes are discussed below) and maintain the current level until a steady state potential prevailed. The current could then be reduced to obtain another steady potential, etc. Thus a potential could be ascertained for each current density considered. Potentials for cathodic 2S aluminum, cathodic and anodic Type 347 stainless steel could be secured without resorting to the use of initially high impressed currents. It was further noted during the anodic treatment of 2S aluminum that fairly long periods were required to obtain steady state potentials, as can be seen by comparing Figures 17 and 18, while for the three other conditions, approximately 40 to 60 minutes sufficed at each current density. When a day's run was completed, the specimen was withdrawn and weighed for qualitative correlations with experimental data. In certain instances, the acids were sampled for analyses.

Similar testing was performed under agitated conditions. The stirrer was inserted in the acid and stirring then maintained continuously for about 4 hours prior to insertion of the electrodes. At this point a sample of acid was secured and it was recorded as the composition of the acid used during that test. Thus it was possible to perform tests without the acid undergoing major changes during the polarization run.
These procedures provided data that enabled the Pourbaix type as well as the Evans type of curve to be constructed.

3. Anodic Polarization Studies of 2S Aluminum

During the course of conducting polarization measurements while the aluminum was the anode, electrochemical passivation occurred in a manner analogous to that indicated in Figure 4 and discussed by Glasstone.


Not only were polarization potentials measured for the 2S aluminum anode but also the potentials and currents associated with this phenomenon. However, a variation in technique had to be developed to secure these data.

These following techniques were employed:

After the acid electrolyte had reached its proper temperature, the resistances for the current control were set at some arbitrary value. The electrodes were then inserted in the acid. If the current and potential held steady for at least 10 minutes, they were considered to be at levels below that required for passivation. Then the samples would be withdrawn, re-prepared, the resistances changed to increase both potential and current, and the electrodes re-inserted. This procedure was followed until the current would fall off and the potential would increase as shown in Figure 4. These critical current and potential values would then be recorded as passivating values. At this or any higher initial values, within the range of the 6-volt storage battery, passivation would take place. The results could be
accurately reproduced by starting at a current and potential well above the initial passivation stage and by increments, reduce these settings until the current no longer fell off. The electrode would then be in the active state.

1. Cathodic Protection Experiments of Type 3167 SS

Acid environments were prepared for the stainless steel cathodes in the usual manner in 1000 ml. Erlenmeyer flasks. An additional flask was used for a control. They were then placed in a constant temperature water bath as shown in Figure 14. The five specimens were abraded on 120 grit paper, washed, weighed, and measured. The four electrodes were then assembled as shown in Figure 16, washed in alcohol and inserted through the central opening of the modified finger-type condensers. The fifth electrode was immersed directly into its acid. The platinum wire anodes were carefully coiled around each electrode, not touching the steel, and extended above the condensers for electrical connections. As soon as all four were immersed in acid, they were connected in series with the selenium rectifier. The resistances were immediately adjusted to provide a current that would yield a desired range of impressed current densities.

At the conclusion of a test run, the current was shut off, and the assemblies dismantled. The electrodes and control were washed with water, rubbed with a rubber stopper, rinsed in acetone and weighed. After abrading, etc., they were ready to be placed in fresh acid under new conditions of temperature, current density, and/or type of acid.

Corrosion rates were determined through use of the formula described earlier. Current densities were calculated for each run
simply by dividing the impressed current by the exposed surface area of the electrode, thus enabling four different current densities to be evaluated per run. The range of the runs was 4.0 to 120 hours.
VI. RESULTS AND DISCUSSION

A. Introduction

This research essentially can be divided into three major phases. The polarization characteristics of the two subject metals, Type 347 SS and 2S aluminum in fuming nitric acid form the basis for these major phases. They have been investigated under the influence of variables such as temperature, acid composition, and static conditions as differentiated from turbulent. Thus the results of this research can logically be grouped as follows, and the ensuing discussion will closely adhere to these divisions:

1. Correlation of Predicted Maximum Corrosion Rates of Subject Couple with Experimental Measurements.
2. The Phenomenon of Anodic Passivation of 2S aluminum.
3. Some Results of Cathodically Protecting Type 347 Stainless Steel.

The polarization data were collected for the following seven environments:

- WFNA @ 122°F, 140°F, 160°F, Static
- WFNA @ 122°F, 140°F, Agitated
- RFNA @ 122°F, 130°F, Static

The phenomenon of anodic passivity of 2S aluminum was investigated under all seven conditions and in particular in WFNA at 122°F and 140°F. The cathodic protection tests were conducted only at the static conditions.

B. Polarization: Application to Prediction of Corrosion Rates

1. Compilation of Data

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To secure the basic current-potential data in this work, tests were run as described under Procedures, in which time-potential curves at constant values of current density were obtained. Examples of the types of curves thus produced are evident in Figures 17 and 18. Each curve by itself yields one potential-current point. It can be seen therefore from these curves that it is possible to conduct such a test at a constant current density over a period of time ranging from 30 minutes to several hours during the reading of potentials, until a "steady-state" potential is obtained. After a test of this nature, the acid is poured out, fresh acid added, the specimen reabraded, etc., and a new current density applied at which a corresponding potential is obtained. However, there is an alternative procedure. Instead of again starting with fresh acid and reabraded sample, it is possible after the very first current density setting has produced a "steady-state" potential to change the resistance of the circuit to another value of current density and get steady potential values at the new setting, etc. and not removing the specimen from the acid. The former method produces curves of the nature indicated in Fig. 17, and also those curves marked 12 m.a./in.² and 20 m.a./in.² in Fig. 18. The latter method yields the 14 m.a./in.² curve of Fig. 18. In either method, the "steady-state" potentials do not vary much, but by using the "step-down" or "step-up" method, a great deal of time can be saved. A typical set of values secured by this latter method is listed in Table 3. If the step-down or step-up method is not used, very long periods are required for the tests. They become prohibitively long at the lower current densities probably because of the slowness of
the reactions as the acid decomposes. By noting Figure 19, the trend of this acid decomposition is apparent. Thus another variable enters the picture during long test periods. The step-down or step-up method may become critical at times at zero currents, but the potentials in these cases can be checked by actually opening the circuit at the end of the preceding run, and later rechecked through careful analysis of the intersection of the cathodic and anodic curves at the zero current ordinate. This will be more readily recognized later. It is to be noted that the problem of using the methods discussed above occurs only when the 2S aluminum is made anodic to platinum and does not occur in any of the other 3 coupled conditions (all of which make use of the inert platinum electrode).

2. Analyses of Pourbaix and Evans Types of Polarization Curves: Corrosion Rate Correlations

   a. Non-Agitated Conditions: WFNA

      (1) Pourbaix Curves

Pourbaix curves have been plotted for all seven conditions of environment. They are presented in Figures 20 through 26. Those for WFNA at temperatures of 122°F, 150°F and 160°F utilizing non-agitated acid are plotted in Figures 20, 21, and 22. It is interesting to note that as the temperature of the acid solution is increased, the 2S aluminum curve in the anodic or oxidation region has become more anodic or less noble. This indicates that more corrosion or reaction is taking place as the temperature is increased, and the fact that it polarizes considerably shows that it is affected by increase of current density in the same fashion. This is demonstrated by reference to Table 4, last column. In all cases where such measurements were
actually made, a high rate of corrosion is manifested. A considerable amount of aluminum nitrate was observed to continuously spall off the aluminum anode and collect at the bottom of the battery jar. This adherent product, it is believed, took an active part in the polarization of the aluminum anode. The anodic portion of the stainless steel curve is quite similar both in shape and magnitude of potential at all three temperatures. This would indicate that neither the current density nor the temperatures of test have very much effect on it. Referring to Table 4 it can be seen that when it is anodic it corrodes rapidly. It is therefore postulated that the reaction is one of dissolution of the metal to form nitrates under the anodic conditions and that the precipitate not being in the vicinity of the electrode or creating any gradients in its vicinity, the metal does not polarize. This is confirmed by the fact that very little corrosion product is discerned in the acid when the steel was the anode. The products were soluble enough in the acid to obviate any effects they might have had on polarization of this electrode. In the cathodic region the steel response to the change in current density is quite analogous and it does polarize in all three cases. However, as the temperature is increased, there is somewhat of an increase in potential. Thus there is more response to the temperature change than in the anodic region for the steel. Reference to Table 4 shows only a slight loss in weight indicating the steel was being cathodically protected much of the time and that the polarization changes were due to acid changes and not to corrosion. A very similar argument
(2) Evans Type Polarization Curves; Equipotential

Points Used for Correlating Corrosion Rates

From the data on the Pourbaix type of polarization curve for
subject couple, polarization curves along the lines of Evans

U. R. Evans, "Metallic Corrosion, Passivity, and Protection," Edward

have also

been prepared for the seven different environments. They are shown
in Figures 27 to 33 inclusive and correspond respectively to the
Pourbaix curves. This now permits one to attempt to obtain a corre­
lation between the predicted theoretical maximum amount of corrosion
in the subject natural galvanic couple with those data obtained from
the 5-48 hour period tests discussed earlier. Since such a type of
test has been performed in which it was shown that aluminum corrodes
sacrificially to the stainless steel, data are available for suitable
comparisons. The corrosion data for the 5-48 hour period of test
under almost all the conditions of test outlined herein, are con­
solidated in Table 5. They are discussed below.

The Evans curves for 2S aluminum and Type 317 SS in WFNA at
122°F, 140°F and 160°F are shown in Figures 27, 28, and 29 respec­
tively. They well exemplify the fact that the tendency for a metal
to corrode is the tendency for the active electrodes to polarize to
to the equipotential point. From these equipotential points, the
the maximum theoretical current generated between subject couple is read off as indicated by the dotted lines. A plot of the equipotential points for the three conditions now being considered is included in Figure 34. Substituting these values in Faraday's law a weight loss rate is calculated which is in turn substituted in equation (24) to yield a corrosion rate in terms of mils per year. These values are compared with those secured from weight losses in the natural couple in Table 6. For these three conditions, a good correlation is evident. The calculated results should be somewhat higher than those observed because of the assumption of no IR drop through the electrolyte. The comparisons for the three subject conditions can also be noted by reference to Figure 35.

b. Effects of Agitated Electrolyte: WFNA at 122°F and 110°F

(1) Pourbaix Curves

Tests were performed, in a manner similar to that discussed above in WFNA at 122°F and 110°F, with the utilization of stirring apparatus. The upper limit of 110°F was chosen because the WFNA supplied for these tests boiled in the vicinity of 160°F. Thus at 110°F a more constant composition would be assured during the runs. The Pourbaix curves for the two tests are shown in Figures 23 and 24. Upon comparing both Figures at 122°F, it is seen that the anodic and cathodic curves for the stainless steel break very similarly to each other. The open circuit potential of the aluminum electrode has dropped considerably in the case of aluminum in agitated acid. The stainless steel again was little affected anodically by the change in current density and corroded considerably. The aluminum anode polarized to
a larger extent in the anodic region in the agitated acid. At 140°F, there was basically no change in the stainless steel curves while the aluminum open circuit potential increased to about the open circuit potential of the non-agitated WFNA at 122°F. Table 4 also indicates trends akin to the results produced in non-agitated WFNA at the same temperatures.

(2) Evans Type Polarization Curves; Equipotential Points Used for Correlating Corrosion Rates

Evans type curves for both runs in WFNA at 122°F and 140°F under conditions of agitated acid are shown in Figures 30 and 31. The correlation between corrosion rates calculated from their equipotential points and the natural couple under the same conditions are shown in Table 6. Fairly good agreement is indicated. When these values are compared with those obtained under conditions of non-agitated acids, they can be seen to be lower. It is believed that the agitating effects may not have altered the composition around the electrodes appreciably. The decrease in attack may be due to increased hydrogen overvoltage. It was noticed during the course of the polarization runs that the potentials in many cases were not steady but fluctuated within a very readable range. These fluctuations appeared to be caused by motion of the acid, reducing the potential to a point of passivity on the one hand and a condition of film breakdown on the other. There might have been a decrease in the potentials of the local anodes. Although the two processes appeared to be competing, corrosion analyses indicated no great overall effects of agitation.
c. Effects of appreciable changes in NO₂ content

(1) Pourbaix Curves

Polarization data were also gathered for subject couple using RFNA at 122°F and 130°F. The upper limit was so chosen because RFNA of the composition listed in Table 1 boils in the vicinity of 110°F. At the two test levels, the changes in acid composition could be expected to be reasonable. The test results are shown in Figures 25 and 26.

The anodic polarization of the steel electrode was very similar to that in WFNA at 122°F. The cathodic portion was slightly higher than that in WFNA at 122°F; open circuit potentials were about equal. The open circuit potential of aluminum was higher in the case of the RFNA. The cathodic reaction for aluminum appeared about the same as in WFNA; as shown in Table 1, no corrosion was thereby noted. Anodically, the aluminum polarized considerably more in the RFNA.

At 130°F, all curves were quite similar in character; the anodic aluminum curve was more noble in the WFNA at 110°F than it was in the RFNA at 130°F.

(2) Evans Type Polarization Curves; Equipotential Points Used for Correlating Corrosion Rates

As in the cases described above, Evans type curves were plotted for RFNA at 122°F and 130°F in Figures 32 and 33 respectively. The corrosion rates calculated for the couple from these curves are compared with experimental measurements of weight losses in Table 6. There was good agreement at the 122°F level but only fair agreement at the 130°F level.
3. General Remarks

A series of curves showing the variation in EMF with temp. at constant current densities was plotted in Figure 36. The break in the data, quite consistent at $140^\circ$F, indicates that another nitrate of aluminum may have been formed, besides the hexahydrate. As discussed in the Literature Survey,


aluminum reacts with nitric acid at concentrations above 81% at room temperatures to form the hexahydrate of aluminum nitrate. Mellor


discusses possible other formations of aluminum nitrate, the trend indicated being that at the higher temperatures, lower hydrates may result. It is therefore postulated that this occurs at about $140^\circ$F, and that this compound may be $\text{Al(NO}_3\text{)}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$. Although only three temperatures were considered, they are believed to be strongly indicative. Each curve should probably be distinctly separated at the $140^\circ$F point. This is so because as shown, the curves not only change slope rapidly and abruptly at $140^\circ$F but they change from concave to convex when the impressed current is below 1.2 m.a./in.$^2$.

Further research along these lines might show more positive verification.

C. The Phenomenon of Anodic Passivation of 2S Aluminum in FNA

1. Introduction: Special Techniques
During the course of the polarization investigations at a certain temperature, it was discovered that if attempts were made to impress current densities above a particular value when the aluminum was anodic to the platinum, it would result in the current falling off to zero or slightly above zero. This occurred similarly at other test temperatures, the maximum current densities varying with temperature. Potential increase during the drop off were extremely rapid in most cases. This phenomenon is termed "anodic passivation" and is discussed in the Literature Survey, par. III.B.4. This passivity is ascribed to the formation of a protective film of aluminum oxide which is highly resistant to the passage of current. Its free energy is such that it will form only at a potential somewhat higher than those values plotted in the preceding polarization curves which are designated the active regions per se (2S aluminum anodic to platinum).

It was found that at the highest temperature of test, 160°F, the current would drop off rapidly with a correspondingly rapid rise in potential. At the lower temperatures, in particular at the 110°F mark, the current and potential transients were more readily handled but in opposition to this, the procedure used in maximum current determination at this level became a rather lengthy one. This can be discerned by viewing Figure 37 which includes several runs made at 110°F. When impressing currents in the vicinity of the maximum possible, the current would always drop and either continue to drop to zero or perhaps later rise as shown, depending upon the value of impressed current. The passivating current for 110°F was actually evaluated to be about 5 m.a./in.². The curves of
Figure 37 were only a portion of those actually secured at 110°F. As such, they indicate that the aluminum anode was still active at a 2.7 m.a./in.² impressed current density. Further testing was performed similarly such that passivating current density of 5 m.a./in.² was obtained for 110°F. Therefore, before any further polarization studies could be attempted, it was necessary to ascertain these current density limits so that proper values could be utilized to guide the polarization runs. The currents for the aluminum-platinum couple in WFNA, under non-agitated conditions, are plotted in Figure 38. The list of results for all seven conditions of test are included in Table 7. Thus it is seen why the graphs of the polarization curves are restricted to their indicated current density limits in most cases at about 10 m.a./in.². It also explains why polarization tests could not be readily applied to the aluminum-stainless steel couple at temperatures below 122°F. Exceptions to this restriction occur at 110°F and 160°F where data at higher currents would not have been contributory to the research and hence were not determined.

When the aluminum-platinum couple was allowed to remain in the active state for 15 to 25 hours, the nitrate film became so protective that current could be increased somewhat into the passivating region and the anode would continue to remain active and at an appreciable dissolution rate. This might be attributed to difficulty in the inward diffusion of the oxidizing elements to the aluminum metal. This nitrate film buildup in turn required a higher application of potential in order to effect passivation. The connotation of current density is extensively employed primarily because of con-
venience and the greater facility it lends in reproducibility of results. Parenthetically, relatively large current density variations with temperature (See Fig. 38) can be explained because of the difference in resistance of the electrolyte being substantially large at small temperature changes while the potentials required for the formation of the passivating film do not necessarily vary within the relatively small temperature span herein considered.

2. Mechanism of Anodic Passivation

In order to properly assess the results of this testing phase and to formulate a possible mechanism for passivation, accurate potentials were required. Since the reaction kinetics were too rapid at 160°F to permit recording of potential data with the equipment used in the test, the 122°F and 114°F levels were focused upon. By using special techniques it was possible to collect pertinent data for these two temperatures. They are listed in Tables 8 and 9 and plotted in Figures 39 and 40 respectively. Close resemblance is found to the graph, Figure 4, previously cited under Literature, page 27. The left hand portions of these curves represent the active region, and are essentially the 2S aluminum anodic polarization curves shown in the Pourbaix and Evans types of curves.

It is postulated that in the active range, aluminum nitrate forms, while in the passive range, aluminum oxide forms. Consider the following reactions and their accompanying free energy changes:

\[
\text{Al} \rightarrow \text{Al}^{+++} + 3 \, e^- \quad 1.67 \text{ volts} \quad (25)
\]
\[
3\text{H}_2\text{O} + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 \text{~} + 6\text{e}^0 + 6\text{H}^+ \quad (26)
\]

For \(\text{Al}_2\text{O}_3\) \(\text{~}\), \(\Delta F^0 = -376.77\) k. cal./mole

and for \(\text{H}_2\text{O}\), \(\Delta F^0 = -54.64\) k. cal./mole

For the reaction:
\[
\Delta F = -376.77 - (3)(-54.64) = -212.77\text{ k. cal.} \quad (27)
\]

\[
e = \frac{-212.77}{(6)(23.060)} = +1.543\text{ volts for reaction (26)} \quad (28)
\]

Similarly:
\[
\text{lH}_2\text{O} + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 \text{~} + \text{H}_2\text{O} + 6\text{e}^0 + 6\text{H}^+ \quad (29)
\]

For \(\text{Al}_2\text{O}_3\) \(\text{~}\) \(\text{~}\) \(\text{H}_2\text{O}\), \(\Delta F^0 = -435.0\) k. cal./mole

\[
e = \frac{-216.41}{(6)(23.060)} = +1.563\text{ volts for reaction (29)} \quad (30)
\]

Continuing:
\[
6\text{H}_2\text{O} + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 \text{~} + 3\text{H}_2\text{O} + 6\text{e}^0 + 6\text{H}^+ \quad (31)
\]

For \(\text{Al}_2\text{O}_3\) \(\text{~}\) \(\text{~}\) \(\text{~}\) \(3\text{H}_2\text{O}\), \(\Delta F^0 = -547.9\) k. cal./mole

\[
e = \frac{-220.06}{(6)(23.060)} = +1.590\text{ volts for reaction (31)} \quad (32)
\]

For the formation of aluminum oxide, the peak potentials for 122°F and 110°F taken from Figures 39 and 40 respectively are:

- at 122°F, \(e = 2.00 -.242 = 1.758\) volts
- at 110°F, \(e = 2.10 -.242 = 1.858\) volts

Subtracting 0.242 puts the resulting voltages on the hydrogen scale.
The free energy of formation of the hexahydrate of aluminum nitrate is calculated:

\[ 6 \text{H}_2\text{O} + 3 \text{NO}_3^- + \text{Al} \rightarrow \text{Al(NO}_3)_3 \cdot 6 \text{H}_2\text{O} + 3 \text{O} \]  \hspace{1cm} (33)

For NO\textsubscript{3}\textsuperscript{-}, \( \Delta F^\circ = -26.41 \text{ k. cal./mole} \)

For Al(NO\textsubscript{3})\textsubscript{3} \cdot 6\text{H}_2\text{O} = -525.82 \text{ k. cal./mole} = \Delta F^\circ

For the reaction, \( \Delta F = -525.82 - (6)(-54.64) - 3(-26.41) \)

\[ = -118.75 \text{ k. cal.} \]

and \( \frac{-118.75}{(3)(23.06)} = +1.715 \text{ volts for reaction (33)} \)

These calculations were all based on free energy values given by Latimer


and Rossini


which apply at 25°C.

It is therefore proposed that the passivating film consists of either Al\textsubscript{2}O\textsubscript{3} or the monohydrated oxide. From the above calculations, a semi-quantitative analysis can be postulated. Since the spontaneity or ease of formation of a compound is less the lower the negative free energy of formation, the oxides, having lower negative free energies of formation than the hexahydrated nitrate of aluminum (See equation (33)), will require more outside energy for formation than the nitrate.
Thus, when impressing currents across the subject couple, the nitrate will form first. At the condition existant at the peak of the curves of Figures 39 and 40, enough energy is supplied so that the oxide starts to form, the speed of which is much more rapid at 160°F than at 110°F or room temperature. Furthermore, this change takes place over a "voltage span" which is the difference between the voltage required for nitrate formation and the voltage required for oxide formation. If more precise instruments had been used, this voltage span would be more accurately defined. It appears from subject graphs to be approximately 0.5 volts. A rigorous experiment would probably produce the flatness usually associated with a voltage span. The equipment so required was considered to be outside the scope of this investigation. At the same time, such equipment would probably have yielded potentials required to form the oxides which more closely approached the theoretical values.

The tri-hydrated aluminum oxide film can probably be discounted because the voltage difference between it and the hexahydrate would be somewhat less than for the other two considered.

3. General Comments

Some substantiating checks on the oxide film proposal were made. An aluminum electrode freshly abraded was heated in an oven for about 5 hours at 500°F. When it was inserted in the acid, anodic to platinum, the current immediately fell off to zero. (The current was set in the active range first.) In another instance, after a freshly abraded aluminum electrode had been passivated, it was removed, exposed to helium for several hours, reinserted, and was still passive. Then open circuit potentials were compared, and they checked closely.
Both type specimens were checked for corrosion rates in the passive range and both failed to lose any significant weights over several hours of test. Alternately making the anode cathodic did not bring it back to the active state at any time.

This phenomenon is extremely sensitive at the change from active to the passive state. Jarring or motion of the solution would cause a rapid current drop off, if the setting was in the active range, near passive values, showing that a state of equilibrium had been prevailing. These two opposing conditions may be noted in the polarization curves where processing is indicated. There, a condition is set up during which the current and potential would regularly fluctuate up and down. Well below this range, steady conditions indicated the active condition and dissolution of the metal; above the critical range, passivity would set in at once.

D. Cathodic Protection of Stainless Steel

As discussed in the Literature Survey, page 29 the criteria for cathodic protection of a metal is that the local cathodes must be polarized to the open circuit potential of the local anodes. This theory is then extended to include the behavior of dissimilar metals, and is further extended to include the use of inert electrodes as anodes, providing that the polarization effects of the anode are not so great that a depolarizer is demanded.

Brown, English, and Williams

discuss a method of calculating local currents which provide excellent data on the criteria for cathodic protection but was considered outside of the intended scope of this work.

The method herein selected for studying the feasibility of cathodically protecting stainless steel in fuming nitric acid was described under Procedures. Three phases were selected for study in white fuming nitric acid (non-agitated), at temperatures of 122°F, 140°F, and 160°F; two phases were chosen for red fuming nitric acid at 122°F and 130°F. A summary of the schedule is included in Table 10. From this schedule, a series of results was obtained for each temperature level, some of which have been plotted. The trends displayed in WFNA at 140°F and 160°F, and in RFNA at 122°F and 130°F are indicated in Figures 41, 42, 43, and 44 respectively. The minimum current density requirements for cathodically protecting stainless steel under the conditions of test are summarized in Table 11.

Reference is made to the polarization curves for the conditions of testing that corresponds to the phase of cathodic protection. In all instances, the cathode curves polarize mostly at the lower ranges of impressed current densities. Then the degree of polarization decreases significantly. This straightening portion of the polarization curve takes place at correspondingly higher current densities as the temperature of test is increased. In fact, it can be seen that the values of the current densities at which cathodic protection is achieved approaches those values at which the above-cited degree of polarization decreases, at the same corresponding temperatures.
A more rigorous determination of the polarization curves for stainless steel might reveal a more striking resemblance than is apparent in these curves.

The results have as bands to show areas rather than single lines in view of the difficulty in maintaining conditions that would yield precise results throughout the experiments. These bands do show on the other hand, that precise control over currents is not a prerequisite to the protection of the steel. When the assemblies were dismantled and reabraded for succeeding tests, it was found that cathodic protection could be detected very readily by visually noting the condition of the specimen surface. The shinier the electrode, the better was the protection. It was further noted that those samples which were partially protected would soon corrode on exposure to air, whereas the well protected specimen remained untarnished. This suggests that a very thin film of oxide had probably formed which on exposure to air was completely oxidized to a thicker film. Weight losses in these cases, however, were only slight. Abrasion of these affected samples was not made difficult by this film covering.

The results indicated that adequate distribution of current was achieved. There were no surface formed irregularities. As stated by Evans,


and as verified herein, the required cathodic current density for preventing corrosion is not the electrochemical equivalent of the
corrosion-rate which would take place in the absence of these measures. This principle is only true where the anodic polarization is small compared to the cathode behavior. These experiments well illustrate this argument. Thus it is deduced that cathodic protection, per se, is feasible for stainless steel in fuming nitric acid in temperatures from room through 160°F. The effect upon the acid was not investigated.
VII. SUGGESTIONS FOR FUTURE RESEARCH

For a continued and perhaps more rigorous pursuit of certain interesting phases in this research, the following fundamental aspects could be selected:

A. Installation of equipment for polarization studies which would utilize distillation methods over the acid bath. The decomposition of the acid would thus be retarded and perhaps enhance more rapid attainment of equilibrium conditions.

B. Polarographic, spectroscopic, interference, or similar type analyses might be attempted in order to facilitate more ready resolution of the products formed in various phases. This would apply to solution properties and compositions, as well as to metal surface variations.

C. Addition of equipment to permit securing accurate values of transients such as potentials at higher temperatures. This might shed more light on free energy changes which may be appreciably altered at the higher temperatures of test.

D. Adaptation of a systematic method of studying the behavior of other couple combinations which would speed up procedures and hence allow a greater number to be studied.

E. Investigate the information stated by Mellor


regarding no corrosion occurring by nitric acid that is 100% pure.
F. Analyses of the spent acid at the termination of cathodic protection runs to discover what ill effects, if any, had ensued during the experiments. This would resolve the total practicability of such investigations as well as furnish information on what might be done to alleviate such adverse consequences if adverse results were actually discovered.

G. Extension of cathodic protection studies to include agitated solutions. This would make the equipment somewhat more complex.


33. Sir Humphrey Davy, "On the Corrosion of Copper Sheeting by Sea Water, and on Methods of Preventing this Effect; and on Their Application to Ships of War and Other Ships," Phil. Trans. Royal Society of London Part 1, (1824) p. 151.


49. R. Boyle, "Considerations Touching the Usefulness of Experimental Natural Philosophy," Oxford, 1663.


Table 1

Range of Acid Compositions Used in Tests *

<table>
<thead>
<tr>
<th></th>
<th>WFNA</th>
<th>RFNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA</td>
<td>96.89 to 99.13%</td>
<td>101.05 to 103.17%</td>
</tr>
<tr>
<td>HNO₃</td>
<td>95.90 to 98.36%</td>
<td>88.15 to 90.74%</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.31 to 1.84%</td>
<td>7.53 to 10.57%</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.98 to 3.37%</td>
<td>0.74 to 1.90%</td>
</tr>
</tbody>
</table>

* All acids used in this research were secured from aluminum drums.
Table 2
Nominal Compositions of Type AISI 347 Stainless Steel * and 2S Aluminum

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>2S Al</td>
<td>99.0% Aluminum</td>
</tr>
<tr>
<td></td>
<td>1% Others</td>
</tr>
<tr>
<td>347 SS</td>
<td>Cr: 17.15%</td>
</tr>
<tr>
<td></td>
<td>Ni: 10.36</td>
</tr>
<tr>
<td></td>
<td>C: 0.07</td>
</tr>
<tr>
<td></td>
<td>Mn: 1.48</td>
</tr>
<tr>
<td></td>
<td>P: 0.018</td>
</tr>
<tr>
<td></td>
<td>S: 0.015</td>
</tr>
<tr>
<td></td>
<td>Si: 0.61</td>
</tr>
<tr>
<td></td>
<td>Cb: 0.97</td>
</tr>
<tr>
<td></td>
<td>Fe: Balance</td>
</tr>
</tbody>
</table>

* This same composition of 347 SS was used throughout the tests, although some of the charts included herein specify Type 347 SS and some specify only 347 SS.
Table 3

Typical Set of Data Obtained to Plot Potential Time Curves *

<table>
<thead>
<tr>
<th>Elapsed Time, min.</th>
<th>Current density ma./in.(^2)</th>
<th>Emf. Volts</th>
<th>Temp. °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>1/4 ma./in.</td>
<td>1.5940</td>
<td>140</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>1.5965</td>
<td>&quot;</td>
</tr>
<tr>
<td>95</td>
<td>&quot;</td>
<td>1.5870</td>
<td>&quot;</td>
</tr>
<tr>
<td>100</td>
<td>&quot;</td>
<td>1.5930</td>
<td>&quot;</td>
</tr>
<tr>
<td>105</td>
<td>&quot;</td>
<td>1.5930</td>
<td>&quot;</td>
</tr>
<tr>
<td>110</td>
<td>&quot;</td>
<td>1.6020</td>
<td>&quot;</td>
</tr>
<tr>
<td>115</td>
<td>&quot;</td>
<td>1.5925</td>
<td>&quot;</td>
</tr>
<tr>
<td>120</td>
<td>&quot;</td>
<td>1.5965</td>
<td>&quot;</td>
</tr>
<tr>
<td>125</td>
<td>&quot;</td>
<td>1.5860</td>
<td>&quot;</td>
</tr>
<tr>
<td>130</td>
<td>&quot;</td>
<td>1.5960</td>
<td>&quot;</td>
</tr>
<tr>
<td>135</td>
<td>&quot;</td>
<td>1.5900</td>
<td>&quot;</td>
</tr>
<tr>
<td>140</td>
<td>&quot;</td>
<td>1.5990</td>
<td>&quot;</td>
</tr>
<tr>
<td>145</td>
<td>&quot;</td>
<td>1.5985</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

* For this table, 96.8% WFNA was used. Acid was not agitated.
Table 4

Qualitative Data on Corrosion Rates Obtained During Polarization Runs of 2S Aluminum and Type 347 SS*

<table>
<thead>
<tr>
<th>Metal Type</th>
<th>Acid</th>
<th>Temp (°F)</th>
<th>Agitated or Static</th>
<th>Anodic or Cathodic</th>
<th>Weight Loss, gms.</th>
<th>Electrode Area, in.²</th>
<th>Duration of Test, Hours</th>
<th>Corrosion Rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>2S Al</td>
<td>WFNA</td>
<td>122</td>
<td>Static</td>
<td>Anodic</td>
<td>0.0026</td>
<td>1.08</td>
<td>9.85</td>
<td>47.6</td>
</tr>
<tr>
<td>2S Al</td>
<td>WFNA</td>
<td>122</td>
<td>Static</td>
<td>Cathodic</td>
<td>0.00026</td>
<td>1.00</td>
<td>2.5</td>
<td>8.45</td>
</tr>
<tr>
<td>3147 SS</td>
<td>WFNA</td>
<td>122</td>
<td>Static</td>
<td>Anodic</td>
<td>0.0189</td>
<td>1.01</td>
<td>9.9</td>
<td>728.0</td>
</tr>
<tr>
<td>3147 SS</td>
<td>WFNA</td>
<td>122</td>
<td>Static</td>
<td>Cathodic</td>
<td>0.00001</td>
<td>1.00</td>
<td>2.5</td>
<td>8.45</td>
</tr>
<tr>
<td>2S Al</td>
<td>WFNA</td>
<td>160</td>
<td>Static</td>
<td>Anodic</td>
<td>0.0009</td>
<td>1.03</td>
<td>3.75</td>
<td>1330.0</td>
</tr>
<tr>
<td>2S Al</td>
<td>WFNA</td>
<td>160</td>
<td>Static</td>
<td>Cathodic</td>
<td>0.0304</td>
<td>1.01</td>
<td>3.75</td>
<td>1330.0</td>
</tr>
<tr>
<td>3147 SS</td>
<td>WFNA</td>
<td>160</td>
<td>Static</td>
<td>Anodic</td>
<td>0.0137</td>
<td>0.993</td>
<td>0.10</td>
<td>670.0</td>
</tr>
<tr>
<td>3147 SS</td>
<td>WFNA</td>
<td>160</td>
<td>Static</td>
<td>Cathodic</td>
<td>0.00005</td>
<td>0.999</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* The Corrosion Rates given above were calculated from average weight changes of the electrodes during the polarization tests, and were incidental to those tests.
<table>
<thead>
<tr>
<th>Metal Type</th>
<th>Acid</th>
<th>Temp °F</th>
<th>Agitated or Static</th>
<th>Anodic or Cathodic</th>
<th>Weight Loss, gms</th>
<th>Electrode Area, in.²</th>
<th>Duration of Test, Hours</th>
<th>Corrosion Rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>2S Al</td>
<td>WFNA</td>
<td>140</td>
<td>Agitated</td>
<td>Anodic</td>
<td>0.0035</td>
<td></td>
<td></td>
<td>239</td>
</tr>
<tr>
<td>2S Al</td>
<td>WFNA</td>
<td>140</td>
<td>Agitated</td>
<td>Cathodic</td>
<td>0.0012</td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>347 SS</td>
<td>WFNA</td>
<td>140</td>
<td>Agitated</td>
<td>Anodic</td>
<td>0.0106</td>
<td>1.016</td>
<td>9.1</td>
<td>865.0</td>
</tr>
<tr>
<td>347 SS</td>
<td>WFNA</td>
<td>140</td>
<td>Agitated</td>
<td>Cathodic</td>
<td>0.0013</td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>2S Al</td>
<td>RFNA</td>
<td>122</td>
<td>Static</td>
<td>Anodic</td>
<td>0.0113</td>
<td>1.05</td>
<td>8.91</td>
<td>23.54</td>
</tr>
<tr>
<td>2S Al</td>
<td>RFNA</td>
<td>122</td>
<td>Static</td>
<td>Cathodic</td>
<td>0.0007</td>
<td>1.05</td>
<td>6.25</td>
<td>20.7</td>
</tr>
<tr>
<td>347 SS</td>
<td>RFNA</td>
<td>122</td>
<td>Static</td>
<td>Anodic</td>
<td>0.0105</td>
<td>1.00</td>
<td>3.91</td>
<td>510.0</td>
</tr>
<tr>
<td>347 SS</td>
<td>RFNA</td>
<td>122</td>
<td>Static</td>
<td>Cathodic</td>
<td>0.0000</td>
<td>1.005</td>
<td>2.20</td>
<td>0</td>
</tr>
<tr>
<td>2S Al</td>
<td>RFNA</td>
<td>130</td>
<td>Static</td>
<td>Anodic</td>
<td>0.0000</td>
<td>0.857</td>
<td>20.70</td>
<td>657.0</td>
</tr>
<tr>
<td>2S Al</td>
<td>RFNA</td>
<td>130</td>
<td>Static</td>
<td>Cathodic</td>
<td>0.0007</td>
<td>0.857</td>
<td>20.70</td>
<td>8.01</td>
</tr>
<tr>
<td>347 SS</td>
<td>RFNA</td>
<td>130</td>
<td>Static</td>
<td>Anodic</td>
<td>0.0192</td>
<td>1.008</td>
<td>4.33</td>
<td>868.0</td>
</tr>
<tr>
<td>347 SS</td>
<td>RFNA</td>
<td>130</td>
<td>Static</td>
<td>Cathodic</td>
<td>0.0003</td>
<td>1.008</td>
<td>11.17</td>
<td>10.0</td>
</tr>
</tbody>
</table>
Table 5

Corrosion Rates of 2S Aluminum and Type 317 Stainless Steel, Singly and Coupled, in Fuming Nitric Acid, mpy. Results are Based on 5-48 Hour Tests. Coupled Designates to 2S Al or to Type 317 SS; Natural Galvanic Couple Only Was Used.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Type Acid</th>
<th>Temp., °F</th>
<th>Static or Agitated</th>
<th>Coupled or Single</th>
<th>Corrosion Rate, m.p.y.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2S Al</td>
<td>WFNA 122</td>
<td>Static</td>
<td>Coupled</td>
<td>Single</td>
<td>90</td>
</tr>
<tr>
<td>2S Al</td>
<td>WFNA 140</td>
<td>Static</td>
<td>Coupled</td>
<td>Single</td>
<td>*</td>
</tr>
<tr>
<td>2S Al</td>
<td>WFNA 160</td>
<td>Static</td>
<td>Coupled</td>
<td>Single</td>
<td>500</td>
</tr>
<tr>
<td>317 SS</td>
<td>WFNA 122</td>
<td>Static</td>
<td>Coupled</td>
<td>Single</td>
<td>1.0</td>
</tr>
<tr>
<td>317 SS</td>
<td>WFNA 140</td>
<td>Static</td>
<td>Coupled</td>
<td>Single</td>
<td>*</td>
</tr>
<tr>
<td>317 SS</td>
<td>WFNA 160</td>
<td>Static</td>
<td>Coupled</td>
<td>Single</td>
<td>1.0</td>
</tr>
<tr>
<td>2S Al</td>
<td>WFNA 122</td>
<td>Agitated</td>
<td>Coupled</td>
<td>Single</td>
<td>35</td>
</tr>
<tr>
<td>317 SS</td>
<td>WFNA 122</td>
<td>Agitated</td>
<td>Coupled</td>
<td>Single</td>
<td>0.5</td>
</tr>
<tr>
<td>317 SS</td>
<td>WFNA 140</td>
<td>Agitated</td>
<td>Coupled</td>
<td>Single</td>
<td>1.5</td>
</tr>
<tr>
<td>2S Al</td>
<td>RFNA Room</td>
<td>Static</td>
<td>Coupled</td>
<td>Single</td>
<td>2.9</td>
</tr>
<tr>
<td>2S Al</td>
<td>RFNA 110</td>
<td>Static</td>
<td>Coupled</td>
<td>Single</td>
<td>135.0</td>
</tr>
<tr>
<td>2S Al</td>
<td>RFNA 122</td>
<td>Static</td>
<td>Coupled</td>
<td>Single</td>
<td>112</td>
</tr>
<tr>
<td>2S Al</td>
<td>RFNA 130</td>
<td>Static</td>
<td>Coupled</td>
<td>Single</td>
<td>178.0</td>
</tr>
<tr>
<td>Metal Type</td>
<td>Temp., °F.</td>
<td>Static or Agitated</td>
<td>Coupled or Single</td>
<td>Corrosion Rate, m.p.y.</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>------------</td>
<td>-------------------</td>
<td>------------------</td>
<td>-----------------------</td>
<td></td>
</tr>
<tr>
<td>316 SS RFNA</td>
<td>Room</td>
<td>Static</td>
<td>Coupled</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>316 SS RFNA</td>
<td>110</td>
<td>Static</td>
<td>Single</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>316 SS RFNA</td>
<td>122</td>
<td>Static</td>
<td>Coupled</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>316 SS RFNA</td>
<td>130</td>
<td>Static</td>
<td>Single</td>
<td>0.56</td>
<td></td>
</tr>
</tbody>
</table>

* No tests
Table 6

Comparison of Predicted Corrosion Rates of 25 Aluminum with Those Obtained Experimentally

<table>
<thead>
<tr>
<th>Type</th>
<th>Temp., °F.</th>
<th>Static or Agitated</th>
<th>Limiting Galvanic Current ma./in.²</th>
<th>Corrosion Rates m.p.y. From Polarization Data</th>
<th>Corrosion Rates m.p.y. From Natural Couple</th>
</tr>
</thead>
<tbody>
<tr>
<td>WFNA</td>
<td>122</td>
<td>Static</td>
<td>1</td>
<td>65.5</td>
<td>90</td>
</tr>
<tr>
<td>WFNA</td>
<td>140</td>
<td>Static</td>
<td>3</td>
<td>187.0</td>
<td>no tests</td>
</tr>
<tr>
<td>WFNA</td>
<td>160</td>
<td>Static</td>
<td>10</td>
<td>655.0</td>
<td>500</td>
</tr>
<tr>
<td>WFNA</td>
<td>122</td>
<td>Agitated</td>
<td>0.7</td>
<td>15.3</td>
<td>35 *</td>
</tr>
<tr>
<td>WFNA</td>
<td>140</td>
<td>Agitated</td>
<td>2</td>
<td>131</td>
<td>90</td>
</tr>
<tr>
<td>RFNA</td>
<td>122</td>
<td>Static</td>
<td>0.2</td>
<td>78</td>
<td>112 **</td>
</tr>
<tr>
<td>RFNA</td>
<td>130</td>
<td>Static</td>
<td>5.6</td>
<td>359</td>
<td>178</td>
</tr>
</tbody>
</table>

* Only 3-48 hour runs were made because of difficulty encountered with equipment.

** Only one run could be utilized here because the aluminum anode developed an oxide film thereafter that made it passive.
Table 7
Current Densities at Which Anodic Passivation of 23 Aluminum Occurs
When Coupled to Platinum Anodes in FNA

<table>
<thead>
<tr>
<th>Acid</th>
<th>Temp., °F</th>
<th>Agitated or Static</th>
<th>Current Density ma./in.</th>
</tr>
</thead>
<tbody>
<tr>
<td>WFNA</td>
<td>110</td>
<td>Static</td>
<td>5</td>
</tr>
<tr>
<td>WFNA</td>
<td>122</td>
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</tr>
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</tr>
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<td>1.055</td>
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* At this point, anodic passivation set in and hence the current falls off rapidly.
Table 9
Variation of Potential with Current Density of 2S Aluminum When Coupled Anodically to Platinum in WFMA (Static) at 140°F (Anodic Passivity Data)

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<th>EMF, Volts</th>
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</table>

* At this point, anodic passivation set in and hence the current falls off rapidly.
Table 10
Summary of the Schedule of Testing Stainless Steel for Cathodic Protection

<table>
<thead>
<tr>
<th>Type Acid</th>
<th>Temp., °F.</th>
<th>Impressed Current</th>
<th>Duration of Runs, Hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Gauge, ma.</td>
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</tr>
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<td>66</td>
</tr>
<tr>
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<td>122</td>
<td>25</td>
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<tr>
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<td>1</td>
<td>115</td>
</tr>
<tr>
<td>WFNA</td>
<td>160</td>
<td>10</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>72</td>
</tr>
<tr>
<td>RFNA</td>
<td>122</td>
<td>5</td>
<td>144.5</td>
</tr>
<tr>
<td>RFNA</td>
<td>122</td>
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<tr>
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</table>
Table 11

Minimum Current Densities Required for Cathodic Protection of Type 347 SS in FNA at the Conditions Indicated

<table>
<thead>
<tr>
<th>Type Acid</th>
<th>Temp., °F</th>
<th>Minimum ( \text{ma./in.}^2 )</th>
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</thead>
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<tr>
<td>WFNA</td>
<td>140</td>
<td>7</td>
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<tr>
<td>WFNA</td>
<td>160</td>
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</tr>
<tr>
<td>RFNA</td>
<td>130</td>
<td>1.5</td>
</tr>
</tbody>
</table>
(a) Action of Local Anodes and Cathodes

(b) Natural Galvanic Couple (after Gladstone)

Fig. 1 Examples of Current Flow in Local and Galvanic Cells.
Reaction reversible in both directions.

Reversible oxidation, irreversible reduction.

Irreversible oxidation, reversible reduction.

Reaction irreversible in both directions.

Fig. 2  Different Types of Polarization Curves (after Pourbaix).
Fig. 3 Graphic Estimation of Galvanic Current (after Uhlig)
Fig. 4  Anodic Passivity
Fig. 5 Illustration of Method of Cathodic Protection. (After Mears and Brown)
Fig. 6 Illustration of a System undergoing Cathodic Protection, (after Pourbaix).
Fig. 7  Schematic, Assembled, and Exploded Views of Galvanic Corrosion Couple
Fig. 8  Apparatus Used to Determine Corrosion Rates of Metals and Alloys in Agitated FNA, Showing Special Condenser, Air-driven Stirrer and Flask.
Fig. 9 Schematic of Apparatus for Polarization Studies

A - Pt electrode
B - 347 stainless electrode
C - 3S AI electrode
Fig. 10 General View of Equipment Used to Conduct Polarization Tests, Showing Constant Temperature Bath and Regulator, Source of Current, Controls, and Potentiometer
Fig. II  Detail of Salt Bridge Construction
Fig. 12 Detail of Holder and Electrode
Fig. 13  Arrangement of Apparatus Used in Agitating WFNA during Polarization Tests Showing Acid Container, Stirrer, and Positions of Electrodes and Salt Bridge
Assembly of Electrodes and Flasks in Constant Temperature Bath for the Study of Cathodic Protection of Type 317 SS in FNA
Fig. 15  Selenium Rectifier and Instrument Panel Used in Performing Cathodic Protection Tests of 316L SS
Fig. 16  Assembled and Exploded Views of Electrode Configurations for Cathodic Protection Tests of Type 316L SS Using Platinum Coils as Anodes, Approx. 1/3 actual size.
Fig. 17 Potential-Time Curve for 2S Aluminum at 140°F in 98.19% WFNA at a Current Density of 1.9 ma./in.² Acid was not agitated.
Fig. 18  Potential - Time Curves for 2S Aluminum at 140°F in 96.85% WFNA at the Higher Current Densities (Acid from aluminum drum.)
Fig. 19 Decomposition of 98.19% WFNA During Polarization Tests of 2S Aluminum conducted at 140°F, using Current Density of 12.5 ma./in.² (Static)
(Acid from aluminum drum)
Fig. 20. Polarization Curves for Type 347SS and 2SAI in WFNA at 122°F. Acid was not Agitated During Test.
Fig. 21  Polarization Curves for 347 SS and 2S Al in WFNA at 140°F. Acid was not Agitated During Test.
Fig. 22 Polarization Curves for Type 347 SS and 2S Al in WFNA at 160°F. Acid was not Agitated during Tests.
Fig. 23 Polarization Curves for Type 347 SS and 2S Al in WFNA at 122°F. Acid was Agitated During Test.
Fig. 24 Polarization Curves for Type 347 SS and 2S Al in WFNA at 140°F. Acid was Agitated During Test.
Fig. 25  Polarization Curves for 347 SS and 2S Al in RFNA at 122° F. Acid was not Agitated during Tests.
Fig. 26 Polarization Curves for Type 347 SS and 2S Al in RFNA at 130°F. Acid was not Agitated During Tests.
Fig. 27 Polarization of Type 347 SS and 2S Al in WFNA at 122°F.
Acid was not Agitated.
Fig. 28  Polarization of Type 347 SS and 2S Al in WFNA at 140°F.
Acid was not Agitated.
Fig. 29. Polarization Curves of 347 SS and 2S Al in WFNA at 160° F. Acid was not Agitated.
Fig. 30  Polarization Curves of 347 SS and 2S Al in WFNA at 122° F. Acid was Agitated During the Tests.
Fig. 31  Polarization Curves of 347 SS and 2S Al in WFNA at 140°F. Acid was Agitated During Tests.
Fig. 32 Polarization Curves of 347 SS and 2S Al in RFNA at 122° F. Acid was not Agitated During Tests.
Fig. 33 Polarization Curves of 347 SS and 2S Al in RFNA at 130°F. Acid was not Agitated During Tests.
WFNA Acid Range
HNO₃: 95.90 to 98.36%
NO₂: 0.31 to 1.84%
Acid from Al Drum

Fig. 34 Equipotential Points (Limiting Galvanic Current) obtained from Polarization Curves of Type 347 SS and 2S Al Static.

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Fig. 35 Comparison of Predicted and Observed Corrosion Rates of 2S Al coupled to Type 347 SS in WFNA.

Acid Range
HN\textsubscript{3}O\textsubscript{3}: 95.90 to 98.36%
NO\textsubscript{2}: 0.31 to 1.84%
Fig. 36  Potential of 2S Al in the active region as a function of the Temperature, when coupled anodically to Pt. electrode. (WFNA)
Fig. 37  Time-Current Curves for Determining the Limiting Maximum Current which could be Impressed across the 2S Al-Pt. Couple at 110° F. in WFNA

(Acid from aluminum drum)
Fig. 38. Current at which Anodic Passivation of 2S Al occurs when coupled to a Pt Cathode at various temperatures, in WFNA, Static.
Acid Range

HNO₃: 96.74 to 98.36%
NO₂: 0.31 to 1.84%

Fig. 39. Anodic Passivation of 2S Al when coupled to Pt. Cathode in WFNA at 122° F. Acid was not agitated.
Acid Range
HNO₃ 95.90 to 98.36%
NO₂ 0.31 to 1.84%

Fig. 40 Anodic Passivation of 2S Al when coupled to Pt. cathode in WFNA at 140° F. Acid was not agitated.
Fig. 41 Cathodic Protection of 347 SS in WFNA at 140°F, using Platinum Anodes.
Fig. 42 Cathodic Protection of Type 347 SS in WFNA at 160° F, using Pt. Anodes.
Fig. 43  Cathodic Protection of Type 347 SS in RFNA at 122°F, using Pt. Anodes.
Fig. 44  Cathodic Protection of Type 347 SS in RFNA at 130°F, using Pt. Anodes.
I, Saul Barron, was born in New York City, February 24, 1917. I received my secondary school education in the public schools of Lakewood, New Jersey. My undergraduate training was obtained at Lafayette College, Easton, Pa., from which I received the degree Bachelor of Science in 1941. After attending The Ohio State University Twilight Graduate School at Wright-Patterson AFB, Ohio, for two years, I received the degree Master of Science in June, 1948. In January, 1953, after completing some of the requirements for the degree Doctor of Philosophy under the same conditions, I received an appointment to a Research Fellowship at The Ohio State University. In July, 1953, I was appointed Research Associate. I held this position for 14 months while completing the requirements for the degree Doctor of Philosophy.