Dedicated to my wife and children
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AN ELECTROCHEMICAL STUDY OF PITTING CORROSION
IN STAINLESS STEELS

I. INTRODUCTION

Pitting is one of the most destructive and insidious forms of corrosion. This type of attack manifests itself as small pits or holes in the exposed metal surface that deepen with time. Usually, the remaining metal surface is relatively unaffected. Because of its localized character, pitting corrosion perforates metal sections with only a small total loss of metal. It is difficult to detect pits because of their small size and the fact that they are often covered by corrosion products. Also, it is very difficult to quantitatively measure and compare the extent of pitting attack because of the widely varying numbers and depths of pits that occur under identical conditions. From the standpoint of equipment design and safety, pitting corrosion introduces a serious problem.

As a class, the stainless steel alloys are more susceptible to damage by pitting attack than any other metal or alloy. Under severe conditions, pits penetrate stainless steel parts at phenomenal rates.
The purpose of this investigation was to study the fundamental mechanisms involved in the pitting corrosion of stainless steels. It is hoped that the results of this study will aid in the understanding and possible mitigation of this mode of corrosion.
II. SUMMARY AND CONCLUSIONS

1. Pitting corrosion is characterized by highly complex, time-dependent electrochemical phenomena. It is impossible to define or describe pitting attack by an ordinary polarization or corrosion diagram, since the electrochemical characteristics of the system change rapidly with time and current flow. To completely describe pitting attack, an infinite series of instantaneous polarization diagrams are required. During the progress of pitting, all types of electrochemical control are operative. Indeed, the idea of electrochemical control becomes quite meaningless when applied to this type of attack.

2. The electrochemical behavior observed during pitting corrosion has been analyzed on the basis of the mixed potential theory. A new concept of the electrochemical action during pitting corrosion has been proposed.

3. The acid theory of pitting corrosion, the most generally accepted theory, has not been supported by the results of this investigation. Indeed, the highly acidic conditions within pit cavities appears to be an effect rather than the cause of pitting corrosion.

4. Ion screening at pit sites has been experimentally observed for the first time. The chloride ions within a
growing pit prevent the migration and diffusion of foreign species to the anode area. Thus, the pitting tendencies of the halide ions are largely due to their ability to prevent the entry of inhibiting ions and dissolved oxygen into the pit anode.

5. The autocatalytic nature of pitting attack has been experimentally verified. Pitting attack is autocatalytic by virtue of the fact that the growth of a pit produces changes that promote its further growth. This autocatalytic action has been always attributed to changes occurring at the pit anode. However, this investigation has demonstrated that pitting corrosion induces self-stimulating electrochemical changes at both anode and cathode areas.

6. In ferric chloride, and possibly in other high conductivity pitting corrosives, there is negligible interaction between two, closely spaced, isolated pit sites. Interactions between pits only occurs on densely pitted surfaces.

7. Pit growth on 18Cr-8Ni stainless steel surfaces has been measured and characterized for the first time. In ferric chloride solutions, the corrosion rate at a pit site is initially very erratic. Pits often become inactive during this early growth period. During the later stages of pit growth, pit corrosion rates steadily increase with time. Pits demonstrate phenomenal increases in corrosion rate
with time. A hundred-fold increase often occurs during the first hour of growth.

8. The factors affecting the growth of pits on 18Cr-8Ni stainless steel immersed in ferric chloride have been determined. Increasing the ferric chloride or ferric ion concentrations markedly increases the rate of pitting corrosion. Pit growth is largely controlled by the amount or concentration of chloride ions contained within the pit cavity. The concentration of chloride ion in the electrolyte has relatively little effect on pit growth. Sulfate and perchlorate ions do not support pitting attack.

9. An entirely new approach to the study of pitting corrosion has been made possible by the development of an artificial pit specimen. This specimen is unique in its almost identical similarity to an actual corrosion pit. These artificial pit specimens permit many measurements which are impossible to make by any other technique.

10. A literature survey has been compiled from the most important literature published during the past thirty-five years. The results, conclusions, and experimental techniques of various investigators have been critically analyzed on the basis of modern theories.

11. Nitrate ion, an inhibitor of pitting attack in ferric chloride solutions, only inhibits the onset of pitting attack and does not retard the attack within growing
pits, except at very high concentrations. Nitrate additions actually stimulate the corrosion rates of growing pits.
III. LITERATURE SURVEY

A. Introduction

The first major section of this literature survey is devoted to the general aspects of pitting corrosion—the nature, occurrence, and the factors affecting pitting corrosion. The second section is concerned with chemical and electrochemical effects, and other more fundamental aspects of the pitting phenomenon. The last two sections describe the theories and the research techniques that have been applied to this form of corrosion. For purposes of clarity and presentation, these four sections have been further subdivided.

This survey represents the more important contributions to the understanding of pitting corrosion published during the last thirty-five years. Because of the fundamental aim of this investigation, the pitting corrosion of metals and alloys other than the stainless steels have been covered to a limited extent. However, almost all of the literature cited is directly related to the pitting attack of 18-8 stainless steels.

Throughout this survey an effort has been made to critically analyze the results, conclusions, and
experimental techniques of various investigators on the bases of modern chemical, electrochemical, and corrosion theories. It is felt that this approach is more desirable than the mere presentation of condensed literature references.

B. General Aspects of Pitting Corrosion

1. Definition of Pitting

Corrosion produces a wide variety of surface structures. It often manifests itself as a uniform attack of the exposed metal surface. In other instances corrosion may be limited to restricted areas of the exposed surface. In this case, it is termed localized attack or localized corrosion. Pitting is an example of highly localized corrosion. The attack is limited to extremely small areas of the metal surface. Usually the remaining surface is relatively unaffected during pitting attack. Pits start at vanishingly small points on the surface and enlarge with time. However, the enlargement of the surface area of a pit is small in comparison with the increase in depth and volume of the cavity. Undermining of the surface is frequently observed during pitting attack. Often, the surface shows only tiny pinholes, while the subsurface metal has been almost entirely removed. Hence, pit growth is mainly growth in depth and volume with a slight increase in the surface area of the pit.
Champion (1) has divided corrosion into two main classes, general and localized, and has subdivided these classes according to the general scheme presented in Table I. Champion further defines pitting as follows:

The term pitting is used when the area of attack is so localized that the width is of the same order as or less than the depth of attack (the dividing line between pitting and uneven local corrosion may be taken at a width/depth ratio of about 6).

Hence, there is a continuous gradation between general corrosion and very localized corrosion such as pitting and cracking. There is no distinct surface structure that can be designated as pitting attack. Any definition of pitting based on surface appearance must be purely arbitrary. Thus, the limiting width/depth ratio quoted above could be chosen as 2 or 10, instead of 6. However, Champion's definition is entirely adequate for most purposes.

There is a lack of distinction between pitting corrosion and crevice corrosion in the literature. Crevice corrosion or concentration cell corrosion is attack that is restricted to shielded areas or crevices on the exposed metal surface. Crevice corrosion is the preferred nomenclature since the term concentration cell implies a mechanism which may not be operative in all cases. This form of attack is associated with surface deposits, scale, gaskets, and other areas where the metal is shielded from direct exposure to the
corrosive medium. McKay (2) and Fontana (3, 4) have discussed the causes and effects of this mode of attack.

Crevice corrosion, because of its localized nature, usually appears as pits or perforations in the metal surface. To differentiate between pitting corrosion and crevice corrosion, the following restriction will be applied: Crevice corrosion is attack that is limited to surface areas that are shielded from direct exposure to the electrolyte, regardless of the form of attack. That is, any corrosion that occurs in shielded areas will be designated as crevice corrosion even though the attack appears as pits or perforations. The importance of this distinction will be shown later.

The term pitting, as used in this paper, will indicate attack that meets the following requirements:

1. It must conform to the width/depth ratio proposed by Champion (1) and/or it must start from a vanishingly small point on the exposed metal surface.

2. It must occur on a freely exposed surface.

In the first requirement, Champion's definition has been modified so as to include newly formed pits which may not meet the maximum width/depth ratio of 6. The second restriction distinguishes pitting corrosion from crevice corrosion.
2. The Occurrence of Pitting

a. Metals Subject to Pitting

Pitting attack has been observed on a great variety of metals. Table II lists some common metals and alloys subject to pitting under certain conditions. This table has been compiled from information presented in The Corrosion Handbook (5). Even titanium has been observed to pit in sodium chloride solutions during anodic polarization studies (6). Thus, it is entirely possible that all metals and alloys will suffer pitting corrosion if exposed to suitable environmental conditions.

The stainless steel alloys as a class are more susceptible to damage by pitting attack than any other metal or alloy. Under severe conditions, pits penetrate stainless steel parts at phenomenal rates.

b. Pitting Corrosives

A pitting corrosive is any reagent which causes pitting corrosion as defined previously. Table III lists the corrosives which have been reported to cause pitting of stainless steel alloys. Table III has been taken from industrial and laboratory corrosion data (7, 8). This table illustrates some interesting aspects of the corrosives that induce pitting of stainless steels. The predominance of inorganic and organic halide compounds is particularly
striking. Reference to Table II indicates that this pitting tendency of halide compounds also applies to other metals and alloys. Oxidizing metal halide salts, such as cupric, ferric, and mercuric bromides and chlorides, are especially aggressive toward stainless steels. Of the halides, the chlorides and bromides show the greatest tendency to produce pitting attack. Fluoride and iodide salts usually demonstrate little or no pitting tendencies.

Table III includes many substances that are not pitting corrosives as defined previously. For example, Stern (9) and Uhlig (10) found that ferric sulfate solutions do not pit freely exposed 18-8 stainless steel surfaces. Thus, ferric sulfate cannot be considered a pitting corrosive. It is also questionable whether many of the other compounds listed in Table III are actually pitting corrosives. These apparent errors in Table III arise from two possible sources. First, the pitting attack might have been due to the presence of contaminating ions. Since supply waters usually contain chloride salts in varying amounts, the pitting may have been caused by the presence of chloride ions. The most probable source of difficulty is the lack of distinction between pitting and crevice corrosion in present-day terminology.

The crevice corrosion of stainless steel alloys is usually most pronounced in halide salt solutions and in
reducing acids. Hence, it is most severe under the same conditions that produce pitting attack. However, the crevice attack of stainless steels can occur in almost any electrolyte. Wyche, Voight, and Laque (11) report that crevice attack sometimes occurs even on stainless steels during exposure to nitric acid. Nitric acid normally passivates stainless alloys.

One must admit that there is a great difference between corrosives that induce localized attack on freely exposed surfaces, and those that cause attack in shielded areas on metal surfaces. Almost every electrolyte can sustain attack in crevices, whereas only specific electrolytes are capable of initiating attack on freely exposed areas. Differentiating between pitting and crevice corrosion is very necessary for the understanding of pitting corrosion.

3. Factors Influencing Pitting

a. Factors Associated with the Metal

(1) Composition. Increasing the chromium content of stainless steels decreases the tendency of pitting in chloride solutions. Huseby and Scheil (12) found no pits in a specimen of Type 310 stainless (24 Cr - 20 Ni) exposed to 10% ferric chloride solution at room temperature, while Type 304 (18 Cr - 8 Ni) pitted under similar conditions. However, it should be noted that increasing chromium
content does not completely prevent pitting attack.

The presence of nickel in stainless alloys improves their resistance to localized attack in neutral chloride solutions and reducing acids (13). The chromium-nickel stainless alloys (300 series) generally show greater resistance to pitting and general attack than do the straight chromium types (400 series).

Carbon content adversely affects the pitting resistance of the stainless steels in 10% ferric chloride solutions. In the case of Type 304 stainless steel, Streicher (14) and Rhodin (15) observed that increasing carbon markedly increased the intensity and extent of pitting in alloys containing less than 0.4% silicon. At silicon levels of 0.5% and greater, carbon contents between 0.01 and 0.09% had negligible influence on the pitting behavior. Huseby and Schell (12) found that carbon content had a deleterious effect on the pitting resistance of sensitized Type 316 stainless exposed to 10% ferric chloride.

Silicon, as seen above, improves the resistance of stainless steels to pitting attack. Streicher (14) found that Type 302B stainless steel (18 Cr - 8 Ni - 2.5 Si) showed relatively few pits after exposure to 10% ferric chloride. However, these pits grew into enormous cavities beneath the surface. Therefore, silicon could be considered detrimental at higher concentrations. Although it
reduces the number of pits formed, it actually increases the
intensity of attack at these points. From the standpoint
of performance, it is more desirable to have an alloy that
supports many shallow pits than one which pits rarely, but
deeply. The chance of perforation is greater in the latter
case. Silicon contents around 2% in Type 316 stainless
steel produce a remarkably pit-resistant alloy. This has
been mentioned by Zapffe (13) and extensive studies of
silicon-containing Type 316 stainless alloys have been made
by Streicher (14) and Rhodin (15).

Molybdenum additions to stainless alloys produce greater
increases in pitting resistance than any other alloy addi-
tion. As little as 2.5% molybdenum in an 18 Cr - 8 Ni stain-
less steel eliminates pitting corrosion in 10% ferric
chloride at room temperature (12). Ordinary 18 Cr - 8 Ni
(Type 304) stainless steel is severely pitted under the
same conditions. Molybdenum additions also markedly improve
the pitting resistance of stainless alloys in all other pitt-
ting corrosives. For this reason, the molybdenum-bearing
alloys, Types 316 and 317, are extensively used in paper
mill construction, marine heat exchangers, and in other
areas where conditions conducive to severe pitting exist.
18 Cr - 8 Ni stainless steels containing 2.5% silicon
together with 3% molybdenum represent the most pit-resistant
class of stainless steels (14, 15).
Minor elements and inclusions often have a pronounced effect on pitting resistance. Sulfur, as sulfide inclusions, noticeably increases the tendency towards localized attack (10, 14). This adverse effect of sulfur has been observed during corrosion studies of iron and steel by Mears (16) and Hoar and Havenhand (17). Selenium additions likewise markedly reduce pitting resistance (10, 14, 18). The normal oxide and silicate inclusions in stainless steels have no detectable effect on pitting resistance (10, 14, 18).

Titanium and columbium alloy additions decrease pitting resistance in ferric chloride solutions, but the effect of these elements is very slight in sodium chloride and sea water (18).

The presence of ferrite phase in austenitic stainless steels increases their pitting tendency in ferric and sodium chloride (19). Also, the presence of ferrite in the very resistant 18 Cr - 8 Ni - 3 Mo - 2 Si alloy reduces the resistance to localized attack (14).

Nitrogen additions cause a slight improvement in pitting resistance. Since nitrogen is an austenite stabilizer, its effect on pitting resistance is believed to be due to the fact that it reduces the amount of ferrite present in stainless alloys (14).
(2) **Heat Treatment.** Holding Types 304 and 316 stainless steels in the sensitizing temperature range (900° - 1600°F) decreases their pitting resistance (12, 18). Uhlig (18) has observed a similar effect for an 18 Cr - 8 Ni stainless alloy containing 0.001% carbon. Austenitic stainless steels exhibit the greatest pitting resistance when solution-quenched from above 1900°F.

(3) **Mechanical Work.** Severe cold work increases the pitting attack of 18 Cr - 8 Ni stainless steel in ferrie chloride (18). Hot rolling tends to concentrate pitting attack at the edges of the sheet. Preferential edge pitting is observed on most wrought stainless products.

(4) **Surface Finish.** Although the original metal surface is rapidly removed by the corrosion process, it can exert a great influence on both the initial and later stages of attack. Pitting and localized corrosion are less likely to occur on polished stainless steel surfaces than on etched or ground surfaces (14, 18). However, the pits that do form are larger and penetrate more rapidly than those on rough surfaces. Generally, rough surfaces show numerous, shallow pits, whereas smooth surfaces have a few large pits. Therefore, the surface finish may greatly influence the probability, the distribution, and the velocity of pitting attack (20). Under severe pitting conditions, surface finish effects often disappear or become negligible.
b. Factors Associated with the Environment

(1) Solution Composition

(a) Ionic Species Present. As discussed previously, the halides and halogen-containing anions are almost invariably associated with the pitting of stainless steels and other alloys. The chlorides, bromides, and hypochlorites are the most aggressive of the halogen-containing anions. Fluorides, iodides, and iodine-containing anions are practically without effect on stainless alloys. Because of the present ambiguous definition of pitting, it is difficult to determine from the published data which of the anionic species, other than halides, have any pitting tendencies. For many of the anionic species listed in Table III, it is very questionable whether they can induce pitting corrosion as defined in this paper. Additional observations will be necessary to establish whether or not anions such as fluoride, sulfate, and acetate can support pitting under specific conditions.

Of the cations, the oxidizing metal ions produce the worst pitting attack. Ferric, cupric, and mercuric halides are the most aggressive of all pitting corrosives. The non-oxidizing metal halides such as aluminum, calcium, and sodium halides, also cause pitting, although to a much less degree than do the oxidizing metal halides. Pitting
corrosives may thus be divided into two classes; the oxidizing metal halides and the non-oxidizing metal halides. These two classes are quite distinct in their pitting behavior.

The behavior of stainless steels in bromides and chlorides and in mixtures of these two anions is most interesting. Mahla and Neilsen (21) observed that 18 Cr - 8 Ni stainless steel (Type 304) was more aggressively attacked by ferric chloride than ferric bromide. However, ferric bromide was more corrosive than ferric chloride toward 18-8 Mo stainless steel (Type 316). The results of their experiments are presented in Table IV. Uhlig and Wulff (22) made similar findings. They also observed that chloride-bromide mixtures were extremely corrosive toward 18-8 and 18-8 Mo stainless alloys. Their results also appear in Table IV. Weight losses give a very rough estimation of the extent of pitting attack. The weight losses reported in these two studies would not be expected to agree since different specimen sizes and exposure times were used.

Pitting attack can be prevented or inhibited by the addition of other ions to the pitting corrosive. Pitting in chloride solutions may be prevented by the addition of suitable amounts of sodium hydroxide (23), sodium chromate (24), sodium nitrate (24), or sodium silicate (25). Perhaps the most striking example of pitting corrosion...
inhibition is the action of nitrate ion additions to ferric chloride solutions. Uhlig (18) found that 18-8 stainless immersed in 10% ferric chloride containing 3% sodium nitrate did not pit, but uniformly corroded at an overall rate of 2 mpy (mils penetration per year) during a 10-year test. Without nitrate additions, the corrosion rate with pitting was a million times greater.

(b) Concentration. The effect of corrosive concentration on pitting attack is somewhat confused in the literature. It has been reported that pitting attack both increases and decreases with increasing halide ion concentration. This confusion may be resolved by relating pitting behavior to the two types of pitting corrosives. For the non-oxidizing metal halides such as sodium or calcium chloride, the corrosion rate first increases and then decreases as chloride ion concentration increases. That is, a plot of corrosion rate vs. chloride ion concentration exhibits a maximum point. Uhlig and Morrill (26) have observed this phenomenon for 18-8 stainless steel and mild steel exposed to 4% sodium chloride.

In the case of oxidizing metal halides, the rate of attack steadily increases with increasing halide ion concentration and shows no maximum point. Experiments by Uhlig (10) indicate that the pitting velocity in ferric
chloride is a linear function of chloride ion concentration.

Another interesting aspect is that pitting velocity is independent of halide ion concentration under conditions of externally applied anodic current as observed by Streicher (14). Under these conditions, pitting attack is a direct function of anodic current density.

(c) **pH**. Hydrogen ion concentration, or pH, markedly affects the pitting behavior of an electrolyte. Uhlig and Morrill (26) have made an extensive study of the effect of pH on the pitting of 18-8 stainless steel by sodium chloride. The authors found that at low pH values pitting ceased and general corrosion occurred while, at high pH values the stainless steel was unaffected. Pitting attack was most severe in neutral (pH-7) sodium chloride solutions.

Ferric and cupric halide solutions are stable only at low pH values. At higher pH values the metal oxides or hydroxides are precipitated, and the solutions lose their pitting tendencies. At very low pH values, solutions of these salts would be expected to produce general corrosion of stainless alloys.

(d) **Atmosphere**. The nature and composition of dissolved gases have a very great influence on the pitting attack occurring in non-oxidizing metal halide
solutions. The amount and composition of these dissolved gases are dependent on the composition and pressure of the atmosphere, above the corrosive media. 18-8 stainless steels do not pit in sodium chloride in the absence of oxygen as shown by Uhlig (10). Thus, the presence of oxygen is necessary for the pitting of stainless steels by non-oxidizing metal halides. Cavalaro and Bighi (28) have observed that the pitting tendency of sodium chloride solutions varied according to the dissolved gases present. For the various dissolved gases studied, the corrosivity increased in the following order: nitrogen, air, and oxygen.

The pressure of the atmosphere above the corrosive electrolyte has a pronounced effect on the corrosion rate. Table V summarizes the effect of oxygen pressure on the corrosion of 18-8 stainless steel in water and sodium chloride solutions. The weight losses reported give a rough indication of pitting intensity. It is unlikely that stainless steel pits in pure water; the weight losses reported are due to general corrosion. The corrosion rate passes through a maximum as oxygen pressure is increased. Oxygen at low pressures stimulates corrosion, while at higher pressures it acts as an inhibitor in sodium chloride solutions. Oxygen pressure, or the amount of dissolved oxygen, would be expected to have only a negligible effect
on pitting attack in oxidizing metal halide solutions. This will be discussed in greater detail later.

(2) Temperature

Temperature has an effect similar to that of halide ion concentration. In the case of non-oxidizing metal halide solutions, the corrosion rate passes through a maximum as temperature is increased. This effect has been observed by Uhlig and Morrill (26) during the attack of 18-8 stainless and mild steel by dilute sodium chloride. It has also been reported by Hackerman (30) for the case of mild steel in water, and by Asselin and Rohrman (31) for copper in sodium halide solutions. In the case of oxidizing metal halides, the rate of pitting attack would be expected to increase with increasing temperature with no indication of maxima. This aspect will be discussed further in a later section.

(3) Agitation

Pitting tends to be most severe under stagnant liquid conditions. Generally, agitation of the pitting corrosive reduces the velocity of pitting attack (32). Fontana (33) has observed that as solution agitation or velocity increases the depth of pitting decreases, while the number of pits increases. Hence, agitation tends to promote general corrosion of the surface.

Copson (34) has suggested that high liquid velocities
may even create stagnant areas because of turbulence. Under these conditions pitting attack would increase at high velocities. Severe agitation or high velocity fluid flow can also introduce mechanical effects such as cavitation and erosion.

C. Fundamental Aspects of Pitting Corrosion

1. Morphological Aspects

Pits are more than mere holes or cavities in a metal surface. Depending on the environmental conditions, they may appear in many forms. Pits, therefore, deserve a more detailed description.

a. Types of Pits

Pits may be conveniently divided into three general classes according to the nature and distribution of the corrosion products produced. The first is the nodular pit or tuberole. In this type, the solid corrosion products bridge the pit and cover it. Externally, the pit site appears as a blister on the metal surface. Nodular pits frequently occur on aluminum (35), copper (36), and steel (37) exposed to natural water or dilute salt solutions.

The second type of pit is the ringed pit. It is so named because the pit is surrounded by a ring or mound of corrosion products. It differs from the nodular type in that the corrosion products are deposited outside of the
pit cavity. Ringed pits have been observed on tin (38) and zinc (39) after exposure to water and neutral salt solutions. Sometimes ringed pits have more than one ring of corrosion products. In this special case, the pit is surrounded by a series of concentric corrosion product rings, or "corrosion rings." These rings are separated by areas which are almost devoid of any deposit. Ackerman (40) has observed this unusual type of ringed pit on iron and steel surfaces exposed to water. Corrosion rings on steel have also been reported by Marende (41) who believes that they are a manifestation of the Liesegang phenomenon.

The Liesegang phenomenon or periodic precipitation was first observed by Liesegang (42) during his studies on reactions in colloid gels. He found that if a solution of silver nitrate was allowed to diffuse into a gelatin gel containing potassium dichromate, silver chromate precipitated in periodic layers rather than continuously. When a drop of silver nitrate was placed on the surface of the gelatin gel, a series of concentric rings was formed similar to the corrosion rings described above. The various theories of periodic precipitation have been summarized by Stern (43). At present, it appears that the phenomenon can best be explained on the basis of ionic diffusion as shown by Wagner (44). Generally, periodic precipitation only
occurs under conditions where liquid convection is restricted, such as in a colloid gel or in capillary passages (45).

The appearance of corrosion rings does not necessarily imply that periodic precipitation has occurred. The rings of corrosion product may be the result of the distribution of the pit-producing reactions. The corrosion ring effect deserves further study.

The third type of pit is the simple pit which is completely free of any corrosion product deposits. That is, simple pits occur when the corrosion products are soluble in the corrosive media. Simple pits have been observed on 18-8 stainless steels exposed to ferric chloride (33) and acidic sodium chloride solutions (46). Prange (47) has observed an unusual type of simple pit on Type 316 stainless steel after exposure to an acidic solution of copper sulfate and sodium chloride. The pit cavity is surrounded by a series of concentric ring-like ditches or grooves. An illustration of this mode of pitting appears on the cover of the June, 1956, issue of Corrosion. The similarity between these grooves and the corrosion product rings observed on ringed pits is particularly striking. This leads one to suspect that there may be a periodicity in the electrochemical reactions that occur during pitting corrosion.
b. Pit Shape

Liebhafsky and Newkirk (48) have made an extensive radiographic study of the pit shapes produced on austenitic stainless steels immersed in ferric chloride. In Types 302 and 304 stainless steels, the pit cross-sections had a "pine tree" structure, with the widest part being at the pit bottom. Pitting often follows crystallographic directions in the metal or alloy. Pearson, Huff, and Hay (49) found that the initial pitting of aluminum in tap water developed as an etch pit structure. During the later stages of attack, the pits became hemispherical.

Pit shape is largely determined by gravitational force. That is, pits usually grow downward from the metal surface. Uhlig (10, 18) has attributed this to the accumulation of high density, soluble corrosion products at the base of the pit. The influence of gravity has been studied by Liebhafsky and Newkirk (48), who whirled corrosion coupons in ferric chloride. The rotation of the specimen provided the analogue of a gravitational field (centrifugal force) in a direction perpendicular to the axis of rotation. Pitting attack was observed to be distorted in this direction on rotated specimens. The authors also found that pitting attack on severely worked stainless steel was not measurably influenced by centrifugal or gravity forces.
This is apparently due to the fact that the directional effects produced by cold work overshadow gravity effects.

o. The Look of Pits

There is considerable controversy as to where pits originate on a metal surface. At first sight, one would expect that they would start at inclusions or other points of surface inhomogeneity. The fact that increasing carbon content increases the number of pits formed on stainless steels (See Factors Influencing Pitting) leads to the assumption that carbide particles might act as pit nuclei. However, Uhlig (18) found that pits readily formed on an 18-8 stainless steel containing only 0.001% carbon. Holding this alloy in the sensitizing temperature range markedly reduced its pitting resistance. Apparently, carbides do not act as pit nuclei. Electron microscope studies of pitted aluminum surfaces likewise indicated no preferential pit sites (49).

During electrolytically accelerated pitting tests in various chloride solutions, Streicher (14) observed that pitting preferentially occurred at grain boundaries, and especially at the intersection of three grain boundaries. However, it is important to note that Streicher's experiments were performed under conditions of impressed anodic current and, therefore, may not reflect true pitting behavior. Indeed, this is shown by Standifer's (46) observations...
during ferroxyl indicator studies. He found that pit sites occurred randomly on solution-quenched stainless steel alloys. Upon the application of small anodic currents, the number and size of these pit sites increased. At higher current values, pit sites appeared along grain and twin boundaries. Thus, Streicher's observations appear to be due to the specific action of externally impressed currents. However, the results obtained with ferroxyl indicator are rather questionable (See Study Methods) and cannot be taken as positive proof.

Summarizing, it seems that the loci of pits are almost completely random, with possibly a slight preference for grain and twin boundaries.

2. Electrochemical Aspects

a. Electrochemical Theory

The electrochemical theory of corrosion is the basic theory of corrosion phenomena. Today it is almost universally accepted by all workers in the field. Simply, it assumes the existence of spatially separated anode and cathode areas on a corroding surface accompanied by electric currents flowing for perceptible distances through the metal (50, 51, 52). At the anode areas dissolution of the metal as metallic ions occurs. A reduction reaction occurs at the cathode areas, and these areas generally remain unattacked during the corrosion process. Corrosion will
occur only if there is current flow between anode and cathode areas. Although there is some question as to the existence of distinct anodes and cathodes during general attack, this does not apply to pitting attack. The anode, or pit, is quite distinct.

Anode and cathode areas can arise in many ways. Basically, a potential difference between two points on an immersed metal surface is due to a physical or chemical difference between the two points. These physical or chemical differences may exist in the metal or in the solution in contact with the metal. Mears and Brown (53) have tabulated the possible sources of potential differences encountered in corrosion. These are presented in Table VI.

b. Electrochemical Reactions

(1) Cathodic Reactions

(a) Oxygen Reduction. Oxygen reduction is the most important cathodic reaction occurring in corrosion processes. An excellent general discussion of this topic appears in a recent literature survey by Lynes (54). Oxygen reduction can proceed along two possible paths depending on the pH of the solution. In acid solutions, the following steps are believed to occur (55):
\[
\begin{align*}
\text{overall: } & \quad 0_2 + 4H^+ + 4e = 2H_2O \\
\text{In alkaline solutions, the steps are (55): } & \quad 0_2 + 2H_2O + 2e = H_2O_2 + 2OH^-
\end{align*}
\]
detected traces of hydrogen peroxide during oxygen reduction on iron electrodes. The amount produced was greater at low current densities and in alkaline electrolytes. The same behavior would be expected for stainless steel cathodes. It is unfortunate that so little attention has been given to the formation and decomposition mechanisms of hydrogen peroxide in the cathodic oxygen reduction process. Hydrogen peroxide is an unstable compound. Therefore, factors that influence its stability, such as pH, temperature, and ions present in the electrolyte, should have a major effect on the velocity and behavior of the oxygen reduction process.

Corrosion involving oxygen reduction as the cathode reaction is thermodynamically much more energetic than corrosion involving hydrogen ion reduction at the cathode areas. That is, there is a greater free energy decrease for oxygen-consuming corrosion than for hydrogen-evolving corrosion. Calculations by Warner (57, 58) and others (59, 60) show this to be true for nearly all metals. However, oxygen-consuming corrosion is usually very slow when compared to hydrogen-evolving corrosion. This is due to the limited availability of oxygen for the cathodic reaction. The solubility of oxygen in water is very low; in electrolyte solutions it is even lower. Thus, the velocity of oxygen-consuming corrosion is dependent on the diffusion
rate of oxygen to the cathode areas. Any factor that influences the diffusion rate of oxygen will therefore influence the velocity of corrosive attack. Decreasing the solubility of oxygen by increasing the temperature or the electrolyte concentration of a solution will reduce the rate of oxygen diffusion to cathode areas. Since the conductivity, or corrosivity, of a solution increases under the same conditions that decrease oxygen solubility, Asselin and Rohrman (31) predicted that a plot of corrosion rate vs. temperature or electrolyte concentration should show maximum points. They found this actually did occur during the attack of copper by halide salt solutions. As mentioned before, Uhlig and Morrill (26) found such maxima in their studies of the pitting of 18-8 stainless steel by sodium chloride solutions. A particularly striking example of the dependence of corrosion velocity on oxygen solubility has been observed by Haohe (61). He determined the oxygen solubility and the corrosion rate of mild steel as a function of sodium chloride concentration. At sodium chloride concentrations up to 10 grams/liter, the oxygen solubility did not vary from the value observed in pure water. Above this concentration, the amount of dissolved oxygen decreased rapidly. The corrosion rate reached a maximum at this critical concentration of sodium chloride.
(b) Hydrogen Ion Reduction. The cathodic reduction of hydrogen ion probably ranks second in importance in corrosion reactions. The reaction is simply the reduction of hydrogen ions to hydrogen gas:

\[ 2H^+ + 2e^{-} = H_2 \text{ (gas)} \]  

This cathodic reaction is most often observed during attack by acid solutions. It is a very rapid reaction; the rapidity depending on several factors, one of which is the concentration of hydrogen ions in solution. As indicated previously, pitting usually occurs in neutral or nearly neutral electrolyte solutions. (There are some important exceptions; these will be discussed in the next section.) For ferrous alloys in neutral solutions, there is an insufficient concentration of hydrogen ions to maintain an active reduction reaction and, hence, other cathodic reactions, such as oxygen reduction, are possible. Therefore, hydrogen ion reduction is not usually an important reaction during pitting attack.

(c) Metal Ion Reduction. This type of cathodic reaction is unique in its effect on pitting. Pitting corrosives containing reducible metal ions often show extremely aggressive pitting actions. The general reaction for this cathodic reaction is:

\[ M^{n+} + ne^- = M^{+(n-m)} \]  

(4)
where \( n \) equals the positive charge of the ion and \( m \) equals the number of electrons involved in the reaction. For solutions containing cupric or ferric ions, the cathode reactions are:

\[
\begin{align*}
Cu^{2+} + e &= Cu^+ \quad (5) \\
Fe^{3+} + e &= Fe^{2+} \quad (6)
\end{align*}
\]

Uhlig (10) determined the pitting tendency of various metal halides toward 18-8 stainless steel. He found that, in the absence of dissolved oxygen, pitting intensity was proportional to the standard oxidation-reduction potential of the metallic ions. At potentials less than 0.15, no pitting occurred. His results are summarized in Table VII. It is important to remember that all of these solutions are capable of pitting stainless steels in the presence of dissolved oxygen. However, metal halides with sufficiently high oxidation-reduction potentials can pit stainless alloys in the absence of dissolved oxygen. Ferric chloride, because of its very high ferrous-ferric potential, causes extremely intense pitting.

Since the cathodic reduction of metal halides is independent of oxygen supply, factors which influence oxygen solubility have no effect on the pitting velocity. Therefore, increasing the temperature or concentration of an oxidizing metal halide solution would be expected to
increase the corrosivity of the solution. There would be no maximum points as is the case with non-oxidizing metal halides in which oxygen reduction is the cathodic reaction.

Most of the oxidizing metal halides are stable only in aqueous solutions at low pH values. At higher pH values, metal oxides or hydroxides are precipitated. For example, ferric chloride solutions are unstable above pH 2-3. Even though these solutions are acidic, hydrogen evolution during pitting corrosion is generally negligible. This is due to the passivating action of these oxidizing metal ions—which suppresses attack by the acid solution. The metal ions also compete with hydrogen ions for reduction at cathode areas.

(d) Effect of Cathodic Reaction on Pitting Behavior. As previously mentioned, there is considerable confusion in the literature as to the effects of various factors on the pitting tendencies of corrosives. This can be attributed to the failure of investigators to recognize the two distinct cathodic reactions that can occur during pitting attack; namely, oxygen reduction and metal ion reduction. Table VIII summarizes the behaviors of oxygen reduction and metal ion reduction types of pitting corrosives toward stainless steels.
(2) **Anodic Reactions**

The anodic reaction during pitting is the solution of the metal as ions. The general equation for this reaction is:

\[ M = M^{+n} + ne \]  

where \( n \) equals the positive charge of the metal ion. Uhlig and Wulff (22) determined the corrosion products produced during the pitting of 18-8 stainless steels. They accomplished this by impressing a current through a divided cell containing stainless alloy electrodes immersed in sodium halide solutions. Their results are tabulated in Table IX. The valence of the corrosion products is most interesting. The 18 Cr - 8 Ni alloys always yielded ferrous and chromic ions as anodic products at the reported current density. However, at higher current densities, the authors observed, by means of indicators, that the 18 Cr - 8 Ni alloys produced ferric ions during the first seconds of current flow. After this initial period, the iron dissolved as ferrous ions. When the current flow was interrupted for a few minutes and then resumed, ferric ions reappeared during the first few seconds. Type 316 stainless behaved strangely. In sodium chloride, the products were ferric and chromate ions. At very low current densities, it produced ferrous ion in sodium chloride. Pure iron was observed to dissolve
as ferrous ions. At very high current densities, it produced ferric ions.

Ferric ion was detected in oxygen-free solutions. From this, the authors concluded that the ferric ions resulted from an electrode reaction rather than the oxidation of ferrous ions. The authors also believed that the appearance of ferric and chromate ions was the result of dissolution from a passive surface.

(3) Polarization Effects

(a) Polarization of Electrode Reactions.

Polarization, or the change of electrode potential with current flow, has received extensive fundamental study and discussion in the literature (62, 63, 64). Polarization results from the slowness of one or more of the processes occurring at an electrode during the discharge or formation of an ion. During anodic polarization, the potential of the anode shifts to a more cathodic potential, while the polarization of a cathode shifts its potential in the anodic direction.

Polarization may be considered as a relative measure of the speed or efficiency of an electrode process. Electrode processes showing negligible polarization are therefore very rapid. Considering the cathodic reactions just described, several interesting points may be observed. Oxygen reduction is a slow process and shows very pronounced polarization
effects. It is slow because of the low solubility of oxygen in aqueous solutions and because the process is controlled by the rate of diffusion of oxygen to the cathode. Metal ion reduction is usually a rapid process and shows slight polarization as compared to oxygen reduction. The reasons are that the concentration of reacting metal ions is usually quite high and the fact that the metal ions are transported to the cathodic areas by both the diffusion and migration. Since the metal ions are positively charged, they tend to travel or migrate to the cathode areas under the influence of the potential gradient within the solution. Thus, positively charged ions will be transported to cathode areas more rapidly than neutral molecules such as oxygen.

(b) Electrochemical Control. Corrosion can proceed under four different types of electrochemical control: anodic, cathodic, mixed, and resistance control (65, 66, 67). If the anode polarizes and the cathode does not, the system is under anodic control. If the cathode polarizes and the anode is non-polarizing, the system is under cathodic control. If both electrodes polarize, the system is under mixed control. For cases where neither electrode appreciably polarizes, the current is controlled by the total resistance of the system, and it is said to be under resistance control. The type of control operating in a corrosion system may be determined if the anode and
cathode areas can be varied. If the corrosion rate increases with increasing cathode area and is independent of anode area, the system is under cathodic control. If corrosion rate is dependent on anode area and is independent of cathode area, the system is cathodically controlled. If the rate is affected by changes in either the anode or cathode areas, the system is under mixed control. Of course, the most accurate method of establishing the type of control is the determination of the anodic and cathodic polarization curves for the system. Often, it is difficult or impossible to separate the anode and cathode elements of the system, and other methods such as described above must be employed.

Considerable effort has been devoted to the determination of the type of control operating during the pitting corrosion of stainless steels. Obviously, the type of control is dependent on the electrode reactions and, therefore, on the type of pitting corrosive to which the alloy is exposed.

For the case of non-oxidizing metal halides, Ellis and LaQue (68) concluded that crevice corrosion of stainless steel in sea water was under complete cathodic control. This conclusion was based on the fact that the weight losses of special crevice corrosion specimens were a linear function of the area outside the crevice which was assumed to
be the total cathodic area. Although these experiments apply to crevice attack, the electrochemical reactions are undoubtedly the same as in pitting attack. Thus it may be assumed that these results indicate that pitting in seawater is under complete cathodic control. The pitting of 18-8 stainless steel by sodium chloride was also studied by Brown and Mears (69). The authors used the "scratch" technique for studying the pitting behavior of 18-8 stainless steel in various media. This method utilized a panel of stainless steel which was completely covered with wax. Scratches were made through the wax and the panel was coupled to an unwaxed panel. The pair were then immersed in the electrolyte under study. The waxed and scratched panels were always anodic with respect to the unwaxed panels. By varying the number of scratches and measuring current and electrode potentials, the authors were able to calculate the polarization diagram of the couple. It was also possible to estimate the type of control by correlating anode area with the percent increase in current (70). The results obtained with a 150 gram/liter solution of sodium chloride were very unusual. The system displayed a behavior that was characteristic of both cathodic and mixed control. The anode and cathode demonstrated considerable polarization, but the corrosion rate was practically independent of anode area. This anomalous behavior was due to the shape
of the calculated anodic polarization curve. It fell nearly vertically from the open circuit anode potential and then became horizontal as current increased. These results tend to support the cathodic control observed by Ellis and LaQue.

Standifer (46) investigated the pitting attack of Type 321 stainless steel in 3 percent potassium chloride solution containing 0.01 normal hydrochloric acid. The author determined the relationship between the anode or pit area, and the corrosion potential. The corrosion potential rapidly increased with slight increases in the anode area at small values of anode area. However, at greater values of anode area, the corrosion potential increased more slowly until it became nearly independent of the anode area. From these results, Standifer concluded that the pitting was initially under anodic control, but shifted to cathodic control as the pitting attack progressed. This shift in control was attributed to the fact that as pitting proceeded the anode area or total area of the pits increased, while the total cathode area necessarily decreased as the pits consumed it.

The mode of control during pitting in ferric chloride has also been considered by Brown and Mears (69) and Benson, Brown, and Mears (70). Using the aforementioned "scratch" technique and the 150 gram/liter sodium chloride solution, the authors added ferric chloride in amounts up to 0.84
grams/liter. Successive additions of ferric chloride progressively decreased the cathodic polarization. At the highest concentration studied, the control was almost completely anodic. Liebhafsky and Newkirk (71), in their studies of the pitting of Type 304 stainless steel in 10% FeCl₃·5H₂O, concluded that the attack was essentially under cathodic control. Two observations supported this idea. First, the corrosion rate soon became constant even though the total anodic area or pit area grew to many times its initial value. Thus, corrosion rate and anode area seemed to be independent. Secondly, the authors determined the corrosion rate as a function of specimen surface area, which was assumed to represent the total cathode area. The authors stated that there was a rough proportionality between specimen area and corrosion rate, indicating cathodic control. However, their experimental results do not show any proportionality between specimen area and corrosion rate. In fact, the results indicate the inverse to be true! These results cannot be considered conclusive, since only runs utilizing two different areas were considered valid by the authors and the rate differences between them were very small.

Stern (72) has recently made an extensive study of the overvoltage behavior of ferric ion reduction on various alloys in 10% ferric sulfate and in 10% ferric chloride
containing nitrate ion as an inhibitor. Types 304, 310, and 316 stainless steels, Hastelloy C, and Hastelloy F were included in the study. Since these materials exhibit great differences in pitting resistance, their cathodic polarization behaviors should differ if the corrosion is cathodically controlled. However, the cathodic polarization characteristics of these alloys were practically identical. Thus, Stern concluded that attack by ferric chloride is not cathodically controlled.

It is apparent that the type of electrochemical control operating during pitting corrosion is not completely understood. The possibility of a change in the type of control during attack is an intriguing hypothesis. The very divergent observations discussed above lead one to suspect that our present-day concepts of electrochemical control may be incomplete or that they may require modification when applied to pitting corrosion.

c. Distribution of Electrochemical Reactions

(1) Statistical Analysis

The application of statistical methods in the study of pitting phenomena has yielded very useful information. Probably the first application of statistical analysis was made by Mears and Evans (73) and Mears (16) who used the now familiar "square drop" method to correlate the corrosion resistance of steel with its composition.
This method employs a sheet of metal which is divided into numerous small squares by wax lines. A drop of corrosive is placed in each square, and a comparison of the number of squares showing attack with the total number of squares indicates the probability of attack. This method, and modifications of it, have been used by Mears and Brown (74), Aziz and Godard (75, 76), and Porter and Hadden (35) in investigations of the pitting corrosion of aluminum. Recently, extreme-value statistics have been successfully used to correlate maximum pit depth with other variables (77, 78). Although most of the published information concerns the pitting of aluminum, many of the observations apply equally well to the pitting of any metal or alloy.

Mears and Brown (74) found that the distribution of pits on an aluminum surface did not correspond to the Poisson formula. Since the Poisson formula is only valid for mutually independent events, the pits must interact with one another. Thus, pitting is not a completely random phenomenon. As indicated earlier, pits are nearly random with respect to surface structure. However, they are not random with respect to each other. The presence of a pit on a surface reduces the probability of another pit appearing at an adjacent area.
Anodic, Cathodic, and Neutral Areas

The interaction between pits is thought to be due to the cathodic reactions that occur on the surface immediately surrounding a pit. Thus, the area adjacent to a pit is cathodically protected from attack. Mears and Brown (74) state that this effect should not only reduce the probability of attack at adjacent areas, but should also reduce the velocity of any corrosion that does occur in these areas. Evans (79) has also emphasized this cathodic protection effect by stating that it is impossible to eliminate pitting attack by removing or isolating the pits on a corroding surface. The elimination of the pits would allow new points of attack, which were previously suppressed, to develop.

Knowledge of the size, shape, and distribution of the anodic and cathodic areas that exist during pitting attack would greatly facilitate a quantitative treatment of the problem. In addition to anodic and cathodic areas, Gatty and Spooner (80) and Akimov (65) have postulated the existence of neutral or non-reactive areas on the basis of electrode potential studies. The determination of the size and extent of these various areas during corrosion is difficult. However, several interesting studies have been made.

Mears and Brown (74), during a study of the pitting of aluminum by sodium chloride containing cupric ions, found
deposits of metallic copper at the mouths and on the walls of pit cavities. No trace of copper was observed at the bases of the pits. Apparently, a cathodic area follows a pit as it penetrates the metal. This idea has also been suggested by May (36). Standifer (46), using ferroxyll indicator, detected the presence of anodic, cathodic, and neutral areas on 18-8 stainless steel. He observed the presence of both anode and cathode regions at the bases of pits. Concentric rings, alternating cathodic and neutral, surrounded the pit sites. Here is another indication of reaction periodicity during pitting corrosion (see: Morphological Aspects). It should be noted that the author used impressed cathodic currents to speed up the development of the indicator colors. The observations could have been readily affected by this treatment. Also, there are several severe criticisms of the ferroxyll indicator method. These are discussed under Study Methods.

Aziz (81) used heavy metal radioisotopes to indicate the cathode areas on an aluminum surface exposed to tap water. The principle of the method was that the radioactive cations would plate out at cathode areas and could be detected by autoradiographic techniques. Aziz found that pits were surrounded by an annular ring of cathodic surface, about which there was an annular ring of neutral area. The remainder of the surface was cathodic.
The electrochemical corrosion process requires that a complete electrical circuit be maintained. That is, electrons must flow through the metal from anode to cathode areas, and current must pass through the corrosive electrolyte. In electrolytes the current is not carried by electrons, but by positive and negative ions. Thus, there is a migration or movement of the ions through the electrolyte. The ions which carry the current are not necessarily those which are created or destroyed by the electrode reactions. The current carrying capacity of an ion is a function of its concentration and mobility, whereas the entry of an ion into an electrode reaction is dependent mainly on its redox potential in the given solution (63). If the current carrying ions play no part in the electrode reactions, they will accumulate at the electrode surfaces. Eventually, a steady state will be reached in the solution adjacent to the electrode when the migration of current-carrying ions into this region is balanced by their diffusion away from it (82).

Baylis (83, 84) was probably the first to observe ion migration during pitting. He analyzed the contents of pit tubercles that appeared on iron pipe after exposure to tap...
water. The analysis showed that there was a substantial quantity of chloride and sulfate ions within the tubercles. Also, the pH of the liquid within the tubercles was around 3.0. Similar analysis of the tubercles formed on aluminum exposed to tap water have been recently reported by Porter and Hadden (35). The authors found chloride ion concentrations ten times as great, and sulfate concentrations twice as great as the tap water levels. The pit contents had pH values around 4.

Parsons, Cudd, and Lochte (85) used synthetic pits for the study of the pitting of iron by sodium chloride. These synthetic pits were self-starting and self-sustaining, and developed nodule-like appearances during exposure. After 80 days' exposure to 0.1 N sodium chloride with a pH value of 8.8, the interior of a typical pit had a pH value of 5.9 and contained: 0.490 N Fe₂⁺, 0.560 N Cl⁻, and 0.070 N Na⁺.

By impressing current through a divided cell, Pryor (37) studied the ion migration occurring during the attack of iron by dilute chloride solutions. Chloride ion concentration in the anode compartment was 3-4 times as great as the original electrolyte. Uhlig (10) used a similar technique to study 18-8 stainless steel in 5% sodium chloride. He found a linear relation between the total coulombs passed through the cell and the concentration of chloride
ion in the anode compartment. With increasing time, the pH of the analyte approached a limiting value of one.

It should be noted that observations of divided cell experiments are only qualitative. The size of the anode compartment in these experiments is much larger than a corrosion pit. A corrosion pit would be expected to contain a greater concentration of chloride ions, and have a lower pH value.

From the above experiments, it is apparent that there is a tremendous buildup of chloride ions at the anode areas during pitting corrosion due to migration effects. Sulfate ions, when present, also accumulate within pits although not as rapidly as chloride ions. The high concentration of hydrogen ions within pits is due to the hydrolysis of the metallic halides within the pits. Iron, nickel, and chromium halides hydrolyze in water to form acidic solutions. Hydrogen ions, because of their positive charge, migrate away from, rather than toward, anode areas.

(2) Autocatalytic Nature

The corrosion pit is a unique type of anode. The first indication of its unusual nature was discovered by Evans (86) in his early experiments on the localized attack of metals. He observed that, on vertically immersed specimens, pits tended to appear in vertical rows, indicating that the corrosion products flowing from a pit
stimulated corrosion at other points. Uhlig (10) also demonstrated the activating action of pit corrosion products. He allowed a thin stream of ferrous chloride to flow over the surface of an 18-8 stainless steel specimen immersed in ferric chloride solution. Within a short time, a groove appeared under the flowing stream of ferrous chloride. Thus, ferrous chloride, the major constituent of stainless steel pit corrosion products, definitely stimulated localized attack.

The term, autocatalytic, was introduced by Edeleanu and Evans (82) and Evans (87) in 1951. Autocatalytic refers to the fact that the working of a pit tends to produce conditions which stimulate its activity. From the above experiments, it is apparent that a pit requires its own corrosion products for active growth, and herein is the essence of its autocatalytic nature. As a result of this autocatalytic nature, newly formed pits are very unstable and often become inactive. Aziz (77) found that one half of the pits formed on aluminum in tap water became inactive in two weeks. Many of the artificial pits of copper used by May (36) were very erratic and often became inactive during the early stages of their growth. The erratic initial corrosion rates of 18-8 stainless steel in ferric chloride solutions, observed by Liebhafsky and Newkirk (71) may also be
an example of this effect although the authors attributed this to possible errors in weighing.

Factors which interfere with the autocatalytic action within pits will reduce the intensity of attack. As mentioned earlier, agitation of the corrosive reduces pitting attack. This is undoubtedly due to the dispersion of corrosion products from the metal surface and from pit interiors. Interference of the autocatalytic pitting action has been used as a basis for the development of pitting resistant stainless steel alloys (38). It was reasoned that, since silver forms insoluble halide salts, the incorporation of this metal in stainless steels should impede autocatalytic action and prevent pitting attack. Early exploratory laboratory tests indicated that 0.2% silver additions to Types 304 and 316 stainless steels caused a pronounced improvement in pitting resistance. However, later observations showed that these silver-containing materials often pitted more rapidly than the silver-free base alloys. This was probably due to the fact that the protection afforded by the silver was incomplete. Under these conditions, a few, but large, pits would be expected.

3. Physicochemical Aspects
   a. Cations

   The role of cations in the pitting corrosion process has been largely covered in the discussion of
cathode reactions. The metal cations, with the exception of the oxidizing metal cations, play no part in the pitting process other than in the carriage of current in the electrolyte. The oxidizing metal cations contribute significantly to the cathodic reactions. None of the cations enter into the anodic reactions.

Brown and Mears (69) and Hay (36) have suggested that the oxidizing metal cations may act as "oxygen carriers." That is, these ions can be reduced at cathode areas and then be re-oxidized by dissolved oxygen to continue the process again. This "oxygen-carrying" effect may contribute to the pitting attack of copper and ferrous alloys by non-oxidizing metal halides. For these alloys, the anodic corrosion products consist mainly of cuprous and ferrous ions. As these ions diffuse and migrate from pits they could be oxidized by dissolved oxygen and reduced on the cathode areas at the pit mouths. Wesley and Lindsley (89) refuted the idea that the formation of ferric chloride was the cause of pitting in sea water since it is extremely insoluble at the pH values normally observed. They may have overstated their conclusion since ferric ions are soluble at the low pH values found in pits, and could contribute to pitting attack. However, as the authors stated, it is very
unlikely that ferric chloride is the sole cause of pitting in sea water.

b. **Anions**

Although the cations present in a solution may greatly affect the velocity of pitting corrosion, the anionic species deserve special study. The pitting attack of stainless steels and other alloys is usually associated with the presence of halide ions—notably chloride and bromide. Other anions have little, if any, tendency to induce localized attack. As was shown, the pit anode requires high concentrations of halide ions, even though these ions are not consumed in the anodic reactions. The halide ions are unique in their corrosive behavior. This section is devoted to a discussion of the various anionic species and their properties. The importance of these properties in determining corrosion behavior is discussed later.

(1) **Anionic Properties**

A summary of the properties of the common anions has been compiled by Piontelli (90). This summary, with additions (91, 92, 93), appears in Table X.

The shape or geometrical structure of the various anions is roughly spherical, with the exception of hydroxide ion, water, and the other ions so noted. The perchlorate and sulfate ions are tetrahedral with the chlorine and sulfur at the center and the oxygen atoms
lying at the corners. The nitrate ion and the water molecule are triangular planar.

The ionic radii are the values obtained from ionic crystals. These values are not absolute, but depend on the crystal lattice and the nature of the cation associated with the anion. They represent an average value as determined by Pauling (94). It should be remembered that these values apply to ions in a crystal lattice and are only a rough measure of ionic radii in aqueous solution.

—Atoms and ions are composed of positive cores or nuclei surrounded by a negative cloud of electrons. If these positive and negative charges are not symmetrical, the center of gravity of the positive charges will be separated from that of the negative charges. The magnitude of this charge displacement is measured by the dipole moment, or product of the charges and the distance between their charge centers. The usual unit is the Debye which is \(10^{-33}\) times the moment expressed as E.S.U. charge units times distance in centimeters. The table indicates that the water molecule and nitrate ion have unsymmetrical charge distributions and, hence, have permanent dipole moments. Although symmetrical atoms and ions have no permanent moments, moments will be induced in them if they are placed in an electric field. Simply, this is caused by the
displacement of the electron cloud and/or the positive nucleus by the applied field. The induced moment is a function of the strength of the applied field:

\[ m = aF \]  

(8)

where \( m \) is the induced moment, \( F \) is the electric field strength, and \( a \) is a constant called the polarizability. It is more convenient to use polarizability since it is a constant for a given ionic species.

Table X lists the polarizabilities of the various anions. Most of the polarizability observed is due to the deformation of the ion electron clouds. The multiplication factors that appear refer to the fact that the total polarizability of molecular ions is assumed to be divided equally among the external atoms. For example, the oxygens of the sulfate are each assumed to contribute one quarter of the total ion polarization. The net effect of ion polarization is an increase in the degree to which electrons are shared, or an increase in covalent character. Syrkin and Dyatkina (95) have presented an excellent discussion of polarizability.

The electron affinity is the energy associated with the addition of an electron or electrons to a neutral atom. The addition of more than one electron involves the input of energy since the addition of an electron to a negative
ion will be opposed by coulombic repulsion. The ionization potential is the energy required to remove the most loosely bound electron or electrons from an isolated atom. The electronegativity of an atom is a measure of its electron attraction based on bond energy relations. It should be noted that electron affinity, ionization potential, and electronegativity are atomic rather than ionic properties. They are a measure of an element's tendency to gain an electron, or its oxidizing power. However, they also reflect the stability of the various ion species. The electron affinity that appears under the hydroxyl ion has probably been estimated by Piontelli. How this has been accomplished is difficult to imagine since there is no hydroxide molecule.

The molecular dissociation energy is the energy necessary to separate an isolated diatomic molecule into the two atoms of the element. Again, this is an atomic property rather than an ionic property. $E_D$ is the reversible electrode potential for the molecule/ion reaction. The equivalent conductance at infinite dilution is a measure of the ionic migrations. The equivalent conductance of a univalent ion is identical to its molar conductance. The multiplication factor in the case of sulfate indicates that the molar conductance is twice the equivalent conductance. The
energy of solvation of an ion is the energy necessary to remove an ion from solution to the gaseous state.

The hydration number of an ion is the number of water molecules that are assumed to be permanently attached to the ion in solution. The reported values of hydration numbers vary widely in magnitude. Brockis (96) and Kortum and Brockis (97) have critically analyzed the reported data and methods used, and have indicated the most accurate of these data and methods. The hydration numbers shown in Table X are those calculated by Ulich (93) from entropy data. These values are very close to the "best values" determined by Brockis (96) and Kortum and Brockis (97) by statistical averaging of the most accurate hydration data. Generally, hydration increases with decreasing ion diameter and increasing ionic charge.

Recently, Hinshelwood (98) has stated that the concept of a hydration sheath surrounding ions in aqueous solution loses much of its significance in view of the more modern ideas of patterned configurations in liquids. To the author, the important point is that water molecules interact to varying degrees with different ionic species. The hydration number is, therefore, a means of expressing this interaction, and does not necessarily imply that ions have a permanently attached sheath of water molecules. Indeed,
the fractional hydration numbers indicate that if the hydration concept is valid, it must be a dynamic phenomenon.

(2) Anionic Species

The halide ions show unique behaviors not only in corrosion reactions, but also in other phenomena, such as ion exchange reactions, complexing tendencies, adsorption effects, electrodeposition, and acid strength behavior. For this reason it would be advantageous to compare the general physicochemical properties and reactions of the halides and other anionic species. Examination of Table X indicates that the halides are quite different from other anions in several respects. They are characterized by their small ionic radii, their great oxidizing power (high values of $E$, $I$, $x$, and $E^0$) and their high polarizabilities.

Fluorine is the most powerful oxidizing agent known and consequently the fluoride ion is one of the most stable ions in aqueous solution. Reference to Table X shows that fluorine and the fluoride ion represent an anomaly in the halogen series. That is, there are greater differences between the properties of fluorine and chlorine than between chlorine and iodine. Indeed, fluorine has often been appropriately termed a "super halogen." In contrast to the extremely violent reactivity of elemental fluorine, the
fluoride ion is rather inert in aqueous solution. It exhibits a low equivalent conductivity due to its great interaction with water molecules (high hydration number) which impedes its mobility. Fluoride ion hydrolyzes in water, especially in acid solutions, forming long, chain-like ions such as: $\text{HF}_2^-$, $\text{H}_2\text{F}^-_3$, and $\text{H}_3\text{F}_4^-(100)$ which would also reduce its mobility.

Ionic complexes are generally covalently bonded, and hence, are formed most readily by ions demonstrating high polarizabilities. Fluoride ion, with its small polarizability, does not form complexes with transition or noble metal ions, but only with small, highly charged cations such as $\text{Al}^{+3}$ and $\text{Si}^{+4} (100)$.

Chlorine and bromine are very similar. Both are oxidizers, although not as powerful as fluorine and their ions are stable in aqueous solutions. Again, their stability is not as great as that of fluoride ion. Both chloride and bromide ions, because of their high polarizabilities, form extensive complexes with the transition, subgroup, and noble metal ions. They do not complex with the alkali or alkaline earth metal ions (100). They also have higher equivalent conductivities because of their lower hydration members.

The iodide ion is the least stable of all the halide ions. It is the only one that is oxidized by atmospheric
oxygen in acid solutions (101). Iodide ion, with a very
great polarizability, forms very extensive complexes with
many metal cations. However, the extent of its complexing
tendency is limited by its instability under oxidizing con-
ditions.

Hydroxide, nitrate, perchlorate, and sulfate ions are
stable in neutral solutions. However, at low pH values or
at high temperatures nitrate and perchlorate ions are
unstable and act as strong oxidizers. These four ions are
only slightly polarizable, and hence, can be considered as
rigid spheres (102). Perchlorate ion is the least polar-
izable of all the ionic species (103). This is evidenced
by the fact that there are no known complexes that contain
the perchlorate radical (104). Hydroxide, nitrate, and
sulfate ions complex to a very limited extent. It should
be noted that chemical bonding or interaction usually occurs
only at one point in an ion, so that only the polariz-
ability at one oxygen is involved when nitrate, perchlorate,
and sulfate ions react chemically. The permanent moment of
the nitrate ion indicates that one of the oxygens in the
ion is more polarizable than the other two (90).

Oxide ion exists only in ionic crystals since it decom-
poses to hydroxide ion in aqueous solutions. The sulfide
ion is somewhat similar to the halide ions. It has an
ionic radius and an electronegativity value very close to chloride ion, and a polarizability even greater than iodide ion. However, it is very unstable in water, being easily oxidized to sulfur as shown by its reversible electrode potential.

Homogeneous ion exchange studies have demonstrated some interesting differences between anionic species. An example of this type of exchange is the electron transfer between ions in different oxidation states:

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

(9)

where \( M^+ \) and \( M^{2+} \) are the two oxidation states of a metal cation and \( e \) is the electron transferred. At equilibrium, the forward and reverse reactions occur at the same rate. By employing radioactive ions it is possible to determine the equilibrium exchange rates. Exchange rates for \( \text{Cr}^{3+}/\text{Cr}^{2+}, \text{Eu}^{3+}/\text{Eu}^{2+} \), and other cation systems, have been observed to be very rapid in the presence of chloride ion (105, 106, 107, 108). The electron exchange in perchlorate solutions is very slow (104, 106), and is sometimes nearly non-existent (107). The chloride ion acts as a catalyst in electron exchange although the mechanism of this catalysis is not completely understood. It is undoubtedly related to the polarizability of the halide ion. Excellent summaries
of ion exchange theories have been prepared by Zwolinski, Marcus and Byring (104), Grahame (109), and Noyes (110).

Adsorption studies have also indicated striking differences between the various anions. Grahame (111) in electrocapillary studies on mercury surfaces found that the adsorption of anions increased in the order:

$$F^- < OH^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < CNS^-$$

Carbonate and sulfate ion adsorbed only slightly. With the exception of nitrate and perchlorate, ion adsorption increases with increasing ionic polarizability. Grahame believes that nitrate and perchlorate ions may be held on the surface by Van der Waals' forces rather than covalent bonds as are the other ions, although the situation is not completely clear.

Hackerman and Stevens (112) have investigated the adsorption of sulfate ions on iron surfaces by means of radioactive sulfate ions. They found that in the presence of chloride ion, the adsorption of sulfate ion increased. This was attributed to a change in the nature of the iron surface. At high chloride/sulfate ratios the authors concluded that chloride was preferentially adsorbed since there was a decrease in sulfate sorption.

Charging curves have been utilized to measure surface adsorption. A charging curve is the change in electrode
potential vs. the total coulombs passed through the system. By rapid charging, through the use of alternating currents, it is possible to study the formation and removal of surface films. Ershler (113), using this technique, observed that the presence of chloride ion reduced the amount of oxygen adsorbed on platinum electrodes. Hickling (114) has reported that an anomaly occurs during rapid charging of platinum in the presence of halides. The electrode potential rises directly to the potential for halogen evolution even when this is higher than the potential at which oxygen can normally deposit. These studies give further indication of the extreme surface activity of the halide ions. Although the analysis and understanding of charging curves is incomplete, they offer an unique means of studying metal surface adsorption in aqueous solutions.

Another interesting property of anions is their symmetric behavior during electrochemical polarization as observed by Piontelli (90, 115) and Piontelli and Poli (116, 117). They are symmetrical in the sense that, for a given metal, the anions that produce the greatest overvoltages during anodic polarization, have an analogous effect during cathodic polarization. Piontelli and Poli observed that, with most metals, the halide ions (chloride, bromide, and iodide) yielded the lowest overvoltages. Perchlorate yielded the greatest overvoltage values while
the other anions occupied intermediate positions. The stimulating effect of the halides on cathodic processes has also been observed by Heyrovsky (102) during studies of the electrodeposition of metals. Heyrovsky found that the presence of chlorides greatly facilitated the deposition of metals such as bismuth and antimony, which usually exhibit large overvoltages during electrodeposition.

The acids corresponding to the various anions vary widely in their relative strengths. Simply, the strength of an acid is a measure of its ability to ionize and release hydrogen ions. The relative strengths of the acids corresponding to the anions listed in Table X decrease in the order:

\[ \text{HClO}_4 > \text{HI} > \text{HBr} > \text{HCl} > \text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HF} > \text{H}_2\text{S} \]

(118). Perchloric acid is the strongest simple acid known (103). It is interesting to note that the halide acids, with the exception of hydrofluoric acid, have high strengths in comparison to the other acids. Here again, fluorine presents an anomaly. Hydrofluoric acid is only weakly acidic.

Summarizing, it is apparent that ionic polarizability has a tremendous effect on ionic behavior. Of course, the other ionic properties also exert considerable influences. However, the unique physicochemical behavior of the halide
ions (excepting fluoride) can be directly related to their high polarizabilities in most instances.

D. Theories of Pitting Corrosion

Strictly speaking, none of the following are actually theories. In most instances they represent only fragmentary conceptual ideas or models of pitting mechanisms. None of them have sufficient experimental proof to warrant the title of theory. For purposes of organization, several of the subsections below have been created to encompass a particular approach to the problem of pitting attack. That is, they are actually a collection of similar ideas rather than a distinct, formalized theory.

1. Imperfection Theory

In 1920, Seligman and Williams (119) advanced what may be termed the imperfection theory to explain the pitting corrosion of aluminum. The authors stated that pitting attack would occur only if crevices or subsurface cavities were originally present in the metal. The authors detected hydrogen peroxide during the corrosion of aluminum in tap water and also observed that additions of hydrogen peroxide to the tap water increased the corrosion of aluminum. From these results they concluded that an autocatalytic reaction involving hydrogen peroxide occurred within corrosion pits. It was believed that surface imperfections provided starting points for this reaction. The authors recognized that
pitting attack required the presence of chlorides but they did not believe this was of major importance.

From the preceding discussions of anodic and cathodic reactions, it is quite obvious that the autocatalytic mechanism postulated by the authors is not possible. The decomposition of two molecules of hydrogen peroxide yields one molecule of oxygen, whereas the reduction of one oxygen molecule yields only one molecule of hydrogen peroxide. Thus, a self-sustaining chain reaction cannot occur. The importance of microscopic surface fissures as pit sites has been indicated by Wulff, as reported by Uhlig (10). Although surface cracks and imperfections can undoubtedly act as starting points for pitting attack, recent experiments such as electron microscope studies (49) indicate that pits can form independently of surface irregularities.

2. Peptization Theory

The peptization theory of pitting attack was proposed by Evans (120) in 1922. It explains the pitting tendency of the chloride ion on the basis of its peptizing action. Peptization refers to the transformation from a bulk precipitate to a colloid suspension. Halide ions are capable of peptizing many substances, including ferric oxide. For example, if freshly precipitated ferric oxide is shaken with a solution containing chloride ions, a colloidal suspension will result. Evans, assuming that the
passivity of iron was due to a surface oxide layer, proposed that chloride ions could destroy this layer at isolated points by peptizing action and allow attack to occur. The peptization concept was also used to explain the corrosion behavior of zinc in sulfate and chloride solutions. (121). A serious objection to this theory is that it is based on a concept of passivity which has yet to be proven conclusively.

3. Penetration Theory

This is perhaps the best known theory of pitting corrosion. In 1927, Evans (122) suggested that the specific pitting tendency of chloride ions was due to their ability to physically penetrate the protective oxide film on iron. This penetrating ability was attributed to the small size of the chloride ion. The theory was brought into prominence in 1930 by the experiments of Britton and Evans (123, 124). The authors immersed two aluminum electrodes in a 0.001 molar solution of potassium dichromate containing 0.05M of various other salts. A potential difference of 2 volts was applied between the electrodes and the resulting current flow was measured. The magnitude of the currents observed for the various salt additions decreased in the order:

KCl > KBr > KI > KF > K₂SO₄ > KNO₃ > Na₂PO₄.

The authors noted that this series closely paralleled the corrosivity of the salts. That is, the halides, with the
exception of fluoride, are very aggressive corrosives, whereas nitrates and phosphates generally inhibit corrosion. During the test the halide salts (excepting fluoride) produced extensive pitting of the aluminum anode. The authors concluded that the current strengths observed were a direct measure of the abilities of the various anions to penetrate the protective oxide layer on the aluminum anode.

Close scrutiny of the experimental technique of Britton and Evans shows that it is not a critical experiment. That is, the results obtained do not conclusively prove or disprove the concept of ion penetration. The current flow observed undoubtedly represents the metal dissolution rate and not the leakage or penetration of ions through an oxide layer.

The penetration theory was effectively refuted, by the work of Burwell and May (125, 126) in 1945. These investigators measured the permeability characteristics of oxide films isolated from aluminum surfaces. Diffusion and osmosis studies demonstrated that potassium chloride and potassium nitrate solutions penetrated the oxide films at almost identical rates. Also, electrical resistance measurements were performed on the films while immersed in solutions of potassium chloride, potassium sulfate, and magnesium chloride at various concentrations. The resistances of the films were roughly proportional to the
resistances of the solutions in which they were immersed. Thus, Burwell and May concluded that the exceptional corrosive action of the chloride ion is not a result of any special case of penetration of the bulk oxide layer on aluminum surfaces. The most obvious criticism of the penetration theory is that it lacks both experimental evidence and theoretical justification. Apparently, the work of Burwell and May has been overlooked by many investigators, since several recent publications infer that the penetration theory is an established fact.

4. Adsorption Theory

The adsorption theory of pitting came into prominence during the period 1945-47, notably due to the work of Ershler (113), Hickling (114), and Kabanov, Burstein and Frumkin (127). The charging experiments on platinum by Ershler and Hickling have been discussed previously. Kabanov and his associates conducted similar experiments using iron electrodes. In general, the adsorption theory postulates that pitting attack commences because chloride ions displace adsorbed oxygen or prevent it from adsorbing at isolated points on a metal surface. Several of the theories of passivity postulate that a film of adsorbed oxygen protects the metal surface from corrosive attack. Hence, according to the adsorption concept, this protective film is ruptured or prevented from forming by the
preferential adsorption of halide ions. This theory is also supported by adsorption studies on mercury (111) and iron (112) surfaces which have been described previously.

5. Acid Theory

It is important to notice that all of the pitting theories so far described, imperfection, peptization, penetration and adsorption are primarily aimed toward an explanation of the onset of pitting attack. With the exception of the imperfection theory, none of the aforementioned theories detail the mechanism that operates in a growing pit. This is a most serious flaw in these theories. The acid theory of pitting attack was the first theory to describe a complete mechanism for pitting corrosion.

Perhaps the first indication of an acid effect was shown by Friend and Marshall (128) in 1914. These investigators determined the relative corrosivity of various salts toward iron by measuring the amount of inhibitor necessary to prevent attack in solutions of these salts. The inhibitors employed were sodium borate, sodium carbonate, and potassium carbonate. The amounts of inhibitor necessary, or the corrosivities of the various salts decreased in the order:

\[
\text{Cl}^- > \text{I}^- > \text{Br}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{F}^- > \text{SO}_3^{2-} > \text{CO}_3^{2-}
\]

The authors observed that this order corresponded to the
relative strengths of the free acids of these anions.

In 1940, Uhlig (10) postulated that the pitting of stainless steels depended on the high acidity and the high concentration of chloride ions within the pits. He experimentally demonstrated that these conditions destroyed the passivity of stainless steel surfaces. Hence, he believed that pit acidity, together with the presence of chloride ions, enabled corrosion to occur by destroying the passivity of the pit interior.

The acid concept was formalized by Hoar (129) in 1947. He postulated that pitting corrosion is caused by pH changes that occur at anode areas. During corrosive attack in a chloride solution, the chloride ions migrate to anode areas and increase the acidity at these regions. If the pH is low enough the metal will dissolve as a soluble salt instead of precipitating as metal oxide or hydroxide. Such a precipitate would tend to stifle the anodic reactions. It is apparent that this is an autocatalytic mechanism since increasing the acidity at anodic regions increases the rate of anodic dissolution which in turn causes a further increase in acidity. This theory is also capable of explaining the onset of pitting attack as stated by Evans (87):

Imagine a piece of metal placed in a solution of pH value high enough to make the discharge of hydroxide ions the main reaction. If for any
reason, anodic current density is momentarily high at one particular point, it produces conditions increasingly favorable to the formation of soluble product. Thus attack at this point becomes permanently faster than at places where film continues to thicken and protect the metal.

Hoar (129) attributed the extreme corrosivity of the halide ions to the high strengths of their free acids as compared to other anionic species. Thus, halide ions would be expected to produce greater acidity at anodic areas than other anions such as sulfate. On the basis of this theory Hoar (130) predicted that perchlorate ions should be similar to chloride ions in their corrosion tendencies toward iron. To illustrate this, he pointed out that these two anions are very similar in all but two aspects:

The equivalent conductivities of sodium chloride and sodium perchlorate in dilute solutions (0.01M) are almost identical. However, at higher concentrations the conductivity of sodium perchlorate is appreciably less than that of sodium chloride.

Both anions form soluble ferrous and ferric salts.

Both are non-oxidizing toward iron and ferrous ions at ordinary dilutions and temperatures.

Both form strong acids (This is the important property in applications of the acid theory).

The chloride ion is more polarizable than perchlorate ion and hence, has a greater tendency to form aqueous complexes.

To test his predictions, Hoar used the technique of Friend and Marshall (128) to measure the relative
corrosivities of sodium chloride and sodium perchlorate toward iron. Carbonate, nitrate, and chromate ions were used as inhibiting agents. The results demonstrated that the corrosive behavior of chloride and perchlorate ions were identical at concentrations of 0.01M or less. However, at higher concentrations, the chloride ion was observed to be more aggressive than perchlorate ion as shown by the amounts of inhibitor necessary to produce the same degree of protection. This was attributed to two factors. First, the greater conductivity of the concentrated chloride solutions would permit greater current flow. Secondly, at any pH value chloride ions would form a higher ratio of soluble to insoluble corrosion products because of their superior complex-forming tendencies. During these tests, both anions produced pitting attack at certain inhibitor/corrosive ratios. At lower ratios, general attack was observed for both anions.

The acid theory provides a justifiable mechanism for pitting corrosion. Today, it is the most generally accepted theory of pitting attack. It has been used to explain the pitting of aluminum by Porter and Hadden (35), Edeleanu, and Evans (82), Evans (87), and Aziz (131). It has been applied to iron by Evans (87) and to stainless steels by Streicher (14). Although the acid theory has been
frequently used in conjunction with the oxide film theory of passivity, this concept of passivity is not an essential assumption in the acid theory. It is an experimental fact that metallic passivity is destroyed in non-oxidizing, highly acidic environments. Thus, the acid theory is valid no matter which theory of passivity is chosen.

6. **Ion Exchange Theory**

Consideration of the pitting theories discussed thus far indicates that all lack a truly fundamental explanation of the pitting tendencies of the halide ions. As mentioned earlier, the halide ions show unique behaviors in many diverse phenomena other than corrosion phenomena. It is very likely that the pitting tendencies of the halide ions is not a separate and distinct property, but is in some way related to the other unique properties of these ions. Thus, a fundamental explanation of the corrosion behavior of the halide ions should also explain most of the other unique properties of these ions. None of the previously discussed theories of pitting are capable of explaining anything but the pitting tendencies of the halide ions. None can be extended to explain even the symmetric electrochemical effects of the various anions.

Piontelli (90), in 1950, advanced what may be termed the ion exchange theory in an attempt to fundamentally
explain the corrosion behaviors of the various anionic species. Strictly speaking, this theory is not really a theory of pitting attack. It is a general concept of all corrosion and electrochemical phenomena which can be applied to pitting corrosion. Piontelli postulated that the influences of the various anions on electrochemical processes is a result of their catalytic effect on electrode ionic exchange reactions. Consider again typical anode and cathode reactions during corrosion:

at the cathode: \[ \text{Cu}^{2+} + e = \text{Cu}^+ \] (5)

at the anode: \[ \text{Fe} = \text{Fe}^{2+} + 2e \] (10)

According to Piontelli's views, the anions influence the electron transfer rates in these reactions by catalytic action. That is, they affect these reactions without being consumed by them. According to this theory, the catalytic influence of anions is essentially determined by their polarizabilities or deformabilities. (90, 115). Highly polarizable anions, such as the halides, catalyze or accelerate the electrode exchange processes; whereas non-polarizable anions, such as perchlorate or sulfate retard these processes.

According to Piontelli, the anions catalyze electrochemical reactions in several ways. First, anions can enter into the constitution of the metal-solution
interphase. The tendency of an anion to concentrate in regions of high electrical fields depends in particular on low hydration and effective radius and high deformability (115). A deformable anion can thus form a surface film that is very responsive to electric fields. This aspect of the theory is best illustrated by Ershler's (113) explanation of the accelerating influence of chloride ions on the anodic dissolution of platinum. He stated that under the influence of anodic potentials, chloride ions form a surface complex (or adsorbed layer) on platinum surfaces. The resulting platinum-chloride ion bond then weakens the metallic bonding of the surface metal atoms and increases their dissolution tendency. Hence the halide ions can aid anodic electron exchange because of their high polarizability and resulting ease of surface adsorption.

Secondly, deformable anions could catalyze ion exchange by directly participating in the transformation of an active complex during electrochemical reactions (90). This catalytic aspect has also been mentioned by Heyrovsky (102) during his studies on the influence of anions on the electrodeposition of metals. He postulated that the accelerating influence of halide ions is due to their stimulation of the electron transfer between the cathodic electrode and the metal cation in solution. Heyrovsky believed that the
deformable halide ions accomplished this by complexing with the metal cations. The cathodic electron transfer then occurred through the polarized halide ion. Thus, the polarized halide ion acts as a bridge between the cathodic electrode and the metal ion. This explanation is very similar to Libby's bridge theory of homogeneous ion exchange as discussed by Grahame (109). Again, the halide ions accelerate ion exchange by virtue of their high polarizabilities and resulting complexing tendencies.

Finally, anions can influence electrochemical reactions by their effect on the surface state of an electrode. The deformable anions preferentially adsorbed, may either prevent the eventual inhibition of other ions, oxygen, water or hydrogen, or also destroy the already existing films of this nature (132).

Thus, the ion exchange theory proposes a direct relation between anionic polarizability and corrosive tendencies. Highly polarizable anions such as chloride and bromide show pronounced corrosivities towards most metals, whereas weakly polarizable anions such as sulfate and perchlorate tend to retard electrochemical reactions. Perchlorate, the least polarizable of all anions would be expected to show the least catalytic influence on electrochemical processes. This prediction is supported by the
polarization studies of Piontelli and Poli (116, 117) which demonstrated that the perchlorate ion produced the highest anodic and cathodic overvoltages in most metal/metal ion systems. However, the acid theory together with corrosion studies by Hoar (130) indicate that the perchlorate ion is a very aggressive corrosive. Thus, the acid theory and the ion exchange theory are diametrically opposed as to the corrosion tendency of the perchlorate ion. The validity of these two theories depends on the correctness of their predictions regarding perchlorate ion. Both theories have valid experimental support.

Summarizing, the ion exchange theory presents a fundamental explanation of the corrosion behaviors of anionic species. In essence, this theory is an application of modern physicochemical concepts to electrode processes. Because of this, it possesses considerable theoretical verification. The distinct advantage of this theory is that it offers a qualitative correlation between the various unique properties of the halide ions. A serious criticism of this theory, especially when applied to pitting corrosion, is its lack of experimental evidence. That is, the importance and extent of anionic catalytic action on the various electrode processes is unknown. Also, the theory, because of its generalized nature, does not detail the mechanisms that operate during pitting attack.
7. Other Minor Theories and Concepts

a. Magnetic Theory

Studies of the pitting of iron and steel by water led Ackerman (40) to the conclusion that the localized attack observed occurred at magnetic poles on the metal surface. These magnetic poles were believed to be induced in ferrite patches by the earth's magnetic field. The author failed to explain how or why such magnetic poles demonstrate localized attack. Although Ackerman's concept of pitting corrosion seems rather dubious, it does suggest several interesting ideas in regard to the pitting of non-magnetic ferrous alloys such as the austenitic stainless steels. Ferrous and ferric salts are strongly paramagnetic. That is, they are strongly attracted by magnetic fields. Hence, the ferrous salt corrosion products produced during exposure to a pitting corrosive would be expected to accumulate at any magnetically permeable areas on an austenitic stainless steel surface and thus, promote pitting at these points. This may be a possible explanation of the lower pitting resistances of ferrite-containing stainless alloys. Also, the high current densities at pit sites might produce local magnetic fields that would influence the distribution of the insoluble, magnetic oxides of iron. Thus, the corrosion rings may be related to a local magnetic field surrounding pit sites. The possible
influence of magnetic fields on pitting corrosion deserves further investigation.

b. Screening Effects

Excepting the adsorption and ion exchange theories, all of the theories of pitting corrosion overlook a very important aspect, namely the stability of a growing corrosion pit. Considering a corrosion pit, one wonders how they maintain their activity in the presence of powerful passivating agents. That is, pits are observed to grow in the presence of dissolved oxygen, oxidizing metal ions such as ferric and cupric ions, and inhibiting anions such as chromate, nitrate, and carbonate. This question is especially applicable to newly formed pits which demonstrate a very small depression in the metal surface and hence, present no major obstacles to diffusion or ion migration. As discussed previously, new pits often become inactive undoubtedly because passivating species in the corrosive have entered the pit interiors. However, the fact that pits remain active in the presence of passivating agents suggests that some sort of screening mechanism must be operative within a pit. This screening effect prevents the passivating agents from contacting the anode surface within a pit.

(1) Chemical Screening

During the pitting of copper by dilute
chloride solutions, May (36) proposed that oxygen diffusion into a growing pit is retarded by a chemical screening reaction. That is, the cuprous ions released at the pit anode diffuse outward rapidly and react with dissolved oxygen to form cupric oxide. Thus, the pit corrosion product reacts with and screens oxygen from the pit interior. Colgate (133) has utilized a similar screening mechanism to explain oxygen screening at pit sites on stainless steels. According to his mechanism, ferrous ions within corrosion pits react with oxygen and prevent it from repassivating the pit anode. Although these mechanisms are convincing and may contribute to the stability of corrosion pits, they are applicable only in a limited number of cases. These mechanisms only explain oxygen screening, and only for metals which release reducing cations as anodic corrosion products. Thus, they do not explain the screening of other passivating species, and likewise cannot be applied to the pitting of aluminum, zinc or nickel.

(2) **Physical Screening**

Standifer (46) has stated that the high concentration of corrosion products at the base of a pit greatly reduces the solubility of oxygen and therefore prevents or retards the diffusion of oxygen to the anode area. Chloride and bromide salts, because of their great solubilities, can reduce oxygen solubility tremendously
Hence, the halides are probably superior to the other anions in their oxygen solubility screening effects. Again, this screening concept can only apply to oxygen screening; it does not explain the screening of ionic species. However, unlike the chemical screening effects, it can be applied to the pitting corrosion of most metals and alloys.

o. **Initiation and Growth Concept**

The concept of initiation and growth during pitting corrosion was introduced by Aziz and Goddard (136) in 1952. The authors stated:

> Experience in this laboratory has suggested the conclusion that pitting should be divided into two separate steps—initiation and propagation. In the opinion of the authors the factors affecting the propagation of a pit are different from those that led to its initiation. A pit can be started by artificial stimulation at an otherwise normal site on the metal surface, yet continue to propagate if given the right environmental conditions.

In 1953, Aziz (131) extended this concept to include three distinct stages—initiation, propagation (or growth) and termination. As mentioned before, corrosion pits, especially those on aluminum surfaces, frequently become inactive after a short period. Aziz's termination stage refers to this phenomenon. Recently, Streicher (14) has also stated that the pitting of stainless steels is divided into distinct initiation and growth steps.
Pit initiation is a most curious technical term. It has never been defined in the literature. True, a pit does start at some point; however, this fact surely does not constitute a definition of an initiation step. If pitting involves two (or more) distinct steps, it must be possible to characterize and separate these steps. Likewise, it must be possible to state the point at which the initiation step ceases and the growth step begins or assumes major importance. If this is not possible, then it is meaningless to discuss pitting in terms of distinct initiation and growth steps. None of the proponents of the initiation and growth concept have even attempted to explain the term pit initiation.

The vague concept of distinguishable initiation and growth steps presents two very real threats to the understanding of pitting corrosion. First, the concept implies a mechanism that may or may not be operative during pitting. There is no experimental evidence to show that pitting is a two-step process. Admittedly, it is quite permissible to divide pitting into any number of purely arbitrary steps. Indeed, May (36) has done this in his discussion of the pitting attack of copper. However, it is very important to realize that the arbitrary division of a process into various stages, is quite different from the actual existence of separate and distinct stages in this process.
Secondly, pit initiation because of its vagueness, can easily become a "theoretical scapegoat." That is, any anomalies or unexplained phenomena in the pitting process can be readily attributed to pit initiation. This practice is already occurring in the current literature.

There is a pressing urgency to either define pit initiation or remove this term from our terminology. In its present form, pit initiation is a very confusing and dangerous term.

3. Study Methods

The study of pitting corrosion is inherently very difficult. The randomness, localization, small size, and varying activities of the corroding areas during pitting attack constitute the inherent difficulty in studying this mode of attack. Perhaps the greatest obstacle to the understanding of pitting corrosion is the difficulty in devising suitable techniques and methods to measure and observe this phenomenon. The following subdivisions describe the various methods that have been used to study pitting corrosion and related phenomena.

1. Visual Observations

The visual observation of the pitting process and pitted metal surfaces has yielded much useful information about the loci and forms of pits and the distribution of corrosion products during pitting attack. The use of
electron microscopy (49) and radiographic techniques (48) has greatly increased the scope of "visual" observations. The major disadvantage of these types of observations is their qualitative nature. It is very difficult to compare or correlate such observations. However, the importance of visual studies should not be underestimated. The auto-catalytic nature of pitting was proposed strictly on the basis of observations made with the naked eye (86).

2. Quantitative Measures of Attack

The study of pitting corrosion is hampered by the difficulty in choosing a suitable way of quantitatively measuring the corrosive attack. Fontana (137, 138) has stated that weight loss determinations and calculated overall corrosion rates do not reflect the localized character of pitting corrosion, and hence, are practically useless for comparison purposes. However, for a given corrosive, weight loss measurements can sometimes be used as a rough estimation of pitting attack. Liebhafsky and Newkirk (71) have used this method fairly successfully during an investigation of the pitting corrosion of stainless steels in ferric chloride. Smith (137) devised a pitting resistance test for stainless steels based on weight loss determinations in a hot, circulating ferric chloride solution. Although the results were reproducible, they cannot be used to predict pitting resistances in solutions other than the test solution for the reasons stated above.
The preferential pitting of specimen edges introduces serious errors into weight loss measurements. Thus, different specimens of the same material often show markedly different weight losses because of edge area differences (18). From a fundamental standpoint, the greatest drawback to weight loss determinations is that they only indicate total pitting attack and cannot be used to study the progress of isolated pits. Thus, individual pit activities are hidden in the overall weight loss measurements.

The depth of pitting has also been used to quantitatively measure and correlate the intensity of pitting corrosion. Both average and maximum pit depths have been utilized for this purpose. As discussed previously, corrosion pits vary widely in intensity, and hence, in depth. For this reason, average pit depth is not a desirable way to measure or compare pitting tendencies. Specimens having identical average pit depths could have widely varying maximum pit depths. At first glance it seems that the measurement of the maximum rather than the average pit depth would be a more desirable measure of pitting corrosion. However, Evans (140) has indicated that the magnitude of the maximum pit depth is meaningless unless the size of the exposed area is also considered. This is due to the fact that as specimen area is increased, the probability of exceeding any given pit depth increases.
Hence, maximum pit depth is a function of specimen size. Evans also stated that another feature of maximum pit depth is that the value obtained will, in general, be different on identical specimens. Thus, schemes for evaluating pitting corrosion based on pit depth measurements, such as proposed by Henke (141), are almost valueless. However, by applying extreme-value statistics to maximum pit depth measurements, Aziz (77) and Eldrege (78) have shown that it is possible to make a quantitative evaluation of pitting intensity.

3. Potential Studies

The time-potential behavior of a metal in a corrosive electrolyte has been used extensively in the study of corrosion phenomena by investigators too numerous to mention. In fact, Gatty and Spooner (80) have devoted an entire book to this subject. It should be observed that the potential of a corroding metal only yields one piece of information, namely, the corrosion potential of the anodic and cathodic reactions occurring on the metal surface. Therefore, the usefulness of such measurements is dependent on how much is known about the anodic and cathodic reactions that are occurring. Although early workers placed much faith in potential measurements, it is generally agreed today that measurements of this sort have little inherent value by themselves. In fact, Mears and Brown (142) have
shown that potential measurements can be very misleading. For example, it is usually considered that if the solution potential of a metal shifts in an anodic direction it indicates an increased corrosion tendency. Likewise a shift in the cathodic direction is usually assumed to indicate an increased resistance to attack. However, the potential of stainless steel immersed in a sodium chloride solution becomes more cathodic upon the addition of ferric chloride. Thus, ferric chloride appears to be an inhibitor on the basis of potential measurements. Potential measurements during pitting attack can often be very misleading.

Mears and Brown (142) and Standifer (46) have shown that potential measurements are relatively insensitive to the onset and growth of pits on a metal surface. This can be attributed to the small size of pits relative to the total area of a specimen.

The micro-solution potential technique developed by Smith and Pingel (143) and used by Standifer (46) might prove useful in pitting studies. These workers measured the solution potentials of small areas on metal surfaces by coating the metal with an insulating plastic and then exposing an area by means of a microhardness indenter. This technique is applicable to grain boundaries and inclusions.
Fenwick (144) devised a potential-break method for estimating the resistance of various steels and stainless steels to chlorides. He measured the potential of a specimen immersed in distilled water or a dilute dichromate solution as hydrochloric acid was added to it. At a certain concentration of hydrochloric acid, the potential of the specimens rapidly shifted in an anodic direction. The amount of hydrochloric acid to produce this potential-break was used as a relative measure of resistance. This method is open to the same criticisms as potential-time studies. Primarily, it lacks interpretation.

4. **Impressed Current Studies**

Impressed current techniques have also been extensively employed in corrosion studies. Piontelli's concepts of the influence of anions in corrosion reactions is largely based on carefully controlled, impressed current polarization studies (90, 115, 116, 117). In the realm of pitting corrosion, perhaps the best known impressed current technique is the break-through potential test developed by Brennert (145) and later used by Mahla and Neilson (21) to evaluate and study the resistance of stainless steels to pitting corrosives. Simply, this test is performed by impressing a continuously increasing potential between a stainless steel anode and an inert cathode and measuring the current flow and the solution potential of the stainless
electrode. As the impressed potential is increased the current flow and the solution potential increase. Finally, a point is reached at which there is a sudden increase in current accompanied by a sudden drop in the solution potential of the stainless steel anode. The solution potential at which this abrupt change occurs is termed the break-through potential and is believed to be the result of the rupture of the passive film at localized points on the surface. Thus, the break-through potential is assumed to be a relative measure of corrosion resistance. Mahla and Nielsen demonstrated that there was a fair correlation between the results of this test and immersion tests in ferric chloride and bromide solutions. However, the results of this test lack fundamental significance. Uhlig (146) has shown that the measured break-through potentials are related to the decomposition potentials of the electrolytes employed in the test. Aziz (147) has criticized this technique because of the complexities introduced, and also the author's contention that the break-through potential is a measure of surface film rupture.

Recently, Streicher (14) has modified the break-through potential test and has developed, what he terms, a pit initiation test. In this test, an increasing potential is applied between a standard size stainless steel anode and a platinum cathode immersed in a pitting electrolyte. The
potential difference is increased to 2 volts and held at this value for 5 minutes. Then the number of pits appearing on the stainless steel specimen is counted. According to the author, the number of pits observed is a measure of the pit initiation tendency of the stainless steel specimen. Streicher stated that there is a direct correlation between the results of the pit initiation test and the results of immersion tests in ferric bromide, ferric chloride, and sea water. However, it is almost impossible to determine the significance of the results obtained by this testing technique. The author does not define pit initiation. In fact, several completely different meanings are implied in the paper. The test in no way duplicates conditions that are present during actual pitting. During the test, vigorous gas evolution (discharged halogens and oxygen) occurs on the stainless steel specimen. That there is correlation between the test and actual pitting tendency is very questionable. Pickled specimens of Type 304 and 316 stainless steel developed nearly the same number of pits during the test. In order to show any appreciable difference between these two stainless steels, Streicher found that it was necessary to pre-expose the specimens to a solution of nitric acid and potassium dichromate. Also, from the data the author presents, it appears that Type 316 stainless steel would show less resistance than Type 304 if the test utilized a lower value of current density. It is
very doubtful if the pit initiation test offers any improvement over the break-through potential test. Purely on the basis of the complexities introduced, the break-through potential test is the more desirable of the two.

As already mentioned, Uhlig (10) and Pryor (37) have also used impressed currents for ion migration and pH studies in divided cells. An evaluation of the divided cell technique is presented under Ion Migration.

Like potential-time measurements, the value of impressed current studies is dependent on a knowledge of the electrochemical reactions involved. Mears and Brown (142) point out that impressed current polarization curves may be misleading because of the existence of local cells on the electrode surfaces. Thus, polarization curves determined by impressed currents only rarely reflect the electrochemical characteristics of an actual corroding system. In duplicating corrosion reactions by impressed current techniques, it is very important to carefully choose the current density or current density range to be used. If this is not done carefully, erroneous results may be obtained. For example, Lal and Thirsk (148) during anodic polarization studies of copper in chloride solutions found that the effect of dissolved oxygen on the polarization measurements depended on the magnitude of the impressed currents employed. Impressed currents greater or less than
those occurring during corrosion can induce electrochemical reactions that are foreign to the actual corrosion process.

It is important to realize that impressed current studies are immensely valuable if they are carefully controlled and properly interpreted.

5. Artificial Pits

Instead of attempting to observe and measure the pitting of a metal surface with all the inherent difficulties that this entails, an artificial cell that closely duplicates the conditions during actual pitting can be constructed and operated. This artificial cell or pit permits a closer control of, and allows a more precise observation of the pitting process than any other study technique. Mears and Brown have made extensive use of artificial pits in studies of the pitting corrosion of iron, stainless steel, magnesium, and aluminum. Their first artificial pits were fabricated from actual pits on aluminum surfaces (149). This was accomplished by exposing two aluminum panels to a pitting environment until distinct pits appeared. Then one panel was completely coated with wax except for the pitted areas, while the other panel was coated on the back, edges, and over the pitted areas of the front face. These were then coupled and replaced in the solution and current flow was measured. Artificial pits utilizing the "scratch" technique (described under
Electrochemical Control During Pitting) were also used by these investigators (69, 70, 149). In a later investigation, Brown and Mears (150) developed still another artificial pit technique. The pits on an aluminum sheet were removed by making a circular cut around them. Then they were replaced in their original positions and insulated from the sheet by beeswax. Electrical connections were made to the pits and the sheet and then the assembly was immersed in an electrolyte. The current flow between the pits and the sheet were then measured by means of a zero-resistance ammeter. All of the artificial pits used by Mears and Brown were self-starting and self-sustaining. That is, upon introduction into the pitting corrosive, the artificial pits began to generate their own current.

Parsons, Cudd, and Lochte (85) have also used an artificial pit in an investigation of the pitting of iron. Their pit consisted of a fine iron wire sealed into the bottom of a glass tube. This wire was connected, by means of an insulated lead, to a spiral of copper wire at the open end of the glass tube. This entire assembly was then vertically immersed in a pitting corrosive with the open end of the tube upward. As discussed under Ion Migration, these cells were self-starting and self-sustaining and permitted the analysis of the pit contents. It should be noted that these artificial pits are actually galvanic
calls with an iron anode and a copper cathode, and hence, only qualitatively duplicate the actual conditions during pitting. Evans and Davies (151) employed an artificial pit of zinc to demonstrate that corrosion currents flow even in high resistance electrolytes such as distilled water. Their pit consisted of a piece of insulating plastic 0.5 cm. thick sandwiched between two sheets of zinc. A 1.5 mm. hole passed through the upper zinc sheet and through the plastic to the lower sheet. The external surface of the bottom sheet and the electrical connections to the two sheets were coated with insulating material. Thus, the pit consisted of a horizontal zinc cathode with a small zinc anode lying at the bottom of a hole through the cathode electrode. In appearance, it closely resembled an actual corrosion pit. The pits were not self-starting in distilled water. However, they could be started by an impressed current after which they became self-sustaining.

Recently May (36) utilized an artificial pit technique for studying the pitting corrosion of copper in dilute salt solutions. His pits were constructed of two electrodes, a freely exposed copper cathode and a copper anode contained in a small, open glass compartment. The anode compartment was packed with a mixture having the same or similar analysis as the contents of actual corrosion pits. In operation, these two electrodes were short-circuited and
immersed in the corrosive medium. Although many of these pits were self-starting others required stimulation by impressed currents before they would start.

There are several criticisms of the artificial pit technique. First, most of the artificial pit designs that have been used are not geometrically similar to actual corrosion pits. The notable exceptions are the "out-out" pits used by Brown and Mears (150) and the pit employed by Evans and Davies (151). As shown by Agar and Hoar (152) and Waber (153) the size and shape of an electrolytic cell influences its polarization characteristics. Thus, to obtain quantitative results from an artificial pit it is necessary that it be geometrically identical to an actual pit. Secondly, local action on the anode electrode of an artificial pit will not be detected during the measurement of current flow between the anode and cathode electrodes. Thus, if this local action is large enough, it could introduce misleading results. This point has been mentioned by Fink (154). Finally, the fact that the artificial pit method only measures the behavior of a single pit, is both desirable and undesirable. It is desirable because it isolates a pit and eliminates interference from other pits. However, because of the random behavior of corrosion pits, an artificial pit cannot be considered representative of all the corrosion pits that occur on a metal surface. Many
artificial pits would have to be constructed and studied before any generalized conclusions concerning overall pitting behavior could be made. Thus, artificial pits are most applicable to micro rather than macro effects.

If constructed and used properly, artificial pits offer an unique means of studying pitting attack. They permit the direct measurement of the actual anodic and cathodic polarization curves that exist during pitting attack. They also permit the continuous measurement of pit corrosion rate. It is interesting to note that one of the verifications of the electrochemical theory of corrosion was accomplished by the use of an artificial pit technique (149).

6. Indicator Studies

Chemical indicators have been used in a variety of corrosion studies to indicate the onset of corrosion and the distribution of the electrochemical reactions occurring on a corroding metal surface. Ferroxylin indicator is the indicator most frequently used to observe anodic and cathodic areas on iron and ferrous alloy surfaces. Although many present day investigators (46, 155, 156) uphold the results obtained with ferroxylin indicator, Bengough and Stuart (157) directed some important and still unanswered criticisms against the ferroxylin technique as early as 1922. These authors stated that results obtained with ferroxylin indicator have little practical or theoretical value.
because of the artificial conditions imposed by the agar gel body of the indicator. They stated that the presence of this gel would interfere with the diffusion of oxygen and metal ions and also alter the formation, precipitation and distribution of normal surface films. The authors observed an anomalous behavior when a modified ferroxyl indicator was applied to copper and brass. No anodic or cathodic areas became visible. Indeed, the validity of the ferroxyl test deserves further study. Alternative indicator compositions might be developed.

The availability of radioactive isotopes in recent years has permitted the extensive development of a new and powerful research method— the radiotracer technique. By utilizing radioactive ions, atoms and molecules, it is possible to follow and observe reactions and phenomena heretofore considered impossible. The sensitivity of radiotracer techniques approaches the fantastic. It is possible to measure as little as $10^{-20}$ gram of matter by these techniques. These techniques offer almost unlimited possibilities for the study of corrosion and surface phenomena.

As mentioned previously, radioactive tracers have been used by Aziz (81) to determine the distribution of electrochemical reactions during the pitting of aluminum. Simnad and Ruder (159) have also used this technique to study the
local action on 18-8 stainless steel surfaces. This method is based on the principle that Co$^{60}$, or other heavy metal radioisotopes, are deposited at cathodic areas by electrolytic action. However, recently Foley, Stark, and Guare (159) have stated that there are three processes by which Co$^{60}$ ions can become associated with metal surfaces: 1) exchange between surface metal atoms and Co$^{60}$ ions in solution; 2) adsorption; 3) electrolytic deposition. Thus, electrodeposition is not the only mechanism by which radiotracers can be deposited on a metal surface. Although these complicating factors do exist, the results of Aziz's studies can be assumed to be at least qualitatively correct. That is, the very heavy deposit of Co$^{60}$ surrounding pit sites is undoubtedly the result of electrodeposition rather than sorption or ion exchange. However, the slight pick-up of the radiotracer on the remainder of the surface may have been due to any one or all three of the processes cited above. Thus, Aziz's conclusion that the bulk surface of the metal is cathodic is open to question. The recent development of high resolution autoradiographic techniques (160, 161, 162, 163) could further extend the usefulness and precision of this indicating technique.

Radiotracers have also been used in other studies that are directly related to various aspects of pitting corrosion. Simnad (164) has prepared an excellent summary of these studies.
IV. APPARATUS AND PROCEDURE

A. Artificial Pit Apparatus

Most of the experimental work performed during this investigation utilized an artificial pit apparatus. The methods used in other minor experiments are described under RESULTS AND DISCUSSION.

1. Artificial Pit Specimen
   a. Description

   The artificial pit specimen is illustrated in Figs. 1 and 2. It consisted of two electrically insulated electrodes mounted in cold-setting plastic. The cathode was a thin sheet of stainless steel alloy, 1 inch square, set in the surface of the plastic mount. A fine wire anode of the same material passed through a small hole in the center of the cathode sheet. The plastic mounting material surrounded this wire and prevented electrical contact with the sheet. Electrical connections to the two electrodes were affected by soldered, plastic coated wires that entered through the base of the specimen. The artificial pit specimen was approximately 1.5 inches in diameter and 0.5 inch thick. Anode wires varying between 5 and 31 mils in diameter were employed in pit construction. The separation between the two electrodes varied between 0.003 and 0.010
inch maximum for all the standard specimens prepared for this investigation. The majority of the specimens had anode-cathode separations of approximately 0.005 inch. In comparison to other artificial pit designs, the artificial pit specimen described above is unique in its similarity to actual corrosion pits. The high cathode/anode area ratio, the planar placement of the electrodes and the small electrode separation lend to this similarity. Also, it is apparent that as dissolution of anode wire proceeds, a depression or pit will be formed. Thus, the behavior of this artificial pit is very similar to the growth of an actual pit.

Several specially modified artificial pit specimens were constructed. The first was a double artificial pit. That is, this specimen contained two anode wires that penetrated the cathode sheet. This type of specimen was specifically designed for the study of interaction effects between pit sites. The double artificial pit specimens had anode-anode separations of 0.038, 0.071, and 0.165 inch, center to center, on 0.020 inch anode wires. To study the effect of anode-cathode separation on specimen behavior, several pits were prepared with very large electrode separations. The largest separation was 0.120 inch which was achieved by passing a 0.020 inch anode wire through a 0.25 inch hole in the cathode sheet.
b. **Preparation**

The cathode electrode was prepared from stainless steel sheet of approximately 0.010 inch thickness or less. It was cut to size and the center hole was pierced by means of a needle or sharp center punch. The protruding burr removed by grinding with emery paper. The anode wire was centered in the hole by means of a microscopic manipulator and held in place by a drop of collodion solution. Then the wire was trimmed off close to the ground surface and 1 inch was left protruding from the other side of the sheet. Next, a lead wire was soldered to the cathode sheet.

A greased ointment tin 1.5 inches in diameter and 0.5 inch deep served as a mold for the pit specimen. The cold-setting plastic mixture consisted of 5 parts by volume of Epon 823 resin together with 1 part by volume of Epon Resin Curing Agent U. Both of these materials were obtained from the Shell Chemical Corporation, New York. The cathode sheet with the attached anode wire and cathode lead was placed, ground surface downward into the ointment tin mold and the tin half filled with the plastic mixture. After the plastic had hardened (4 to 6 hours) a lead was soldered to the anode wire, and the mold was filled to the top with plastic mixture. The mold was then stripped away from the hardened plastic specimen and the projecting anode wire was ground level with the cathode electrode. Before use, the
artificial pit specimen was ground with 400 grit emery paper, scrubbed with soap and water, rinsed in distilled water, and dried.

2. Test Cell

a. Description

The test cell and its component parts are illustrated in Figs. 3, 4, and 5. By this arrangement the environmental conditions during test runs were carefully controlled. Fig. 3 is the test assembly. This assembly fitted into a wide-mouth, 1000 ml. flask as shown in Fig. 4. The artificial pit specimen rested on the Teflon support and was completely immersed in the corrosive solution. A close-up view of the specimen and support is shown in Fig. 5. The atmosphere and dissolved gas in the solution were controlled by continuously admitting the desired gas through the gas inlet tube. Electrical connection between the artificial pit specimen and external measuring circuits was made through the stopper. Although not shown in these illustrations, an additional glass tube, passing through the stopper to the specimen support, was used to contain a salt bridge during polarization studies. The glass and Teflon construction of the test cell together with the plastic coated specimen leads prevented contamination of the corrosive solution.
b. Operation

In this study, the following standardized operating conditions were maintained in the test cell. 400 ml. of electrolyte were used in every test run. With the artificial pit specimen resting on the specimen support, the two electrodes were approximately 0.5 inch below the surface of the electrolyte. During all tests, except those so noted, the corrosive was continuously saturated with oxygen entering the inlet tube at 0.5 liter/minute. All tests were conducted at an ambient temperature of 80° ± 2°F.

3. Electrical Circuit

a. Description

The electrical circuit used in the artificial pit studies is schematically illustrated in Fig. 6. The actual circuit consisted of four circuits identical to Fig. 6 with a switching arrangement for connecting the pH meter and the potentiometer into any one of them. This arrangement was constructed to permit electrical measurements of more than one artificial pit. It also permitted the measurement of double, triple or quadruple pit specimens. The upper portion of Fig. 6 illustrates the circuit for controlling impressed current. The current was supplied from a 150 ohm, 25 watt bleeder resistor across a 6 volt storage cell. The bleeder resistor insured a steady supply by reducing transient polarization effects in the storage
cell. The impressed current was controlled by voltage dividing across variable resistors. This was done to reduce the total resistance in the measuring circuit. The potential across the artificial pit specimen was measured by a potentiometer. Current flow through the pit specimen was measured by the voltage drop across a precision 3000 ohm resistor accurate to ±1 percent. The potentiometer circuit included a Rubicon Type B High Precision Potentiometer together with an Eppley low temperature coefficient standard reference cell. Potential balance was indicated by a Rubicon Spotlight Galvanometer with a sensitivity of 5.7 microvolts/mm, and an internal resistance of 24 ohms. This potentiometer circuit was capable of measuring potentials with an accuracy of 0.01 percent. The solution potentials of the artificial pit electrode were measured by a Model G Beckman pH Meter in conjunction with a saturated calomel electrode. With this arrangement it was possible to measure electrode potentials within 5 millivolts or less. The maximum current flow to or from the pH meter during electrode potential measurements was $5 \times 10^{-13}$ amperes. Contact between the calomel electrode and the artificial pit specimen was made by means of a string soaked in saturated potassium chloride solution. The string bridge, together with an intermediate vessel containing saturated
potassium chloride solution, prevented contamination of the calomel electrode by the corrosive electrolyte.

b. Operation

(1) Impressed Current Studies

The electrical circuit permitted the study of impressed current polarization behavior. This was accomplished by connecting the potentiometer across the precision resistor and adjusting the current controls until the desired current intensity was achieved. The electrode potentials of the anode and cathode electrodes could be measured by coupling the pH meter to either of these electrodes. Also, the potential across the artificial pit could be determined by setting the potentiometer switch to the potential position.

(2) Short Circuit Current Measurement

The electrical circuit could also function as a zero-resistance ammeter when used with self-sustaining artificial pits. To make short circuit current measurements the potentiometer was set to a potential value of zero and was connected across the artificial pit specimen. The current controls were then adjusted until the potential across the pit specimen was equal to zero. Then the potentiometer was switched across the precision resistor and the short circuit current measured. It is important to note that even though an external current was impressed
during these measurements, the measured current value was the true short circuit current. This zero-resistance ammeter circuit is similar to that used by Brown and Years (149) and Godard (165).

(3) Polarization Studies

The circuit also permitted the determination of the actual anodic and cathodic polarization behavior of a self-sustaining artificial pit. The corrosion potential or apex of the polarization diagram was obtained by determining the short-circuit current of an artificial pit and measuring the anode and cathode electrode potentials under this condition. Additional points on the anodic and cathodic polarization curves were obtained by allowing finite potential differences to exist across the artificial pit and measuring the electrode potentials and current intensities under these conditions. Open circuit electrode potential measurements were made by disconnecting the pit specimen from the external current source. Polarization curves determined in this manner indicate the actual polarization behavior of the electrodes during corrosion.

B. Materials

The materials used in this investigation are listed in Table XI. The stainless steel wire was obtained from the Wilbur B. Driver Company, Newark, New Jersey. The Type 304 stainless steel sheet was purchased from the Alloy Metal
Wire Company, Prospect Park, Pennsylvania. The metallurgical history of these materials was not available. It is believed that they were all in the solution quenched condition. The majority of the artificial pit specimens were constructed from the stainless sheet and wire in the as-received condition. Several specimens were prepared from sheet and wire after solution quenching from 2050°F.

All of the electrolytes investigated were prepared from reagent grade chemicals and double distilled water. Exceptions to this were ferric bromide and ferric perchlorate. These compounds were prepared in the laboratory by adding sodium hydroxide to a solution of ferric chloride. The resulting precipitate of ferric hydroxide was carefully washed several dozen times with double distilled water by decantation. After washing, the precipitate was dissolved in an appropriate quantity of hydrobromic or perchloric acid and the resulting solution was diluted with distilled water to the desired concentration. The final concentrations of both solutions were somewhat inaccurate since some of the ferric hydroxide always failed to dissolve in the acid solutions.
V. RESULTS AND DISCUSSION

A. Artificial Pit Experiments

1. Introduction

Most of the experiments with artificial pits were directed toward the pitting attack of Type 304 stainless steel in ferric chloride solutions. Ferric chloride was also used as a basis for comparing the pitting corrosivities of other media. The oxidizing metal halides have the distinct advantage of producing rapid and intense pitting attack. Such corrosives produce high corrosion current intensities and are readily studied by the artificial pit technique. All of the following figures and reported results refer to Type 304 stainless steel, except where noted otherwise.

At the beginning of this investigation it was decided to make all tests at a constant pH value. pH of 2.0 was arbitrarily chosen and many of the solutions studied contained acid additions to increase their acidity to this value. However, it was observed that the acidity of the test solutions changed rapidly with time. Also, the pH of a given solution varied from batch to batch. Because of these difficulties and also the fact that the pitting behavior of the solutions changed only slightly with age or
pH value, pH control was stopped midway in the investigation. No further acid additions were made to any of the test solutions except the ferric chloride solutions which contained 0.05 N hydrochloric acid to prevent decomposition. The pH values of all the electrolytes investigated varied between 1.5 and 2.5.

2. Pit Growth Studies
   a. Open Circuit Behavior

   The open circuit potential differences of Type 304 stainless steel pit specimens were measured in solutions of ferric bromide, ferric chloride, ferric perchlorate, ferric sulfate, sodium bromide, sodium chloride and sodium nitrate. In every instance, the wire always became anodic after the passage of sufficient time. These open circuit potential differences were not reproducible for a given specimen and solution. Also, no trends or correlations were found between the observed potential differences and the solutions under study.

   The anodic behavior of the wire electrode is an example of the area/perimeter ratio effect. This was first observed by François and coworkers (166) during the corrosion of stainless steels by ferric chloride. They found that a 18-8 stainless steel panel with a wax grid painted on its surface coupled to a similar bare panel in ferric chloride solution always became anodic. The attack on the
waxed panel was concentrated along the waxed lines. Current flow between the panels was found to be proportional to the relative area/ perimeter ratio of the waxed panel. This effect is undoubtedly a crevice effect. The wax-metal interface provides an ideal site for crevice corrosion. Hence, an area with a large edge length will contain a greater proportion of anodic sites than an identical area with a shorter edge length. Considering an artificial pit, it is apparent that the wire has a very low area/ perimeter ratio compared to the sheet and, therefore, is more anodic.

b. Pit Activation

The Type 304 stainless steel pit specimens used in this investigation were not always self-starting. Thus, when they were short-circuited through the zero-resistance ammeter circuit and immersed in a pitting corrosive, they did not always become self-sustaining. Several techniques were used to activate the inert specimens. The most common method was the application of an impressed current (wire anodic) through the specimen. Currents between 10 and 60 microamperes were applied for periods up to 5 minutes after which the pits usually became self-sustaining and generated their own current. It was found that high impressed current values were not as effective as low currents in activating pits. The higher currents often retarded pit activation. Inactive pits were often activated by opening
the circuit between the electrodes and leaving them in the corrosive until an appreciable potential difference developed between the two electrodes. More violent measures were used to activate pit specimens which were not stimulated by the above methods. One technique consisted of placing a drop of concentrated hydrochloric acid on the anode wire while the specimen was immersed in the corrosive. Also, inactive pits could often be activated by starting them in a very severe pitting corrosive, such as concentrated ferric chloride, and then transferring them to the solution under study. This is the transfer technique which is described in a later section.

The artificial pit specimens showed very erratic activation tendencies. Some became active immediately after immersion, whereas several remained inactive even after the anode wire had been almost entirely dissolved away by various stimulation attempts. Also, a given specimen usually showed a variable activation behavior in identical experiments. In general, previously used specimens were more readily activated than unused specimens. Also, the ease of activation increased with increasing ferric chloride concentration.

It should be noted that although a pit specimen was considered inactive, a current flow was usually observed. This current flow was very small, usually 0.1 microampere
or less. Such current flows were observed even for specimens immersed in non-pitting electrolytes such as ferric sulfate and sodium nitrate. These small currents are a result of the area/perimeter effect between the wire and the sheet. Thus, during artificial pit studies the area/perimeter ratio effect tends to exaggerate the pitting tendencies of the solutions under study.

**c. Pit Growth Characteristics**

The growth of a Type 304 stainless steel pit specimen in 0.1 molar ferric chloride is shown in Fig. 7. The current shown is the self-generated short circuit current and is directly related to the corrosion rate of the anode electrode. Pit growth is characterized by a very erratic corrosion or growth rate during the early stages of pit development. Many of the artificial pit specimens tested suddenly lost their activity during the first few minutes of growth. This initial instability of corrosion pits has been observed by other investigators (36, 71, 77), and is an indication of the autocatalytic nature of the pit anode. The stability of the pits increased with time and the loss of pit activity during the later growth stages was only rarely observed.

Pit growth is also characterized by a rapid increase of corrosion rate with time. The pit specimen illustrated in
Fig. 7 shows a 25-fold increase in corrosion rate during its first 90 minutes of growth. Note also that the corrosion rate begins to level off at longer times. No limiting corrosion rate was observed even in three hour tests; the rate continued to increase slowly. It was not possible to appreciably accelerate the corrosion rate of a pit specimen by impressed currents. Although some stimulation was possible, high current values could only be obtained by allowing the pit to remain short-circuited for long periods of time. In many instances, the application of even small currents to a growing pit reduced its corrosion current value. This inability to speed up the pitting process in artificial pits by impressing currents has also been reported by May (36). Apparently, the conditions within a pit are extremely critical, and the conditions leading to increased pit activity are time-dependent and cannot be appreciably hastened by external currents.

It is important to emphasize that Fig. 7 is not representative of all pit specimens tested in ferric chloride. Pit growth characteristics were not reproducible in identical tests even when the same pit specimen was used in both instances. Several specimens refused to become self-sustaining under any conditions. Some became inactive after a short growth period, while others showed extremely rapid increases in corrosion rates with time. A few pits
demonstrated an almost constant corrosion rate that increased very slowly with time. The magnitude and duration of the initial corrosion current fluctuations varied from specimen to specimen and also during identical tests with the same specimen. However, Fig. 7 does qualitatively illustrate the growth behavior of most active pits—namely, an erratic and unstable incubation period followed by a period of increasing pit activity.

The highly variable behaviors of the artificial pit specimens closely corresponds to the observed behaviors of actual corrosion pits. Hence, it is an indication of their similarity to real corrosion pits. May (36) has observed similar non-reproducibility in his artificial copper pit studies in water and dilute salt solutions.

The wire anode was not attacked uniformly during the pitting studies, but showed numerous localized pits. Also, edge attack along the wire-plastic interface was frequently observed. Thus, the currents observed during pit growth studies actually represented the activities of more than one pit. However, it is entirely permissible to consider the wire electrode as a single pit. The localized attack of the anode increases the error in quantitative calculations such as anodic current density. However, the localized attack of the wire was fortunate because it permitted
the electrochemical observation of anode or pit enlargement which would not have been possible if the wire anode had corroded uniformly. These observations are discussed in later sections.

The localized attack of the wire suggested that local corrosion action may have occurred on the wire surface with the unattacked portions of the wire acting as cathodic sites. Indeed, local corrosion action did occur on the wire as shown by measurements described in later sections. However, the magnitude of these local currents were very small compared to the measured corrosion currents. This is illustrated by the fact that open-circuited pit specimens showed no visible attack of the anode wire or no enlargement of existing pits when exposed to the ferric chloride solutions for periods up to 24 hours. Thus, the measured current flow closely approximated the total corrosion current flow.

The corrosive solutions were chosen so that no pitting occurred on the cathode sheet during a normal test run (up to 3 hours). However, with longer exposures all of the pitting corrosives invariably produced pitting and edge attack of the cathode electrode. Ferric chloride concentrations of 0.2 molar or less did not pit the cathode sheet during experimental runs. However, 0.3 molar concentrations
produced pitting in less than an hour, and, hence, were not extensively used for test purposes.

Several estimates were made of the anodic and cathodic current densities during pitting attack in ferric chloride. The values of anodic current density were based on visual estimates of the total anodic area. Cathodic current densities ranged from 10 to 100 microamperes/square inch while anode values ranged from 1 to 10 amperes/square inch. This high anodic current density explains the extremely rapid pit penetration often observed in ferric chloride solutions.

d. Factors Affecting Pit Growth

(1) Heat Treatment

Because the heat treatments of Type 304 stainless steel sheet and wire were unknown, tests were conducted to compare the corrosion characteristics of the materials in the as-received condition with the solution quenched condition. Several pit specimens were constructed from sheet and wire and were water quenched after 20 minutes at 2050° F. in an argon atmosphere. No observable differences were noted between these pits and pits constructed from the as-received material. They demonstrated similar open circuit and pit growth behaviors. Of course,
slight differences may have existed but they would have been completely hidden by the inherent non-reproducibility of the pit specimens.

The heat treatment of the wires and thin sheets was very difficult. The cathode sheets warped severely during quenching and the oxide scale that formed on the materials was hard to remove. Because of this, and since heat treatment produced no changes in corrosion characteristics, all of the remaining specimens were made from the as-received materials.

(2) **Anode Wire Diameter**

Type 304 stainless steel pit specimens with wire diameters of 5, 10, 20 and 31 mils were tested in ferric chloride. Because of the localized attack of the anode wire, the diameter of the wire had no effect on the pit growth characteristics. The 5 and 10 mil wires were difficult to mount and were often undermined and dropped out during corrosion attack. Pits with 20 mil anodes were considered the most desirable since they were easy to assemble, and were not usually destructively undermined during testing which allowed them to be reused. From the standpoint of geometric similarity to actual pits, the 20 mil anode was more desirable than the 31 mil anode.
(3) **Solution Age**

Pure solutions of ferric chloride precipitated ferric hydroxide upon standing. Hydrochloric acid additions prevented this decomposition. However, acid stabilized solutions also showed pronounced changes with time. The pH values of the solutions generally increased with time although this change was often erratic and in some cases it increased with time. The most noticeable change was a darkening of the solution color. Ferric chloride solutions containing 0.05 normal hydrochloric acid were yellow-orange when freshly prepared and became more orange upon standing.

Old ferric chloride solutions (standing 1 month or more) appeared to be slightly more sluggish in their pitting action than freshly prepared solutions. That is, old solutions usually demonstrated a slower increase in corrosion rate with time. However, no difference was observed in the maximum pit activity reached in either solution; both supported ever increasing pit activities. The difference between old and new solutions was very slight and it was not possible to conclusively verify it because of the inherent non-reproducibilities of the pitting tests. The difference is probably related to the formation of stable ion complexes. pH seemed to have relatively no effect.
since fresh ferric chloride solutions containing various amounts of acid between zero and 0.1 normal showed similar growth tendencies.

(4) Agitation

Agitation of ferric chloride solutions slightly increased the activity of growing pits. This increase in activity was often only momentary. Agitation apparently increased the supply of ferric ions at the cathode electrode and did not disturb the autocatalytic conditions existing at the pit anode. Even violent shaking of the test cell failed to cause any reduction in the activity of stable, growing pits. This suggested that the autocatalytic pit corrosion products were not merely resting in the pit cavity, but were held there by some force other than gravity. This was further substantiated by the observation that the localized pits on the anode wire were generally shallow and open, and should have created no barrier to diffusion.

(5) Atmosphere

The atmosphere within the test cell produced no observable effect on the pitting tendencies of ferric chloride solutions. The substitution of nitrogen for the usual oxygen atmosphere did not effect pit growth characteristics. From previous discussions of the effect of oxygen on the corrosivity of oxidizing metal halides,
this is the expected result. The cathodic reduction of oxygen is a minor reaction during pitting in ferric chloride. Stagnant solutions showed a slightly slower increase in pit activity than solutions with gas bubbling through them. This was undoubtedly due to the stirring effect of the gas bubbles rather than any specific chemical action. Oxygen was used as the standard test atmosphere to keep test conditions identical and to retard any build-up of ferrous ions during long test runs.

(6) Current Interruption

Fig. 8 illustrates the effect of current interruption on the activity of an artificial pit immersed in 0.1 molar ferric chloride. The points were obtained by opening the circuit of an active pit specimen and making very rapid short circuit current measurements at various time intervals. Each current determination took 5 seconds or less to perform. It was felt that the duration of the measurements was so short that no increase in pit activity occurred during the measurements. Thus, the curve represents the activity that a pit specimen, originally at 90 microamperes, would have after being interrupted for a given time period. Notice that even momentary current interruptions produced marked decreases in pit activity. Fig. 8 is probably the first direct experimental evidence of the autocatalytic nature of pitting corrosion.
The apparent logarithmic relationship shown in Fig. 8 suggests the phenomena of non-steady state diffusion. The general equation of the current decay curve in Fig. 8 is:

$$\log I = Kt + k \quad (11)$$

Where \( I \) is current flow at time \( t \), \( K \) and \( k \) are constants. The diffusion of the concentrated pit contents into the bulk solution during open circuit conditions can be closely approximated by the expression:

$$\log C = K't + k' \quad (12)$$

Where \( C \) is the concentration of the chloride ions within the pit at time \( t \), \( K' \) and \( k' \) are constants. Thus, pit activity or pit current appears to be directly related to the concentration or amount of chloride ion within the pit.

The decay of the anode and cathode potential difference during open circuit was also determined. The potential decay was observed to be much slower than the current decay. For example, a pit specimen in 0.1 molar ferric chloride with an initial open circuit potential difference of 0.339 volt, dropped to 0.200 volt after 12 minutes. It was not possible to determine whether potential decay was a logarithmic function because of the short range of potential values. The area/perimeter effect prevented accurate determinations at low potential difference values. The slow decrease in potential difference compared to the rapid decrease in corrosion current suggested that the
current decay was mainly due to a shrinkage of the anodic area within pits. Changes in anode area are discussed further in a later section.

(7) Pit Interaction

Possible interaction effects between pit sites were studied with double artificial pit specimens containing two 20 mil anode wires separated by distances of 0.165, 0.070 and 0.038 inches, center to center. These were tested in 0.2 molar ferrie chloride. Several techniques were employed to detect pit interaction effects. The first method consisted of activating one of the pits and observing its short circuit current while an anodic current of 100 microamperes or more was impressed through the other anode wire. In the second method, both pits were activated and their short circuit current behaviors were observed to determine if there was any relationship between the activities of the pits. In the third technique, the two pits were stimulated to active growth and the short circuit current behavior of one was watched while the other was inactivated by opening its circuit.

No detectable interactions were observed during tests on the three double pit specimens. However, reduction of the cathode electrode size by masking with Glyptal enamel produced marked interaction effects. The reduction of the cathode size of an artificial pit specimen is equivalent to
the existence of numerous corrosion pits on the cathode sheet. It is similar in that it increases the cathode current density and causes greater cathodic polarization as would the existence of numerous pits. Fig. 9 illustrates the observed interaction on a double pit specimen with a reduced cathode electrode size. The cathode area measured 0.099 by 0.055 inch. Note that upon opening the circuit of one pit, the activity of the other increased. Likewise, closing the circuit of a pit reduced the activity of the other. This effect was most noticeable during the inactivation and activation of pit number 2. These observations suggest an unusual hypothesis. In ferric chloride, and possibly other high conductivity pitting corrosives, there is negligible interaction between two closely spaced, isolated pit sites. Pit interactions apparently only occur on densely pitted surfaces. This concept represents a departure from the commonly accepted idea that a single pit suppresses attack in its immediate vicinity (74, 79). It also explains the frequently anomalous observation of two or more corrosion pits in extremely close proximity (35).

The determination of pit interaction was very difficult because of the repeated and rapid balancing and switching operations that were required. For these reasons pit interaction studies on triple and quadruple pit specimens were not attempted.
e. Other Growth Studies

Exploratory experiments were performed with Type 304 stainless steel specimens exposed to 0.1 molar ferric bromide and cupric chloride solutions. Both of these electrolytes demonstrated pit growth tendencies similar to that of ferric chloride. Intense corrosion currents that increased rapidly with time were observed. Pit growth in cupric chloride was characterized by a very steady increase in corrosion current with time. Unlike ferric chloride, cupric chloride produced only small current fluctuations during early growth stages.

Tests with Type 316 stainless pit specimens demonstrated that ferric chloride solutions up to 0.3 molar would not sustain any pitting corrosion. The open circuit potential differences of these specimens was observed to be close to zero.

3. Transfer Studies

a. The Transfer Technique

Because of the inherent non-reproducibility of pit growth behavior, it was impossible to measure the relative pitting tendencies of various electrolytes by duplicate tests. However, this difficulty was avoided by transferring an actively growing pit specimen from one corrosive medium to another and observing any resulting changes in current intensity. The pit specimens were transferred by
moving the entire test assembly shown in Fig. 1 from one test cell to another. During the transfer, the electrical connections were maintained. Also, the test assembly was always held so that a layer of electrolyte remained on the surface of the pit specimen during the operation. Such pit transfers usually took no more than 5 seconds. Tests in which a pit was transferred between two identical solutions demonstrated that a careful transfer operation caused no change in pit activity. In all of the experiments conducted, the transfer operation was repeated several times to insure that the observed effects were qualitatively reproducible.

b. **Factors Affecting Pit Activity**

(1) **Anionic Species**

(a) **Sulfate**

Fig. 10 shows the relative pitting tendencies of ferric chloride and ferric sulfate. The change from a solid line to a dashed line indicates the transference of the pit specimen from the chloride to the sulfate solution. As shown by the last transfer to the sulfate solution, the pit current rapidly fell toward zero. However, interference from the area/perimeter ratio effect prevented it from actually reaching zero current. It is quite evident from Fig. 10 that the presence of chloride
ion is essential to pit activity. The sulfate ion shows no pitting tendency. This non-pitting nature of ferric sulfate has been shown by Stern (9) and Uhlig (10) and also by corrosion tests described later under Other Studies.

(b) Perchlorate

The pitting tendency of ferric perchlorate is demonstrated in Fig. 11. Like sulfate, perchlorate shows no pitting tendencies. Notice the interference from the area/perimeter effect at the end of the fourth transfer to the perchlorate solution. The corrosion current leveled off. The observed inertness of ferric perchlorate is not in accord with the acid theory of pitting or Hoar's experiments with iron (129, 130). Ferric perchlorate should have a pitting tendency similar to that of ferric chloride according to the acid theory. Thus, the high acidity within a pit is probably an effect rather than the cause of pitting attack.

(2) Ferric Chloride Concentration

Fig. 12 illustrates the effect of ferric chloride concentration on pit activity. It is quite evident that increasing the concentration markedly increased pit activity. The first transfer to the 0.3 molar ferric chloride illustrates one of the activation techniques described in Pit Activation. Note that the specimen, initially at a very low activity level, was stimulated to a higher
activity by transferring to the 0.3 molar solution for a short period. Additional transfers further increased the pit activity in the 0.2 molar solution. No pitting of the cathode electrode occurred during this test because of the short overall exposure to the 0.3 molar solution.

(3) Ferric Ion Concentration

During pitting in ferric chloride, both the anion and cation are involved in the corrosion process. The chloride ion is essential to autocatalytic anodic process as already shown by the transfer studies in sulfate and perchlorate solutions, and the pronounced effect of current interruptions. Likewise, the ferric ion is consumed in the cathodic reduction reaction. This introduces the question of which ion is the more important to the overall pitting process.

The effect of ferric ion concentration on pit activity was determined by transferring between pure chloride and chloride salt mixtures containing only one half as much ferric ion. The results of these transfers are pictured in Fig. 13. Note that the mixtures contained only 0.05 equivalent of ferric ion per liter compared to 0.1 per liter for the pure solution. The chloride ion concentration was nearly identical in all three solutions, 0.4 equivalents per liter. Sodium and aluminum cations cannot be cathodically reduced, and therefore, have no effect on
the pitting process. It can be seen from Fig. 13 that reduction of the ferric ion concentration noticeably reduced the pit specimen activity. Hence, pitting attack in ferric chloride is controlled to a large extent by the concentration of ferric ion. The accelerating influence of ferric ion has also been observed by Brown and Mears (69) and Benson, Brown and Mears (70). The tremendous influence of ferric ion is also apparent if one considers the relative pitting intensities produced by ferric chloride and sodium chloride (see Table VII).

(4) Chloride Ion Concentration

The effect of chloride ion concentration was investigated by transferring between pure ferric chloride and ferric salt mixtures containing only one half as much chloride ion. Fig. 14 shows the effect of transferring into a ferric chloride-sulfate mixture. Most unusual is the tremendous burst in pit activity following the transfer to the chloride-sulfate mixture. The reasons for this behavior are discussed later. In general, it can be seen that after the initial burst in pit activity subsided, the chloride-sulfate mixture showed little effect on pit activity. Thus, the concentration of the chloride ion on the bulk solution had little effect on pitting intensity. Indeed, from the open circuit current decay behavior it appears that the chloride ion concentration at the pit
anode is the controlling factor rather than the concentration of the bulk solution. Of course, the bulk solution composition will exert some influence on the anode chloride concentration. This is evidenced by the results of the transfer studies in ferric sulfate and perchlorate solutions. Evidently, the pit anode requires a continuous supply of chloride from the surrounding solution to offset the loss of chloride by diffusion.

The effect of chloride ion concentration was also studied by transferring between 0.2 molar ferric chloride and a solution containing 0.1 molar ferric chloride and 0.1 molar ferric perchlorate. However, the pit specimen lost all activity in this mixture. An effect similar to Fig. 11 was obtained. Apparently, the perchlorate ion possesses a greater inhibiting power than the sulfate ion.

(5) Nitrate Additions

The effect of nitrate additions on pit activity is shown in Fig. 15. Concentrations of sodium nitrate up to 0.5 molar stimulated the activity of growing pit specimens. A concentration of 1.0 molar first stimulated and then destroyed pit activity. Other transfer tests showed that a 0.05 molar sodium nitrate addition to 0.1 molar ferric chloride produced no observable change in pit activity. Thus, increasing amounts of nitrate
increased pit activity except for large additions which destroyed pit activity.

The results shown in Fig. 15 are most unusual considering the fact that nitrate ion is a very powerful inhibitor of pitting corrosion in ferric chloride. It was observed that it was impossible to activate pit specimens in 0.1 and 0.2 molar ferric chloride containing 0.05 molar or more of sodium nitrate. Although activation tests were not made at concentrations lower than 0.05 molar, corrosion test results, shown in Table XII and described later, indicated that a 0.018 molar addition of sodium nitrate was sufficient to prevent pitting in 0.1 molar ferric chloride. Fig. 15 shows that growing pits were not retarded when transferred to a solution containing 25 times the amount of nitrate necessary to inhibit the onset of pitting. In fact, such nitrate ion concentrations actually stimulated pitting attack! This unusual behavior of nitrate ion was further verified by the fact that, if growing pit specimens were open-circuited in the nitrate-inhibited ferric chloride for a period sufficient to drop their activity to the vicinity of zero, they could not be reactivated by impressed currents. Thus, nitrate ion only inhibits the onset of pitting attack and does not retard growing pits except at very high concentrations.
c. Ion Screening

It has been demonstrated that nitrate ion does not effect the cathodic reduction of ferric ion (9), and therefore the inhibiting influence of this ion must be due to its effect on the anodic reactions occurring during pitting. Considering Fig. 15 and the activation studies described above, it is evident that nitrate ion concentrations that retard the anodic reactions during pit activation do not suppress the anodic reactions during pit growth. It follows that the nitrate ions must not contact the anodic reaction sites during pit growth except at very high concentrations. Thus, the contents of a growing pit in some way screen or prevent nitrate ions from inhibiting the anodic reactions that are occurring. Likewise, considering the effects of ferric sulfate and ferric chloride-sulfate mixtures on pit activity shown in Figs. 10 and 14, it is apparent that sulfate ions must also be screened from the anodic sites in growing pits.

The existence of a screening effect at pit sites has been predicted from the characteristics of pitting corrosion (see, Screening Effects). The transfer and activation studies described above represent the first experimental indication of such a screening effect during pitting attack. This effect is undoubtedly caused by the high chloride ion
concentrations at pit anodes. The nature and mechanism of this screening action is open to speculation. Specific adsorption of chloride ions could keep other ions from anodic sites. There is also the possibility that high chloride ion concentrations might produce a migrational block to other anions. The conductivities of highly concentrated solutions (167) indicate that chloride ions possess greater mobilities than any other anions under these conditions. Hence, in the highly concentrated chloride salt solutions in pit cavities, the migration of chloride ions might be much greater than other anions.

It is quite evident that the acid theory of pitting is incapable of explaining any screening action at pit sites. The highly acidic conditions within a pit would not be expected to interfere with the migration of inhibiting anions to the electrode surface. Here, as in the case of the pitting tendency of ferric perchlorate, the acid theory fails to explain observed behavior.

Naturally, the concept of a screening action at pit sites is not a complete explanation of the pit anode mechanism. The nature of the screening action and the reasons why the halides cause this effect remain to be explained. However, this idea does explain some of the observed behavior. The concept of an anodic screening
action is entirely consistent with the adsorption and ion exchange theories of pitting.

d. Pit Inertia and Pit Memory

There are two unusual characteristics of pitting corrosion that deserve mention. The first is pit inertia. That is, during rapid increases or decreases in corrosion current, the current tended to overshoot its final value. This behavior was often observed after pit transfers. Figs. 12 and 13 show the pit inertia effect during decreases in corrosion current, and Figs. 14 and 15 illustrate this effect during increases and decreases in pit current. Pit inertia was also often observed during the early erratic state of pit growth. This unusual behavior is undoubtedly due to the disturbance of the migration-diffusion balance within corrosion pits. During rapid current changes ion migration rate probably changes more rapidly than ion diffusion rate and a temporary unbalance results.

Pit memory is illustrated in Figs. 10 and 11. The most interesting feature of these curves is the very rapid increase in corrosion current following transfers to the ferric chloride solution. This increase was much faster than that obtained during any pit growth studies and it showed no evidence of early erratic behavior. The pits appeared to remember their original activity and returned
immediately to it. Fig. 11 shows that this effect is very similar to actual memory phenomena. Thus, the longer the pit remained in the inactive solution, the slower it returned to its original value. Note that the ferric chloride curves in Fig. 11 decrease in slope with increasing previous exposures to the perchlorate solution. If the pit specimens were allowed to remain in the sulfate or perchlorate solutions for long periods, they were observed to be inactive when transferred back to ferric chloride.

Pit memory apparently results from the re-activation of the original pit anode areas. This suggests that the stability of passive surfaces increases with time. Thus, newly passivated areas are more readily destroyed, or activated than old passive areas.

4. Polarization Studies

a. Potential Measurements and Conventions

The signs of the potentials reported in this study follow the conventions adopted by the Electrochemical Society. Potentials more anodic than the reference electrode have negative values, while those more cathodic have positive values. All potential measurements were made with a saturated calomel reference electrode. The potential of this electrode relative to the hydrogen electrode potential is 0.2415 volt at 77° F (25° C).
Tests indicated that the position of the string salt bridge within the test cell produced no observable difference in the measured potentials of the pit specimen electrodes. All polarization studies were conducted in 0.2 molar ferric chloride.

b. Instantaneous Polarization Behavior

(1) Instantaneous Polarization Curves

The autocatalytic nature of the pit anode produces a most unusual phenomenon; namely, that there is no open circuit anode potential. Under steady state, open circuit conditions, the potential of the pit anode will be identical with that of the bulk metal surface. This can be readily seen by noting that under conditions of zero current flow, there will be no migration of chloride ions to the pit site. Hence, if steady state conditions are achieved, the composition of the solution in contact with the pit interior will be identical to that in contact with the remaining metal surface.\(^1\) Thus, since the metal and solution at both areas have identical compositions, there can be no potential difference.\(^2\) All of the literature

\(^1\)Actually, this only applies to the ideal case in which the diffusion rates of ionic species at both areas are equal. Shallow, open corrosion pits containing no re-entrant angles will closely approach this ideal case.

\(^2\)This is based on the assumption that the metal has an homogeneous composition.
pertaining to the electrochemistry of pitting fails to recognize this inherent anomaly. Polarization curves of pitting corrosion which indicate open circuit potential differences (69) give an erroneous impression of the pitting process.

From the discussion above, it is apparent that ordinary polarization curves cannot be used to study the electrochemical reactions during pitting. Because of this, a new type of polarization curve has been utilized in this investigation--the instantaneous polarization curve. This curve is obtained by rapidly introducing resistance into a short-circuited electrode system and measuring the corresponding electrode potentials. Fig. 16 illustrates an instantaneous polarization diagram of an artificial pit in ferric chloride. This diagram was obtained by allowing a short-circuited pit specimen to grow until its activity reached a value of about 17 microamperes. Then the potentials of the two electrodes were measured. Next, electrode potentials were measured as arbitrary amounts of external resistance were rapidly introduced into the circuit. The open circuit electrode potentials were then obtained by disconnecting the specimen terminals from the electrical

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3 The resistance was introduced by unbalancing the zero-resistance ammeter circuit and allowing finite potential differences to exist across the pit specimen terminals.
circuit. The determination of Fig. 16 took less than 30 seconds.

It is important to emphasize the significance of an instantaneous polarization diagram. It is not an equilibrium polarization diagram. If performed fast enough, it represents the polarization characteristics of a system under the conditions that existed during short circuit operation. Thus, the differences in solution composition at the electrode surfaces during short circuit current flow are maintained during the polarization measurements. The open circuit anode potential shown in Fig. 16 is not an actual open circuit potential, but the instantaneous open circuit potential. On open circuit, it rapidly became less anodic and approached the potential of the cathode sheet. However, the area/perimeter effect imposed by the pit specimen prevented it from actually reaching the cathodic potential.

Because the instantaneous anodic and cathodic polarization curves were observed to be nearly linear, only the corrosion current, corrosion potential and the open circuit potentials were measured in most of the following experiments. In this manner, it was possible to determine the polarization diagrams in 3 seconds or less. Such short times greatly reduced the chance of errors arising from diffusion during the measurements.
It is important to emphasize that all of the instantaneous polarization diagrams prepared in this investigation represent the characteristics of the self-generated potentials and currents of artificial pit specimens. They were not obtained with impressed currents.

(2) **Effect of Time**

The polarization diagram pictured in Fig. 16 only represents the electrochemical characteristics of a pit at a specific current value. However, the activity or corrosion current of a pit changes markedly with time as shown by the previously described growth studies. Hence, the polarization characteristics of a pit must also change with time.

Fig. 17 illustrates the effect of time on the instantaneous polarization characteristics of a pit specimen. This diagram was obtained by measuring the polarization behavior of a specimen after it had reached a corrosion current indicated by the curves marked by number 1. After the open circuit potentials were measured, the specimen was again short-circuited and allowed to grow to a greater corrosion current, and the process was repeated. The specimen never returned to its original short circuit current after the open circuit potentials were measured because of current decay during open circuit conditions (see Fig. 3). The final short circuit current was always less than the
original value. The numbers do not refer to any standard time interval. A standard time interval between tests would be meaningless since the specimen did not grow normally because of the repeated current interruptions during polarization measurements. The numbers merely indicate the change in instantaneous polarization behavior with corrosion current, which increases with time. The cathodic polarization curves for diagrams 3 to 10 have been drawn as a single line to avoid a confusing array of lines. The open circuit cathodic potentials for diagrams 3 to 10 varied between -0.007 and 0.001 volt, and thus the single cathodic curve closely approximates the actual curves.

Fig. 17 demonstrates that the electrochemical behavior of pitting corrosion is most unusual. The open circuit anodic potential became more anodic with increasing time. Also, the slope of the anodic polarization curves decreased with increasing time. The cathode electrode showed similar, but less pronounced, changes with time. These changes in electrochemical characteristics with time will be analyzed in a later section. The important point is that pitting corrosion cannot be represented by a single polarization diagram. Since there is an instantaneous polarization diagram for every pit corrosion current value, an infinite number of diagrams is required to completely picture
pitting corrosion. This conclusion marks a distinct departure from the usual concepts of pitting, and corrosion phenomena in general.

(3) Effect of Cathode Electrode Area

The cathode electrode areas of the standard pit specimens were altered by masking various amounts of the cathode sheet with insulating enamel. In all cases, the reduced cathode areas were square in shape. From the standpoint of symmetric current distribution, circular cathode areas would have been more desirable. However, the painting of accurate circular areas was very difficult. Small, accurate, square areas were easier to mask and permitted very precise area measurements. All areas were measured with a microscope fitted with a micrometer eyepiece.

Figs. 18 through 22 illustrate the effect of cathode electrode area reductions on polarization behavior. Fig. 18 illustrates that a fourfold reduction in area produced no observable changes in the polarization curves compared to the 1 square inch electrode. The "creeping" cathode curve shown in Fig. 18 resulted from the fact that polarization measurements were started before the open circuit potential of the cathode had stabilized. This phenomenon frequently occurred during the polarization studies. Note that, if the cathodic polarization curves of the four
diagrams are superimposed, a series of curves similar to Fig. 17 results.

Figs. 19 and 20 show that further reductions in cathode area produced marked changes in the polarization characteristics of the pit specimens. The instantaneous open circuit cathodic potential shifted to more noble potentials with increasing time. Also, the slopes of the cathodic polarization curves decreased with time. The symmetric electrochemical behavior of the anode and cathode pictured in Fig. 19 is most striking. Comparison between Fig. 19 and Fig. 20 shows that decreasing the cathode area produces a greater suppression of the open circuit cathodic potential. Another interesting aspect of these two figures is the relatively constant corrosion potentials.

It is evident that as the area of the cathode electrode is decreased its area/perimeter ratio also decreases. At very small cathode areas interference from this effect was encountered. Fig. 21 illustrates this interference. Note that the open circuit cathodic potential for diagram number 1 is very high in comparison to all the previously cited figures. Also, the suppression of the cathodic open circuit potential does not follow the trend observed in Figs. 17, 18, 19 and 20. Obviously, at a cathodic area of 0.003 square inch, the area/perimeter effect exerted considerable influence on the cathodic behavior. As Fig. 21 shows, the
cathodic electrode was actually quite anodic when compared to the previously observed open circuit anodic potentials. This area/perimeter interference is not catastrophic since the curves still show the same qualitative polarization characteristics. Also, 0.003 square inch represented the smallest area possible with 20 mil anode specimens. At this area value, the sides of the square cathode area were tangent to the hole in the cathode sheet.

The time behavior of the instantaneous open circuit cathode potential also changed with a reduction in cathode area. At cathode areas of 0.25 and 1 square inch the open circuit cathodic potentials of growing pits did not vary appreciably with time. This, of course, did not apply to specimens showing "creeping" cathode potentials (see Fig. 18). However, after the open circuit potentials of such specimens settled at a steady value, the above behavior was observed. The open circuit cathodic potentials of the specimens with very small cathode areas (0.020 square inch or less) varied rapidly with time. Immediately after open-circuiting, the potentials usually rapidly shifted to a more noble potential and then gradually become more anodic with time. The initial shift in the noble direction indicates that a localized depletion of ferric ions (concentration polarization) existed at the small cathode electrodes.
during pit growth. The potential shift was caused by the diffusion of ferrous ions away from the electrode surface.

The growth rates of the small cathode pit specimens appeared to decrease with decreasing cathode area. The specimen with the 0.003 square inch cathode electrode showed a very slow increase in pit activity with time. However, because of the non-reproducible nature of pit growth it was impossible to make any quantitative correlations between cathode electrode size and growth characteristics.

A reduction in the cathode electrode area can be considered to be equivalent to three different circumstances that arise during pitting attack. First and most obvious, a reduction in cathode size is equivalent to the reduction of the area of a specimen in an ordinary corrosion test. Thus, the cathode electrode area studies can be used to show how the polarization characteristics of a single pit change with specimen area.

Secondly, the reduction of the cathode electrode area can be considered to be qualitatively equivalent to the enlargement of the pit anode. In either case, the cathode/anode area ratio decreases. In applying the effects of cathode area reduction to the enlargement of a single pit, it must be remembered that the absolute electrode sizes in
the two systems are not identical. The absolute size of a corroding system can have a pronounced effect on its polarization characteristics (152, 153). However, the relatively high conductivity of the electrolyte and the almost uniform cathode current distribution to be shown later, indicate that such comparisons are probably valid for the systems studied.

Third, the reduction of the cathode electrode area is equivalent to the existence of other pit sites on the cathode sheet. Such area reductions increase the cathodic current density at a given value of pit corrosion current as would the existence of other pits on the unpainted cathode electrode. Consider an actively growing pit specimen with a cathode area of 0.01 square inch. This is equivalent to a pit specimen with a 1 square inch cathode electrode containing 100 random pit sites each with an activity equal to the pit under study.\(^4\) When instantaneous polarization measurements are made on a reduced area pit specimen, the cathodic current density falls to zero. Hence, the polarization changes produced by cathode electrode reductions indicate how the electrochemical characteristics of all pits change as their number per unit area

\(^4\)This assumes that the current is evenly distributed over the entire cathode electrode. This condition is approximated by the system studied. (See Cathode Current Distribution.)
increases. The pit interaction shown in Fig. 9 therefore demonstrates how the activity of a single pit changes when numerous other pits on the surface are open-circuited.

(4) Polarization Curve Shape

Fig. 16 illustrates that the anodic and cathodic polarization curves on a pit specimen were virtually linear. Fig. 22 shows the shape of polarization curves obtained with a pit specimen with a reduced cathode electrode area. These curves were obtained in the same manner as those in Fig. 16. The anodic polarization curves were calculated from the cathodic polarization curves and the potential differences that existed across the specimen terminals. Both anodic and cathodic polarization curves are nearly linear. The non-linear behavior of the cathodic curve at low current values may have resulted from the noble shift of the cathodic potential during the measurements. In any case, no serious error is introduced by assuming that the cathodic curve is exactly linear as was done in Figs. 19, 20 and 21.

(5) Electrochemical Control

As discussed in the literature survey, there is considerable dispute over the type of electrochemical control operating during pitting corrosion. From the preceding polarization diagrams, it is apparent that all types of control occur during pitting attack. Fig. 17
illustrates a series of polarization diagrams showing complete anodic control. Polarization diagram number 2 in Fig. 20 demonstrates a high degree of cathodic control and Fig. 19 shows a series of diagrams under mixed control.

From the results of the cathode area studies, it is evident that as pitting corrosion progresses, the electrochemical control shifts from anodic to cathodic control via mixed control. The progress of pitting corrosion refers to the enlargement of a single pit or the appearance of more pit sites on the exposed area. This observed shift in control type is identical to that predicted by Standifer (46).

The concept of electrochemical control when applied to pitting corrosion becomes quite meaningless. One must think in terms of an instantaneous electrochemical control. However, in view of the complex, time-dependent electrochemical phenomena that occur during the progress of pitting attack, the type of control operating at any instant is of minor importance.

(6) **Transfer Effects**

Polarization studies were made to determine the causes of the unusual increases in pit activity following the transfer of pit specimens to a ferric chloride-sulfate mixture (Fig. 14). Fig. 23 illustrates the changes that occur during transfer from a 0.2 molar ferric chloride
solution to a chloride-sulfate mixture containing 0.2 molar ferric ion. It was obtained by allowing a pit specimen to grow to an activity of 112 microamperes in pure ferric chloride. An instantaneous polarization diagram was then determined (diagram number 1). Next, the specimen was short-circuited until its activity almost returned to its original value. At this point it was transferred to the chloride-sulfate mixture and a polarization diagram was immediately determined (diagram number 2).

As Fig. 23 shows, there was a rapid increase in corrosion current following the transfer operation. This increase was caused by the suppression of the potential of the cathode electrode by the chloride-sulfate mixture. The anodic electrode was relatively unaffected by the transfer. The slight difference in the slopes of the two anodic polarization curves is undoubtedly due to the fact that the specimen was transferred before it reached its original activity value. The open circuit cathodic potential in the chloride-sulfate mixture became more anodic with time, thus explaining the decrease in pit activity following the initial rise in activity shown in Fig. 14. The transfer effects observed in nitrate-inhibited ferric chloride (Fig. 15) were undoubtedly caused by the same phenomenon—the suppression of the cathode electrode potential.
Fig. 23 further substantiates the idea of a screening action at pit anodes. The transfer to the chloride-sulfate mixture enables the cathode electrode, but produces relatively little effect on the anode electrode.

(7) Effect of Anode-Cathode Separation

The artificial pit specimens used in this study differed from actual corrosion pits in that there was a finite separation between the anode and cathode electrodes. Although this separation was very small, it still represented a departure from the geometry of actual pits. To check the effect of this anode-cathode separation on pit behavior, several pit specimens were constructed with very large separations.

Figs. 24 and 25 illustrate the polarization diagrams obtained with the specimen having the greatest anode-cathode separation. It is evident that this special specimen behaved very similarly to the standard specimens. As evidenced by the high corrosion currents, it showed a rapid growth rate. Also, reduction of the cathode area produced effects similar to those observed with standard specimens. The only observable difference between this special specimen and standard specimens was the corrosion potential behavior. With standard specimens, the potentials of the anode and cathode electrodes under short circuit conditions
were always within approximately 2 millivolts of each other. However, the special specimen consistently showed a potential difference of approximately 3 to 5 millivolts under the same conditions. It should be noted that the ranges of the observed potential differences lay at the limit of accuracy of the pH meter. Hence, the actual magnitude of the difference between the two types of specimens is questionable. It was concluded that the anode-cathode separations of the standard pit specimens did not affect their similarities to actual corrosion pits.

**c. Cathode Current Distribution**

The fact that large anode-cathode separations did not markedly affect the polarization characteristics of the pit specimens indicated that the current distribution on the cathode electrode was nearly uniform. Additional tests were performed to determine cathode current distribution. Impressed current polarization studies were conducted using artificial pits immersed in 0.1 molar ferric sulfate. The specimens were allowed to remain open-circuited in the ferric sulfate until the cathode reached a steady potential value. Then cathodic polarization curves were obtained by two different methods: by impressing current through the anode wire or through an auxiliary horizontal anode. If the cathodic current is evenly distributed over the entire cathode electrode, the polarization curves obtained by the
above methods should be identical. Tests using specimens with cathode areas of 1.0 and 0.25 square inches indicated that either method produced nearly identical polarization curves. Likewise, if the cathodic current is evenly distributed, then polarization curves obtained by impressing current across a pit specimen should be independent of cathode electrode area. Fig. 26 shows the cathodic polarization curves obtained by impressing current through pit specimens with 1.0 and 0.25 square inch cathode electrodes. The open circuit potential of the 1 square inch specimen was 0.600 volt, while that of the 0.25 square inch specimen was 0.499 volt. The difference is due to the area/ perimeter effect. Because of this, tests were not performed on smaller cathode electrodes. As Fig. 26 illustrates, the curves are almost identical. However, the smaller electrode shows a slightly lower potential at a given current density indicating that cathodic current is probably not completely uniform. Experimental errors might have caused this difference.

Impressed current studies, utilizing indicator reagents, were also used to check cathodic current distribution. By placing a piece of filter paper moistened with an indicator solution on the surface of a pit specimen and impressing a current between the electrodes, it was possible to obtain current distribution patterns on the paper. Sodium
chloride solutions containing phenolphthalein and sodium iodide solutions were used as indicators. Phenolphthalein changes from colorless to pink in the presence of a base, and hence, indicates the distribution of cathodic areas. To use the sodium iodide solutions, it was necessary to reverse the polarity of the pit specimen. The wire was made cathodic and the sheet anodic. Iodide ion is anodically oxidized to free iodine. Although the pit polarity was reversed in the iodide indicator studies, the observed current distribution can be equated to cathodic current distribution. At low concentrations of sodium iodide, the current was concentrated immediately around the hole in the cathode. Little or no iodine was released on the remaining area. However, as the concentration of the sodium iodide was increased, the current distribution became more even. A nearly saturated solution produced an almost perfectly uniform distribution of iodine. A similar observation was made with a concentrated solution of sodium chloride containing phenolphthalein. Thus, in low conductivity electrolytes, cathodic current distribution is not uniform. As conductivity increases, cathodic current distribution becomes more uniform.

The uniform current distribution and the horizontal cathodic polarization curve of a one square inch cathode electrode explain why no pit interaction was observed with
the standard double pit specimens. The current generated by a single pit did not affect the potential of the cathode electrode (Fig. 17) and, since the current distribution was nearly uniform, the pit would not influence the activity of another pit adjacent to it.

d. Analysis of the Electrochemistry of Pitting

As shown by the results of the pit growth and polarization studies, pitting corrosion is an extremely complex, time-dependent phenomenon. The following analysis is a generalized and simplified explanation of the observed behavior of pitting attack. No attempt has been made to relate pitting corrosion to any specific theory of passivity. Indeed, this is one of the failings of many of the theories and explanations of this mode of attack. Instead, the analysis is based on the observed behavior of passive surfaces. Actually, the fundamental mechanisms involved during the pitting attack of stainless steels will not be completely explained until the nature of the passive state is thoroughly understood. However, it is felt that a generalized analysis of pitting that is consistent with the known properties of the passive state will have a more lasting value than one which has been rationalized to include a particular theory of passivity.

(1) Mixed Potential Concept

Simply, the mixed potential concept states
that, if an electrode is immersed in a solution containing an oxidation-reduction system, its open circuit potential will depend on the electrochemical reactions which occur on its surface. If the electrode is chemically inert, its potential will be equal to the oxidation-reduction potential of the system. However, if the electrode is attacked by the solution, the open circuit potential will lie between the oxidation-reduction potential of the system and that of the metal dissolution reaction. This potential is termed the mixed potential. Associated with this potential is a local action current on the electrode surface which is equivalent to the corrosion rate of the metal.

The mixed potential concept was first proposed by Wagner and Traud (168) and has been discussed by Kolthoff and Miller (169) and Petrocelli (170). Recently, Stern and Geary (171) applied this concept to the analysis of polarization curve shapes. Although the mixed potential theory does not depend on the concept of discrete anodic and cathodic elements, this concept can be treated as a special case under the theory. In this analysis, the idea of local elements is used for the sake of simplicity.

(2) Local Action on Electrodes

The reversible oxidation-reduction potential of a ferric salt solution varies between approximately 0.65 and 0.75 volt (vs. S.C.E.) depending on the amount of ferrous ion present (172). However, the cathode electrode
potentials of the pit specimens were always observed to be much more active than this in ferric chloride solutions. Therefore, it is evident that the cathodic electrode potentials of a pit specimen are actually mixed potentials and local corrosion currents exist on its surfaces. Likewise, the pit anode potentials are also mixed potentials.

The electrochemical characteristics of pitting corrosion can be interpreted by three interdependent, instantaneous polarization curves as shown in Fig. 27. $E_a^0$ and $E_c^0$ are the reversible electrode potentials for the anodic and cathodic reactions. $I_a$ and $I_0$ are the currents flowing between the local elements on the electrode surfaces. $I_{corr.}$ is the corrosion current flowing between the two electrodes. $E_a$ and $E_c$ are the instantaneous open circuit electrode potentials. It is important to note that $E_a$ and $E_c$ are equal under steady state, open circuit conditions.

Fig. 27 is schematic and linear polarization diagrams have been chosen for purposes of simplicity. The first diagram represents the superposition of all the local action currents occurring on the pit anode. The second diagram portrays the current between the local elements on the cathode electrode surface. The last diagram illustrates the resulting instantaneous polarization behavior of the two electrodes. The first two diagrams were arbitrarily drawn. The final, resultant polarization diagram was constructed from the two local action diagrams by a method
described by Pope (173). Thus, the open circuit potential and the polarization behavior of a mixed potential electrode are directly related to the local cell reactions in its surface.

Fig. 28 schematically illustrates how the electrochemical characteristics of a mixed potential or corroding cathode change as a result of changes in its local cell action. The upper diagrams are local cell polarization diagrams corresponding to the second polarization diagram in Fig. 27. The lower curves are the resultant cathodic polarization curves. These correspond to the cathodic polarization curve in the final diagram pictured in Fig. 27. The anode area is the total area of the anodic elements on the surface. The cathodic area is the combined area of all the non-corroding cathodic elements. As the three cases illustrate, variations in local cell action have a pronounced effect on the electrochemical characteristics of a mixed potential cathode.

(3) Effect of Time and Current

The effects of time and corrosion current flow on the electrochemical behavior of pitting attack are mutually dependent. The time-dependent changes are dependent on the existence of corrosion current flow. Therefore, it is only possible to discuss the observed changes in terms of both of these variables.
The observed changes in electrochemical behavior that occurred during the progress of pitting attack are most unusual. The cathode electrode became more noble, while the anode became more active. This effect was not due to cathodic protection or anodic stimulation, since it persisted even during open circuit conditions. This persistence was only temporary, of course.

The causes of this unusual effect can be explained by referring to Fig. 28. Cases 2 and 3 illustrate that a reduction in the relative area of the anodic elements on a corroding cathode shifts its potential in the noble direction. This must have occurred during the progress of pitting attack. Time and current flow suppressed anodic sites on the cathode electrode surface. Since the reduction of the anodic area must be followed by an increase in the total cathodic area, the instantaneous cathodic polarization curves generally followed the behavior illustrated in case 3. The changes in the electrochemical behavior of the pit anode can be attributed to an increase in the relative anodic element area with time and current flow. Referring to Fig. 27 it is evident that, as pitting corrosion progresses, the local action polarization curves are constantly changing. $E_a$ and $E_0$ move further apart with time, while the values of $E_a^0$ and $E_0^0$ remain fixed. The reasons
why the local cell distribution changes with time and current flow is not known. It is obviously related to the destruction and repair of the passive surface state.

The change in the electrochemical activity of a metal surface with current flow and time has also been observed by Pearson (174). He found that the minimum cathodic current necessary to protect buried iron structures decreased with time. The iron surface became more noble with current flow and time. Recent studies by Pryor (175) and Pryor and Keir (176) with galvanic couples of aluminum-iron and zinc-iron have also demonstrated the enoblement of iron by cathodic currents. These investigators used instantaneous polarization techniques similar to those of the present investigation in many of their experiments (177).

The changes in the instantaneous polarization diagrams pictured in Figs. 17 to 22 are direct experimental evidence of the autocatalytic nature of pitting. Not only do these diagrams offer further proof for the conclusions of the current interruption experiments, but they illustrate the mode of this autocatalytic nature. Considering the pit anode, it is evident that the changes induced by time and current flow tended to increase pit activity.

Examination of the polarization diagrams obtained with pit specimens having reduced cathode electrode areas leads to an interesting conclusion. That is, the autocatalytic
nature of pitting corrosion is not restricted to action at the anode. Pitting corrosion produces self-stimulating electrochemical changes at both anode and cathode areas.

(4) Pit Anode Definition

Since the anode wire of the pit specimens did not corrode uniformly, it is evident that the shift of the anodic open circuit potential in the active direction is due to the enlargement of the corroding area with time. This introduces the question of defining the pit anode. If the pit anode is defined as that area on which only anodic reactions occur, then it would not be a mixed potential electrode. The open circuit potential of this electrode would equal $E_a^0$ in Fig. 27 and there would be no local action currents. The only effect of time and current flow would be a decrease in the slope of the anodic polarization curves. The instantaneous open circuit potential would remain constant. However, if the pit anode is defined so as to include some cathodic area, as in the present study, then an anodic potential shift would be observed with the passage of time and corrosion current. This definition is probably the more realistic since there are undoubtedly some rapidly corroding areas within pit cavities that also support cathodic reduction reactions.

It is interesting to note that it was particularly fortunate that the anode wire did not corrode uniformly.
If the wire corroded uniformly, it would have been impossible to observe the effects of anode area expansion during the progress of pitting.

(5) Pit Development

In view of the autocatalytic nature of pitting, it is quite evident that once started, a pit site causes changes which tend to promote its further growth. However, the question of how a pit site originates remains unanswered. From the literature and the results of this investigation, there is no reason to suspect that the condition leading to the formation of a pit site is fundamentally different from that which promotes growth—namely, the localized accumulation of halide ions. This initial accumulation could arise from any current flow occurring on the metal surface. Table VI lists numerous sources of such current flow. This does not deny the fact that there may be a fundamentally distinct pit initiation stage in the pitting corrosion process. However, since no experimental or theoretical justification for such a stage has been shown, it is pointless to introduce such a concept. It contributes nothing to the understanding of pitting phenomena.

3. Other Studies

1. Nitrate Inhibition Tests
Corrosion tests were performed to determine the amount of nitrate ion necessary to inhibit the pitting corrosion of Type 304 stainless steel exposed to various concentrations of ferric chloride. The results of these tests appear in Table XII. As shown in Part A, the amount of sodium nitrate necessary to prevent pitting in 10 percent ferric chloride solution was only 0.5 percent. This is much less than the 3 percent additions used by Uhlig (18) in his inhibition studies. However, it has been shown that nitrate ions are consumed in the inhibition process (14) and thus, greater amounts of sodium nitrate would be necessary to prevent pitting during long time exposures. Also, other tests, not reported herein, indicated that nitrate additions were not very effective in preventing crevice attack on 18-8 stainless steel surfaces. Hence, the results of the above studies are only applicable to freely exposed stainless surfaces.

The most interesting result of these tests was the almost constant nitrate/chloride ion ratios necessary to prevent pitting attack in the three ferric chloride concentrations tested. Considering the fact that the nitrate additions were arbitrarily chosen the agreement is excellent. One nitrate ion per approximately 20 chloride ions is sufficient to prevent the onset of pitting attack.
2. Pitting and Crevice Corrosion Tests

Because of the questionable pitting tendencies of many of the corrosives listed in Table III, tests were conducted to check the corrosivity of the following solutions:

- 10% alum
- 10% aluminum sulfate
- saturated aluminum sulfate
- 10% ferrous sulfate
- 10% ferric sulfate
- 40% formaldehyde
- 10% magnesium sulfate
- 10% nickel sulfate
- moist sodium acetate crystals

These particular solutions have been reported to cause pitting attack of 18-8 stainless steels (8). 3.5 x 0.5 inch specimens were cut from a 0.005 inch Type 304 stainless steel sheet (analysis given in Table XI). All of the specimens were ground with 400 grit emory and carefully washed and dried before testing. Two types of specimens were immersed in each solution. One was a flat sheet as described above while the other was crimped to produce a very thin crevice in the center of the specimen.

After a 30 day exposure at 80°F, none of the specimens showed any visible signs of pitting or crevice corrosion. Even microscopic examination failed to reveal any localized attack. Weight loss determinations were not performed. These tests seem to substantiate the predications (see, Pitting Corrosives) that many of the substances listed in Table III are not true pitting corrosives. There is a
possibility that a longer test duration might have produced some crevice attack or even pitting. However, it is more likely that the results reported in Table III were due to chloride contamination. The solutions used in this study were virtually chloride-free since reagent grade chemicals and double-distilled water were used in their preparation.
VI. RECOMMENDATIONS FOR FUTURE WORK

A review of the results of the present investigation indicates that the following suggestions might aid the planning of future studies of pitting corrosion.

A. Expansion of Artificial Pit Studies

1. The present studies of the pitting of Type 304 stainless steel in ferric chloride solutions should be continued.

   a. Transfer studies should be conducted to determine the effect of low pH values on the pitting tendency of ferric chloride solutions.

   b. Transfer and activation experiments should be performed to further substantiate the ion screening action of the halide ions. Ferric chloride solutions inhibited with chromate or perchlorate ions might be used.

   c. Tests should be made in very dilute ferric chloride solutions (0.01 molar or less) to determine the effect of electrolyte conductivity on pit growth, polarization characteristics, and cathodic current distribution.

   d. Instantaneous polarization measurements should be made during double pit interaction tests to determine the exact mode of pit interaction.
2. Pit growth and instantaneous polarization characteristics should be measured in other pitting systems.

a. Other oxidizing metal halides such as ferric bromide, cupric chloride, and mercuric chloride should be thoroughly investigated. Also, the unusual behavior of ferric bromide-chloride mixtures (22) might be explained.

b. Tests in non-oxidizing metal halides such as aluminum chloride, calcium chloride, sodium chloride and sodium bromide should be attempted. Exploratory tests in this investigation indicated that hydrogen peroxide additions to non-oxidizing metal halide solutions often produced appreciable pit specimen corrosion currents. High currents would eliminate area/perimeter interference during studies in these weakly pitting corrosives.

c. Tests with other stainless steel alloys should be conducted. The superior resistance of Type 316 and the "3P" (14, 15) stainless steels might be explained. Tests made in this investigation indicate that very severe pitting environments will probably be required to obtain self-sustaining pits of these materials.

d. Artificial pit tests could be conducted with pure iron, nickel, and chromium specimens. Such tests might facilitate the study and interpretation of the reactions involved in the pitting of stainless steels.
3. Indicator studies could be incorporated into artificial pit tests.
   
a. Suitable acid-base indicators could be used to determine the pH at the anode of a growing pit specimen. Microscopic observations of the wire anode could be used to detect color changes at pit sites. Possible correlations between corrosion current and anode pH might be obtained.

b. Cathodic current distribution under conditions of impressed current or during actual pit growth should be investigated. Radioactive tracers, acid-base indicators, or redox indicating techniques such as described by Wada (173) might be employed. Relations between corrosion current flow and cathodic current distribution could be developed.

B. Suggested Apparatus Modifications

1. The introduction of an auxiliary anode electrode into the pit specimen test cell would extend the usefulness of the artificial pit apparatus.

   a. An auxiliary electrode would permit the study of pit growth and instantaneous polarization behavior during external polarization of the pit specimen cathode. The external polarization of a pit specimen cathode is equivalent to the existence of other pit sites on its surface. However, this effect differs from that produced by cathode
area reduction in that the cathode electrode remains polarized during polarization measurements. Thus, the activity of a single pit can be related to the activity of other pits existing on the surface.

b. Pit interaction studies could be determined as a function of the activity of other pit sites.

c. Cathodic protection studies could be investigated by impressing a current between the pit specimen electrodes and the auxiliary anode. Changes in pit activity and polarization characteristics could be related to the impressed current intensity.

2. The present measuring circuit is cumbersome and difficult to manipulate. The varying pit activity necessitates continuous manual adjustment of the zero-resistance ammeter circuit.

a. The use of a self-balancing zero resistance ammeter such as described by Godard (165) or the electronic circuit developed by Makar and Francis (179) would greatly improve the present apparatus. Pit interaction tests could be performed on multiple anode pit specimens.

b. The development of an electronic interrupter circuit to measure instantaneous polarization behavior would also improve the present apparatus. If polarization curves could be determined in 0.1 or 0.01 second, the results would be much more accurate. If such a circuit
were used, the actual shape of instantaneous polarization curves could be accurately determined. Also, the electrochemical changes accompanying pit growth could be measured without disturbing the growth process.

3. The artificial pit specimens might be changed or improved to extend the scope of the artificial pit technique.

   a. Large macroscopic pits, such as used by Evans and Davies (151), could be used to study the electrochemical behavior of large, well developed pits in ferric chloride and other aggressive pitting corrosives.

   b. It might be possible to redesign the artificial pit specimens so that area/parameter ratio effects could be eliminated or compensated. Thus, it might be possible to study the non-oxidizing halides by this method.

   c. The artificial pit technique might serve as the basis for a pitting resistance test. Although test results are highly non-reproducible, a common basis might be devised for comparing the pitting resistances of various metals and alloys.

   d. From the good correlation between the results of corrosion tests and pit activation tests, a short-time pitting inhibitor test appears to be quite feasible.
C. New Studies

1. There is a pressing need for additional knowledge concerning pitting corrosives.
   a. A corrosion study should be made to determine what salts and anions are capable of supporting the pitting attack of stainless steels. At present, it is known that practically all soluble chloride and bromides definitely pit stainless steels. However, whether other anions can cause pitting attack is unknown. Theoretical interpretations of pitting mechanisms are hampered by this fact. The corrosives listed in Table III would be an excellent starting point for such a study.
   b. The pseudo-halides such as cyanide, cyanate, thiocyanate, and azide have physicochemical properties very similar to the halides (130). A survey of their properties and possibly experimental tests might show that they have pitting tendencies. If so, theoretical correlations between ionic properties and inherent pitting tendencies could be made.

2. Additional electrochemical experiments would be very useful in future studies.
   a. Transference and electrical conductivity measurements in very concentrated solutions should be made. The screening action of the halide ions may be largely due to their superior mobility in highly concentrated solutions.
Studies should also be made in solution mixtures to determine the relative ability of various ions (e.g. nitrate) to migrate through saturated or nearly saturated chloride salt solutions.

b. The micro solution potential technique (46, 143) might be applied to the sulfide and selenide inclusions in Type 303 stainless steel to explain the very low pitting resistance of this alloy.

c. The charging curve technique (113, 114) might be applied to stainless steel surfaces immersed in halide salt solutions. Such a technique might be very useful in observing and explaining surface reactions during pitting.

3. The effect of nitrate ion additions on growing pits could be investigated by making continuous weight loss measurements on stainless steel coupons immersed in ferric chloride (71). Sodium nitrate could be added to the system after pitting was in progress. Such tests would further substantiate the observations made with artificial pit specimens.

4. The effect of magnetic fields on the pitting attack of stainless steels might be studied. Ackerman's (40) concepts of magnetic effects (see: Theories of Pitting Corrosion) may provide explanations for the distribution of pitting attack and pit corrosion products. An exploratory
experiment performed in this investigation indicated that a magnetic field did influence the mode of attack of stainless steel immersed in sodium chloride solution. Further experiments should be performed.
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### TABLE I
Classification of Corrosion

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<th>General Corrosion</th>
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<table>
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<tr>
<th>Localized Corrosion</th>
<th>pitting</th>
<th>wide</th>
<th>medium</th>
<th>narrow</th>
<th>cracking</th>
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Source: Champion (1).
<table>
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<th>Materials</th>
<th>Environments</th>
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<tbody>
<tr>
<td>Aluminum</td>
<td>fresh waters, sea water chlorides, sulfates, nitrates</td>
</tr>
<tr>
<td>Copper and Cu-Zn Alloys</td>
<td>fresh waters, sea water</td>
</tr>
<tr>
<td>Iron and Steel</td>
<td>fresh waters, sea water</td>
</tr>
<tr>
<td>Lead</td>
<td>soils, dilute chloride solutions</td>
</tr>
<tr>
<td>Magnesium</td>
<td>sea water, HF, halides, sulfates, hypochlorites</td>
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<tr>
<td>Nickel and Ni-Cu Alloys</td>
<td>hypochlorites</td>
</tr>
<tr>
<td>Stainless Steels</td>
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<tr>
<td>Tin</td>
<td>halides, sulfates, nitrates, chlorates, perchlorates</td>
</tr>
<tr>
<td>Zinc</td>
<td>water, sea water</td>
</tr>
</tbody>
</table>

# TABLE III

Pitting Corrosives for Stainless Steels

| Acetic acid | Magnesium oxychloride |
| Acetic anhydride | Magnesium sulfate |
| Acetylene tetrachloride | Mercury chloride |
| Allyamine (vapor) | Manganese chloride |
| Alum | Lithium chloride |
| Aluminum sulfate | Monosodium glutamate |
| Ammonium chloride | Nickel chloride |
| Ammonium sulfate | Nickel sulfate |
| Ammonium stannichloride | Oleic acid |
| Ammonium thiocyanate | Phenol |
| Amyl acetate | Phthalic anhydride |
| Barium chloride | Potassium bromide |
| Boric acid | Potassium chloride |
| Calcium chloride | Potassium ferrocyanide |
| Calcium hypochlorite | Potassium ferriyanide |
| Carbon tetrabromide | Potassium hypochlorite |
| Carbon tetrachloride (wet) | Silver bromide |
| Chromic acid | Sodium acetate |
| Copper chloride | Sodium chloride |
| Ethylene dibromide | Sodium ferriyanide |
| Ferric chloride | Sodium fluoride |
| Ferric sulfate | Sodium hypochlorite |
| Ferric sulfate | Sodium sulfide |
| Formaldehyde | Sodium tetaborate |
| Fluoboric acid | Stannic chloride |
| Glutamic acid | Stannous chloride |
| Hydrogen sulfide | Trichloroethylene (wet) |
| Iodine (moist) | Fresh water (pH = 7, at 500°F) |
| Lactic acid | Sea water |
| Magnesium acid | Zinc chloride |
| Magnesium chloride |  |

**Sources:**
Nelson (7)
Crucible Steel Company (8).
### TABLE IV
Pitting of Stainless Steels by Bromides and Chlorides

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<tr>
<th>Solution</th>
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<td></td>
<td>18-8</td>
<td>18-8 Mo</td>
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<tr>
<td>10% FeCl₃</td>
<td>0.874</td>
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<tr>
<td>10% FeBr₃</td>
<td>0.352</td>
<td>0.0360</td>
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Source: Mahla and Nielsen (21).

<table>
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<td></td>
<td>18-8</td>
<td>18-8 Mo</td>
</tr>
<tr>
<td>1. 10% FeCl₃ - 0.05N HCL</td>
<td>1.10</td>
<td>0.122</td>
<td>0.0035</td>
</tr>
<tr>
<td>2. FeBr₃ 10%</td>
<td>1.02</td>
<td>0.042</td>
<td>0.042</td>
</tr>
<tr>
<td>3. No. 1 plus 100 gm NaBr/l</td>
<td>0.75</td>
<td>0.798</td>
<td>0.171</td>
</tr>
<tr>
<td>4. No. 1 plus 42.1 gm NaCl/l</td>
<td>1.03</td>
<td>0.530</td>
<td>0.0096</td>
</tr>
</tbody>
</table>

Source: Uhlig and Wulff (22).
## TABLE V

**Effect of Oxygen Pressure on the Corrosion of 18-8 Stainless Steels at 22° to 25° C**

<table>
<thead>
<tr>
<th>Oxygen Pressure (atmospheres)</th>
<th>Weight Loss (mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O</td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.04</td>
<td>0.0</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>0.2</td>
<td>0.25</td>
</tr>
<tr>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9.86</td>
<td>---</td>
</tr>
<tr>
<td>61.3</td>
<td>---</td>
</tr>
</tbody>
</table>

Source: Frese (29).
# TABLE VI

Sources of Potential Differences

<table>
<thead>
<tr>
<th>1. Potential Differences Associated with the Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Grain Boundaries</td>
</tr>
<tr>
<td>B. Orientation of Grains</td>
</tr>
<tr>
<td>C. Differential Grain Size</td>
</tr>
<tr>
<td>D. Differential Thermal Treatment</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2. Potential Differences Associated with the Metal Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Surface Roughness</td>
</tr>
<tr>
<td>B. Local Scratches or Abrasions</td>
</tr>
<tr>
<td>C. Difference in Shape</td>
</tr>
<tr>
<td>D. Differential Strain</td>
</tr>
<tr>
<td>E. Differential Pre-Exposure to Air or Oxygen</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3. Potential Differences Associated with the Corroding Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Differential Concentration or Composition</td>
</tr>
<tr>
<td>B. Differential Aeration</td>
</tr>
<tr>
<td>C. Differential Heating</td>
</tr>
<tr>
<td>D. Differential Illumination</td>
</tr>
<tr>
<td>E. Differential Agitation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4. Potential Differences Associated with External Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Contact with Dissimilar Metals</td>
</tr>
<tr>
<td>B. Complex Cells</td>
</tr>
<tr>
<td>C. Externally Applied Potentials</td>
</tr>
</tbody>
</table>

Source: Mears and Brown (53).
<table>
<thead>
<tr>
<th>Solution (0.5M)</th>
<th>$E_0$ (Standard)</th>
<th>Presence of Pits</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl$_3$</td>
<td>+0.77</td>
<td>yes</td>
</tr>
<tr>
<td>CuCl$_2$ (Cu$^{2+}$ + Cl$^-$ = CuCl)</td>
<td>+0.57</td>
<td>yes</td>
</tr>
<tr>
<td>SnCl$_4$</td>
<td>+0.15</td>
<td>no</td>
</tr>
<tr>
<td>NiCl$_2$ (no lower valence salt)</td>
<td>0.00</td>
<td>no</td>
</tr>
<tr>
<td>MnCl$_2$ (no lower valence salt)</td>
<td>0.00</td>
<td>no</td>
</tr>
<tr>
<td>TiCl$_4$ in 0.5N HCL</td>
<td>+0.04</td>
<td>no</td>
</tr>
<tr>
<td>CrCl$_3$</td>
<td>-0.4</td>
<td>no</td>
</tr>
</tbody>
</table>

Source: Uhlig (10).
<table>
<thead>
<tr>
<th></th>
<th>Oxygen Reduction</th>
<th>Metal Ion Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Examples:</strong></td>
<td>NaCl, NaBr, CaCl₂</td>
<td>FeCl₃, FeBr₃, CuCl₂</td>
</tr>
<tr>
<td></td>
<td>MgCl₂, AlCl₃</td>
<td>HgCl₂</td>
</tr>
<tr>
<td><strong>Relative Rate of Attack:</strong></td>
<td>slow</td>
<td>moderate to rapid</td>
</tr>
<tr>
<td><strong>Increasing Temperature:</strong></td>
<td>corrosion rate increases, then decreases. Maximum point</td>
<td>corrosion rate increases. No maximum point</td>
</tr>
<tr>
<td><strong>Increasing Concentration:</strong></td>
<td>corrosion rate increases, then decreases. Maximum point</td>
<td>corrosion rate increases. No maximum point</td>
</tr>
<tr>
<td><strong>Increasing O₂ Content:</strong></td>
<td>increases attack</td>
<td>negligible effect</td>
</tr>
<tr>
<td><strong>Effect of pH:</strong></td>
<td>low pH—general attack</td>
<td>solutions stable only at low pH</td>
</tr>
<tr>
<td></td>
<td>neutral pH—pitting</td>
<td>neutral and high pH—no attack</td>
</tr>
<tr>
<td></td>
<td>high pH—no attack</td>
<td></td>
</tr>
<tr>
<td><strong>Corrosion Products:</strong></td>
<td>usually insoluble</td>
<td>usually soluble</td>
</tr>
</tbody>
</table>
TABLE IX
Corrosion Products of Stainless Steels

Part A: Valences of Corrosion Products.
Divided cell: Stainless steel electrodes 8 x 8 cm.
Current: 1 amp for 30 minutes

<table>
<thead>
<tr>
<th>Anode</th>
<th>Electrolyte</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>18-8</td>
<td>4% NaCl</td>
<td>Cr$^+$</td>
<td>Fe$^+$</td>
<td>Ni$^+$</td>
</tr>
<tr>
<td>18-8</td>
<td>4% NaBr</td>
<td>Cr$^+$</td>
<td>Fe$^+$</td>
<td>Ni$^+$</td>
</tr>
<tr>
<td>18-8 Mo</td>
<td>4% NaCl</td>
<td>CrO$_4^{-2}$</td>
<td>Fe$^+$</td>
<td>Ni$^+$</td>
</tr>
<tr>
<td>18-8 Mo</td>
<td>4% NaBr</td>
<td>Cr$^+$</td>
<td>Fe$^+$</td>
<td>Ni$^+$</td>
</tr>
</tbody>
</table>

Part B: Composition of Corrosion Products.
Divided cell: Stainless steel electrodes
Current: 0.5 amp for 2 hours, anode current density: 0.0108 amp/cm$^2$

<table>
<thead>
<tr>
<th>Alloy Analysis</th>
<th>Solution Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr 18.17</td>
<td>Cr/Ni = 2.04</td>
</tr>
<tr>
<td>Ni 8.94</td>
<td></td>
</tr>
<tr>
<td>Fe 72.07</td>
<td>Fe/Ni = 8.07</td>
</tr>
</tbody>
</table>

Source: Uhlig and Wulff (22).
### TABLE X

#### Summary of Anion Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>H(_2)O</th>
<th>F(^-)</th>
<th>Cl(^-)</th>
<th>Br(^-)</th>
<th>I(^-)</th>
<th>OH(^-)</th>
<th>NO(_3)^-</th>
<th>ClO(_4)^-</th>
<th>SO(_4)^-</th>
<th>O(^-)</th>
<th>S(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geom. Structure</td>
<td>trian.</td>
<td>trian(91)</td>
<td>tetr.</td>
<td>tetr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r_x) (Å)</td>
<td>0.97</td>
<td>1.34</td>
<td>1.91</td>
<td>1.95</td>
<td>2.17</td>
<td>1.54</td>
<td>(1.18)*</td>
<td>(1.51)**</td>
<td>(2.15)**</td>
<td>1.4</td>
<td>1.34</td>
</tr>
<tr>
<td>a (Å x 10(^2))</td>
<td>1.5</td>
<td>1.0</td>
<td>3.7</td>
<td>4.3</td>
<td>7.6</td>
<td>(2.3)</td>
<td>3 x 1.5</td>
<td>4 x 1.3</td>
<td>4 x 1.5</td>
<td>(3)</td>
<td>10</td>
</tr>
<tr>
<td>(\mu) (Debye)</td>
<td>1.87</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E) (volt)</td>
<td>4.1</td>
<td>3.8</td>
<td>3.5</td>
<td>3.2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I) (volt)</td>
<td>17.42</td>
<td>13.01</td>
<td>11.84</td>
<td>10.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(x) (volt)</td>
<td>4.0</td>
<td>3.0</td>
<td>2.8</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(D) (volt)</td>
<td>2.75</td>
<td>2.47</td>
<td>1.97</td>
<td>1.54</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E_H) (25°C)</td>
<td>2.9</td>
<td>1.36</td>
<td>1.08</td>
<td>0.54</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(l\text{o}(180\°C))</td>
<td>146</td>
<td>65</td>
<td>67</td>
<td>66</td>
<td>166</td>
<td>61.4</td>
<td>58.4</td>
<td>2 x 67.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(W_x) (volt)</td>
<td>4.0</td>
<td>2.8</td>
<td>2.3</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H. N.</td>
<td>5</td>
<td>2</td>
<td>1.5</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8</td>
</tr>
</tbody>
</table>

* G1-0 for two electrons
** S-0
*** 0-0 (92)

- \(r_x\) = crystal ionic radius
- \(a\) = ionic polarizability
- \(\mu\) = permanent electric moment
- \(E\) = electron affinity
- \(I\) = ionization potential (92)
- \(x\) = electronegativity (92)
- \(D_0\) = energy of molecular dissociation
- \(E_H\) = reversible electrode potential
- \(l\text{o}\) = reversible electrode potential
- \(W_x\) = equivalent conductance at dilution
- \(H. N.\) = energy of solvation of gaseous ion

Source: Piontellii (90)--Modified
## TABLE XI
Composition of Materials

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Form</th>
<th>Percent Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>Type 304 Stainless Steel</td>
<td>0.005 in. wire</td>
<td>18.68</td>
</tr>
<tr>
<td>Type 304 Stainless Steel</td>
<td>0.010 in. wire</td>
<td>18.72</td>
</tr>
<tr>
<td>Type 304 Stainless Steel</td>
<td>0.020 in. wire</td>
<td>18.65</td>
</tr>
<tr>
<td>Type 304 Stainless Steel</td>
<td>0.031 in. wire</td>
<td>18.85</td>
</tr>
<tr>
<td>Type 304 Stainless Steel</td>
<td>0.005 in. wire</td>
<td>18.74</td>
</tr>
<tr>
<td>Type 316 Stainless Steel</td>
<td>0.010 in. wire</td>
<td>17.33</td>
</tr>
<tr>
<td>Type 316 Stainless Steel</td>
<td>0.030 in. sheet**</td>
<td>16-18</td>
</tr>
</tbody>
</table>

* Nominal Composition

**Cold-rolled to 0.011 inch prior to use in artificial pits.
### TABLE XII

**Inhibition of Pitting in Ferriox Chloride by Sodium Nitrate Additions**

**Specimen:** Type 304 stainless steel, 3.5 x 0.5 x 0.005 inches. (See Table XI for composition.)

**Exposure:** 3 days in 120 ml. of solution

#### A. 10% FeCl₃ · 6H₂O (0.387 molar)

<table>
<thead>
<tr>
<th>Percent NaNO₃ (by weight)</th>
<th>Molar Concentration</th>
<th>Presence of Pits</th>
<th>Weight Loss (mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.000</td>
<td>yes</td>
<td>evident attack</td>
</tr>
<tr>
<td>0.10</td>
<td>0.012</td>
<td>yes</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.20</td>
<td>0.025</td>
<td>yes</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.30</td>
<td>0.037</td>
<td>yes</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.40</td>
<td>0.049</td>
<td>yes</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.50</td>
<td>0.062</td>
<td>no</td>
<td>1.8</td>
</tr>
<tr>
<td>0.60</td>
<td>0.074</td>
<td>no</td>
<td>0.0</td>
</tr>
<tr>
<td>0.70</td>
<td>0.087</td>
<td>no</td>
<td>0.0</td>
</tr>
</tbody>
</table>

#### B. 0.2 Molar Ferriox Chloride

<table>
<thead>
<tr>
<th>Percent NaNO₃ (by weight)</th>
<th>Molar Concentration</th>
<th>Presence of Pits</th>
<th>Weight Loss (mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.000</td>
<td>yes</td>
<td>evident attack</td>
</tr>
<tr>
<td>0.10</td>
<td>0.012</td>
<td>yes</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.20</td>
<td>0.024</td>
<td>yes (1 sm. pit)</td>
<td>0.3</td>
</tr>
<tr>
<td>0.25</td>
<td>0.030</td>
<td>no</td>
<td>0.0</td>
</tr>
<tr>
<td>0.30</td>
<td>0.035</td>
<td>no</td>
<td>0.0</td>
</tr>
<tr>
<td>0.35</td>
<td>0.042</td>
<td>no</td>
<td>0.0</td>
</tr>
<tr>
<td>0.40</td>
<td>0.049</td>
<td>no</td>
<td>0.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.061</td>
<td>no</td>
<td>0.0</td>
</tr>
</tbody>
</table>
### TABLE XII (Continued)

#### C. 0.1 Molar Ferric Chloride

<table>
<thead>
<tr>
<th>Percent NaNO₃ (by weight)</th>
<th>Molar Concentration</th>
<th>Presence of Pits</th>
<th>Weight Loss (mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.000</td>
<td>yes</td>
<td>evident attack</td>
</tr>
<tr>
<td>0.05</td>
<td>0.006</td>
<td>yes</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.10</td>
<td>0.012</td>
<td>yes</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.15</td>
<td>0.018</td>
<td>no</td>
<td>0.0</td>
</tr>
<tr>
<td>0.20</td>
<td>0.024</td>
<td>no</td>
<td>0.0</td>
</tr>
<tr>
<td>0.25</td>
<td>0.036</td>
<td>no</td>
<td>0.0</td>
</tr>
<tr>
<td>0.30</td>
<td>0.042</td>
<td>no</td>
<td>0.0</td>
</tr>
<tr>
<td>0.35</td>
<td>0.048</td>
<td>no</td>
<td>0.0</td>
</tr>
</tbody>
</table>

#### D. Maximum Amount of Nitrate Needed to Inhibit

<table>
<thead>
<tr>
<th>Ferric Chloride Concentration</th>
<th>Minimum Nitrate Concentration</th>
<th>Minimum NO₃/Cl⁻ Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.387 molar</td>
<td>0.062 N</td>
<td>1:19</td>
</tr>
<tr>
<td>0.20 molar</td>
<td>0.030 N</td>
<td>1:20</td>
</tr>
<tr>
<td>0.10 molar</td>
<td>0.018 N</td>
<td>1:17</td>
</tr>
</tbody>
</table>
Fig. 1 The Artificial Pit Specimen

Wire Anode

Cold Setting Plastic

Cathode

Insulated Leads
Fig. 2. Artificial Pit Specimen Top Surface
Fig. 3 Test Assembly

- Gas inlet
- Electrical Connection
- Gas exit
- Rubber stopper
- Fritted glass gas dispersion tube
- Glass support rods
- Teflon specimen support
Fig. 4. Artificial Pit Test Cell

Fig. 5. Close-Up View of Specimen Holder
Fig. 6 Circuit Diagram for Artificial Pit Studies

6V

"Bleeder Resistor"

Current Controls

Anode → Cathode

S.C.E. Sat'd KCl

String Bridge

Artificial Pit

Precision Resistor

Potential

Current

Potentiometer
Fig 7  Growth of an Artificial Pit in 0.1M FeCl₃ + 0.08N HCl

Cathode Area: 1.0 Sq in  Anode Wire Dia.: 20 Mils
Fig. 8 Current Decay of an Artificial Pit During Open Circuit Conditions (Points are instantaneous Readings)
Cathode Area: 1.0 in$^2$  Anode Wire Diam.: 20 Mils.
Fig. 9 Pit Interaction During Growth in 0.2M FeCl₃ + 0.05N HCl
Cathode Area: 0.005 in.² Anode Wire Diam.: 20 Mils.
Anode Separation: 0.038 in. (Center to Center)
Fig. 10 Transfer Studies in Ferric Sulfate
Cathode Area: 1.0 in.²    Anode Wire Diam.: 31 Mils.

Current (Microamperes)

0.1M FeCl₃ + 0.08N HCl
0.1M Fe₂(SO₄)₃

Time in Minutes
Fig. 11 Transfer Studies in Ferric Perchlorate
Cathode Area: 1.0 In.  Anode Wire Diam.: 10 Mils.

- \(0.1\overline{M} \text{FeCl}_3 + 0.08\overline{M} \text{HCl}\)
- \(0.1\overline{M} \text{Fe(ClO}_4)_3 + 0.01\overline{M} \text{HClO}_4\)
Fig. 12 Transfer Studies in Ferric Chloride
Cathode Area: 1.0 in²  Anode Wire Diam.: 31 Mil.

- 0.2M FeCl₃ + 0.05N HCl
- 0.3M FeCl₃ + 0.05N HCl
Fig. 13 Transfer Studies in Chloride Salt Mixtures

Cathode Area: 1.0 in.$^2$  Anode Wire Diam. 20 Mils.

- $0.10\text{M FeCl}_3 + 0.08\text{N HCl}$
- $0.05\text{M FeCl}_3 + 0.05\text{M AlCl}_3 + 0.07\text{N HCl}$
- $0.05\text{M FeCl}_3 + 0.15\text{M NaCl} + 0.11\text{N HCl}$
Fig 14 Transfer Studies in a Ferric Chloride—Sulfate Mixture
Cathode Area: 1.0 in²   Anode Diam.: 20 Mil.

- 0.1M FeCl₃ + 0.08N HCl
- 0.05M FeCl₃ + 0.02N Fe₂(SO₄)₃
**Fig 15** Transfer Studies in Ferric Chloride–Sodium Nitrate Mixtures
Cathode Area: 1.0 in.²  Anode Wire Diam.: 10 Mils.

![Graph showing current changes over time for different concentrations of FeCl₃ and NaNO₃.]

- **○** 0.1 M FeCl₃ + 0.08 M HCl
- **○** 0.1 M FeCl₃ + 0.5 M NaNO₃
- **○** 0.1 M FeCl₃ + 1.0 M NaNO₃

**Current (Microamperes)**

**Time in Minutes**
Fig. 16 Instantaneous Polarization Curves in $0.2\text{M FeCl}_3 + 0.05\text{N HCl}$

Cathode Area: 1.0 in.$^2$  Anode Wire Diam.: 31 Mils.

- Measured Anodic Potentials
- Measured Cathodic Potentials
- Calculated Cathodic Potentials

$(E_c = E_a - \Delta E)$
Fig. 17 Effect of Time on Instantaneous Polarization Curves in 0.2M FeCl$_3$ + 0.05N HCl
Cathode Area: 1.0 in$^2$  Anode Wire Diam.: 20 Mils.

Increasing Time 1 to 10
Fig. 18 Effect of Time on Instantaneous Polarization
Curves in 0.2M FeCl₃ + 0.05N HCl
Anode Wire Diam.: 20 Mil. Cathode Area: 0.25 in.²
Fig. 19 Effect of Time on Instantaneous Polarization Curves in 0.2 M FeCl₃ + 0.05 M HCl

Cathode Area: 0.020 in.² Anode Wire Diam.: 20 Mils.

Increasing Time 1 to 10
Fig. 20 Effect of Time on Instantaneous Polarization Curves in 0.2M FeCl₃ + 0.05N HCl
Cathode Area: 0.013 in.²  Anode Wire Diam.: 31 Mil.
Fig. 21 Effect of Time on Instantaneous Polarization Curves in 0.2 M FeCl$_3$ + 0.05 M HCl
Cathode Area: 0.003 in.$^2$, Anode Wire Diam: 20 MIL.
Fig. 22 The Shape of Instantaneous Polarization Curves in 0.2 M FeCl₃ + 0.05 M HCL.

Cathode Area 0.006 in², Anode Wire Diameter 20 mils.

Increasing Time
1 to 2

- Measured Cathodic Potentials
- Calculated Anodic Potentials

\( E_a = E_c + \Delta E \)
Fig. 23 Changes in Instantaneous Polarization Curves During Transfer from Ferric Chloride to Chloride-Sulfate Mixture
Cathode Area: 1.0 in.², Anode Wire Diam: 20 Mil.

1. $0.2\text{M FeCl}_3 + 0.05\text{N HCl}$

2. $0.1\text{M FeCl}_3 + 0.05\text{M Fe}_2(\text{SO}_4)_3$

Transferred from Ferric Chloride When Pit Activity was 94 Microamperes
Fig 24  Effect of Anode—Cathode Separation on Instantaneous Polarization Curves in 0.2M FeCl₃ + 0.05N HCl
Cathode Area.: 1 In²  Anode Wire Diam.: 20 Mils.
Separation: 0.120 In.
Fig. 25  Effect of Anode–Cathode Separation on Instantaneous Polarization Curves in 0.2 M FeCl₃ + 0.05 M HCl
Cathode Area: 0.120 in.²  Anode Wire Diam.: 20 Mils
Separation: 0.120 in.

Increasing 1 to 2
Time
Fig. 26 Impressed Current Cathodic Polarization Curves For Pit Specimens Immersed in 0.1M Ferric Sulfate.

- 0.25 in$^2$ Cathode Area
- 1.0 in$^2$ Cathode Area
Fig. 27 Relation Between Local Action at Pit Anode and Cathode and Overall Polarization Behavior.

Local Action at Pit Anode

Local Action at Pit Cathode

Resultant Polarization Diagram for Pit

- Local Action at Pit Anode
  - $E_a^0$ to $E_a^-$
  - $E^a$ to $E_a^-$

- Local Action at Pit Cathode
  - $E_c^0$ to $E_c^-$
  - $E^c$ to $E_c^-$

- Resultant Polarization Diagram for Pit
  - $E_a$, $E_c$, and $E_{corr}$
Fig. 28 Effect of Varying Anode and Cathode Areas on the Polarization Characteristics of a Corrodinig Cathode (Schematic)

Case 1: Anode and Cathode Areas Increase Proportionately

Case 2: Anode Area Decreases, Cathode Area Remains Constant

Case 3: Cathode Area Increases, Anode Area Remains Constant.
I, Norbert D. Greene, Jr., was born on September 7, 1931, in Rochester, New York. I received my secondary school education in the public schools of that city. From 1949 to 1953, I attended the University of Rochester, where I received the degree of Bachelor of Science in Chemical Engineering in June, 1953. In 1954, I received the degree of Master of Science in Metallurgy from The Ohio State University. In 1953, while in residence at The Ohio State University, I received an appointment as a Research Fellow which I held until 1955, when I was appointed a Research Associate. I held this appointment for two years while completing the requirements for the degree of Doctor of Philosophy.