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PASSIVITY OF IRON AND ITS BREAKDOWN IN ALKALINE SULFIDE SOLUTIONS

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PASSIVITY OF IRON AND ITS BREAKDOWN IN ALKALINE SULFIDE SOLUTIONS

by

JOSE RAFAEL VERA

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE DOCTOR OF PHILOSOPHY

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HOUSTON, TEXAS

MAY 1984
ABSTRACT

PASSIVITY OF IRON AND ITS BREAKDOWN

IN ALKALINE SULFIDE SOLUTIONS

by

Jose Rafael Vera

The passivity of iron in borate buffer solutions and its breakdown in presence of sulfide ions was studied using standard electrochemical techniques (e.g., galvanostatic, potentiodynamic, potentiostatic) and complemented with microscopic examination and electron microprobe analysis of the surface. Mass transport effects and the nature of dissolved species were investigated using rotating disc and ring-disc electrodes. The electronic properties of the oxide film, and their relationship with the breakdown of passivity, were studied using photoelectrochemical techniques.

Initial passivation of iron in sulfide-containing solutions is due to coverage of the surface by an iron(II) oxide phase, which competes with the formation of a non-protective iron sulfide (mackinawite) film. The passive layer is gradually converted into non-stoichiometric $\gamma$-$\text{Fe}_2\text{O}_3$. This oxide is an n-type semiconductor. At higher positive potentials, mackinawite is oxidized to $\text{Fe}_2\text{O}_3$ and $\text{S}$. Sulfur can also be produced by direct oxidation of $\text{HS}^-$, and $\text{FeS}_2$ (pyrite) can precipitate from the solution.

The resistance of the passive film to breakdown is affected not only by its thickness, but also by its composition (expressed as
deviation from stoichiometry). Both are controlled by the potential at which the electrode is passivated and the time of passivation prior to sulfide injection.

The mechanism of localized corrosion on passive iron is associated to the formation of mackinawite patches on the surface. The extent of corrosion is determined by the kinetics of nucleation and growth of mackinawite.

The nucleation of mackinawite patches, is a fast process related to the adsorption of HS⁻ on weak spots of the passive film. The growth of the nuclei occurs by dissolution of the adjacent oxide, and its rate is controlled by the diffusion of Fe(II) species away from the surface.

Pitting corrosion occurs underneath the mackinawite deposits by a mechanism similar to that of crevice corrosion.
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I INTRODUCTION

Passivity can be defined as a decrease in the corrosion rate of a metal in a given environment under conditions where it has a marked thermodynamic tendency to react [1]. Observations of passivity on iron have been reported since 1782 [2-4], but the first theory of passivity was developed by Faraday [5] in 1834. His basic postulate, that a surface oxidative process is a fundamental requirement of passivity, has proved to be essentially correct.

In the last century, a great deal of effort has been dedicated to the study of the chemical composition, crystallographic structures, and physical and electronic properties of the passive film [6-11]. However, controversy still continues regarding not only these problems, but also the mechanism that leads to passivity. It is generally agreed that initial passivation can be best described in terms of adsorption of some oxygen-containing species, followed by the growth of a finite oxide phase. Previous studies performed in this laboratory have corroborated the formation of an oxide film with semiconductor properties on iron passivated in borate buffer [12,13]. The corrosion resistance of the metal depends on the composition and thickness of this passive film.

The thermodynamic equilibria at the metal/film/electrolyte interface can best be analyzed using potential vs. pH (E/pH) diagrams, also called "Pourbaix diagrams" [14]. This diagram defines domains of stability beyond which the system is thermodynamically unstable. Whether the system remains in an unstable condition or reverts to a stable state is a question that can only be answered by examining the
kinetics of the reaction and the associated activation energies.

Figure 1 presents a schematic Pourbaix diagram of iron in pure water showing the areas of immunity, corrosion and passivity [14]. If the metal is in the "immunity" area, the metal is stable as Fe, i.e. no corrosion or formation of surface films occur. In the area marked "corrosion", the metal tends to dissolve as soluble Fe$^{2+}$ species and there is no thermodynamic reason for the corrosion to stop. Finally, if the metal is in the area marked "passivity", an insoluble iron oxide (or hydroxide) film would form on the metal surface and, when completely covered, metal corrosion would be inhibited.

Passivity can be induced by a variety of mechanisms, e.g., oxidizing inhibitors and anodic polarization [14,15]. For the purposes of this thesis, the discussion will be limited to electrochemical passivation via anodic polarization.

Figure 2 illustrates a typical potentiostatic anodic polarization (current vs. potential) curve for iron.

Metal dissolves as Fe$^{2+}$ in the region AB. This portion of the curve is referred to as the active region. If the metal remained active, the anodic current, which is proportional to the corrosion rate, would continue to increase exponentially with the applied potential (point C). The onset of passivity is observed by a sharp decrease in the anodic current by several orders of magnitude.

This type of polarization curve was first obtained by Flade [16] and the critical potential of transition from passive to active is known as the "Flade potential", $E_p$. Unfortunately, this term now has a variety of connotations. Many investigators, following Flade's original
FIGURE 1

Schematic Potential vs. pH Diagram

of the System Fe-H2O
FIGURE 2

Schematic Current/Voltage Curve of Iron

in Alkaline Solutions
definition, assign this name to the potential at which an already passivated metal begins to lose passivity [17-19]. Some authors, however, prefer to assign this term to the passivation potential (point D) at which the current is maximal [20], or even to the point B where the oxygen begins to adsorb on the metal surface [21]. All discussions in this report will refer to the original definition of \( E_p \), a value which is slightly anodic to the potential of complete passivation (point E).

The potential region between E and F is called the "passive region" and the current density in this region is the passive current, \( i_{\text{pas}} \). The region positive to F, where either oxygen evolution or another oxidation reaction occurs, is the transpassive region.

The successful commercial and industrial use of non-noble metals, such as iron, aluminum, titanium and their alloys, is based on their passivation properties. Breakdown of passivity is the principal reason for corrosion failures, such as pitting, stress corrosion cracking, crevice corrosion, intergranular corrosion, corrosion fatigue, etc. It is, therefore, of crucial importance to be able to understand the process that produces these most damaging forms of corrosion in order to develop ways to control them.

The passive layer can be destroyed by mechanical, chemical or electrochemical means. However, in the absence of "aggressive" ions (e.g., chlorides, sulfides) the metal surface usually repassivates and no localized corrosion occurs. In this work, only the passivity breakdown caused by the presence of sulfide ions in the solution will be considered.
Corrosion of iron (or mild steel) in aqueous solutions containing sulfide ions is a significant technical problem in the oil and gas industry [22-26], in the production of heavy water by the Girdler-Sulfide process [27], in the pulp and paper industry [28] as well as in the corrosion caused by sulfate reducing bacteria [29].

The nature of the iron sulfides produced during iron corrosion in sulfide solutions, and their relative effect in the uniform corrosion of iron based alloys have been subject of numerous studies and reviews [30,31]. Depending on the system conditions and exposure time, sulfide compounds with different stoichiometries or crystal structures can be found. Some of these compounds are: mackinawite (Fe₇₅S with x = 0.057 to 0.064), pyrrhotite (Fe₁₋ₓS with x = 0.14 to 0.00), troilite (hexagonal FeS), marcasite (orthorhombic FeS₂), and pyrite (cubic FeS₂) [31]. The iron sulfide compounds most commonly found in corrosion deposits are mackinawite [32-35] and pyrite [32,33]. Crystallographic studies, necessary to distinguish polymorphs of the same general composition, were out of the scope of this research. Therefore, for purposes of this work, the term "pyrite" will in general refer to a ferrous disulfide, and the term "mackinawite" to a non-stoichiometric ferrous monosulfide. For simplicity, they will be adverted as FeS₂ and FeS respectively.

The electrochemical behaviour of iron in the presence of soluble sulfide species is very complex and has been extensively studied under a wide variety of environmental conditions (pH, temperature, sulfide concentration, aeration) [36-48].
A number of E/pH diagrams for the iron-sulfur-water system at 25 °C has been reported [49-52]. This system consists of many solid compounds and dissolved species. For example, at room temperature, seven crystalline phases of hydrated ferric sulfate, ten mineral iron sulfides, six ferrous and ferric oxides and eight aqueous iron species have been reported [53]. Consequently, the complete E/pH diagram for the Fe-S-H₂O system is exceedingly complex, and it is usual to select the species that are specific to the problem of interest. Accordingly, for corrosion studies at room temperature, the following species were selected: S, FeS₂, FeS, Fe₂O₃, Fe³⁺, Fe²⁺, H₂S(aq), HS⁻, S²⁻, and SO₄²⁻.

Figure 3 presents an E/pH diagram for iron in water containing 10⁻¹ M of total dissolved sulfur. Bouet and Brenet [52] used this diagram to ascertain the regions of potential corrosion of iron in a sulfide environment, considering that all iron sulfides and oxides were passivating. In this case, the region of assumed passivity in the presence of sulfides extends over a larger range of potential and pH than that for passivation in pure water (cf. Figure 1). Therefore, corrosion would appear to be less likely where sulfide is present. However, the iron sulfide films are, in general, not as protective as the oxide films and true passivity is not maintained. Besides, local destruction of the passive film can occur even in the region of stability of the iron oxide.

In alkaline sulfide solutions, the anodic polarization of iron is characterized by, at least, two anodic current peaks (cf. Figure 4). The first peak appears in the same active-passive transition potential
FIGURE 3

Schematic Potential vs. pH Diagram

of the System Fe–S–H₂O
FIGURE 4

Schematic Current/Voltage Curve of Iron in Alkaline Sulfide Solutions
range as in sulfide-free solutions. It was originally assigned to the formation of a protective layer of pyrite on the electrode surface [43-45]. More recent voltammetric studies [36,37] showed that this peak is most probably due to the formation of a defective oxide layer [48]. The second anodic current peak occurs at potentials ~ 0.4 V more positive than the active-passive transition peak and is absent in sulfide-free solutions. For this reason, several authors assigned this peak to the oxidation of sulfide ions [45-48], and others to the oxidation of pyrite to magnetite and of sulfide to sulfate [44]. Conversely, this peak has also been ascribed to the onset of pitting [36,39,40].

Considerably less work has been directed towards an understanding of the passivity breakdown of iron in alkaline sulfide solutions.

Shoesmith et al [36] suggested that the passivity breakdown in strongly alkaline (pH > 12) sulfide solutions was related to the dissolution of Fe$^{3+}$ at potentials positive to the second peak, forming a soluble ferric sulfide complex. No sulfide film was formed on the surface at this pH, but in a later work at lower pH, mackinawite patches were observed [37]. The nucleation of these patches was assumed to start at fault sites in the pre-formed oxide layer, by direct reaction of the metal with HS$^{-}$ [37]. The spread of the nuclei across the surface was controlled by the dissolution of the oxide film due to a local decrease in pH [37]. No data on pit morphology nor experimental evidence of potentials related to passivity breakdown were reported.
It has been shown recently that nucleation and growth of mackinawite occurs during pitting corrosion of iron not only in highly alkaline sulfide solutions, but also in phosphate-borate-sulfide solutions (pH = 8.0) [39,40]. Isolated pits were reported to initiate beneath the mackinawite film [40], but the kinetics of mackinawite formation could not be discriminated from that of pitting corrosion. In neutral solutions, pit initiation was ascribed to the formation of two-dimensional iron sulfide islands on the metal surface [40], similar to the mechanism proposed for halide containing solutions [54].

Most of these investigations were performed on iron (or mild steel) passivated in the presence of sulfide ions, and the effect of the composition and thickness of the passive film on the passivity breakdown process were not considered. It has been suggested, however, that film composition plays an important role in the pitting process in sulfide solutions [40].

Summarizing, the evidence regarding the electrochemical behaviour of iron in alkaline sulfide solutions is still inconclusive and, in some cases, contradictory. There is scarce information about the initial steps of the corrosion process leading to the passivity breakdown although it is believed to be related to the formation of mackinawite patches. The relationship between the kinetics of nucleation and growth of mackinawite and the initiation of pitting corrosion is not clear. And finally, the kinetics of localized corrosion and the formation of iron sulfide on passive iron have not been fully studied.
The main objective of this research was to obtain a better understanding of the process of passivity breakdown of iron in alkaline sulfide solutions, with more emphasis on the kinetics of iron sulfide formation and pitting initiation on passive iron. The initiation of breakdown of passivity was of major concern because it usually determines whether or not a metallic structure will fail by localized corrosion, under given conditions. Once the passivity has been locally destroyed, different forms of accelerated localized corrosion can occur.

On the basis of the previous results, this investigation was directed towards the following goals:

1. To understand better the electrochemical behavior of iron in alkaline sulfide solutions.
2. To identify positively the process leading to localized corrosion on passive iron.
3. To study the kinetics of nucleation and growth of iron sulfides and their relationship with the passive film thickness and composition.
4. To propose a mechanism for the localized corrosion beneath the sulfide deposits.

In order to fulfill these objectives, standard electrochemical techniques (e.g., potentiodynamic, potentiostatic, galvanostatic) were used on both static and rotating electrodes, and were complemented with microscopic examination and electron microprobe analysis. In addition, a photoelectrochemical technique was used to study the effect of the oxide film properties on the passivity breakdown process.
II. THEORY

II.1 KINETICS OF ELECTROCHEMICAL REACTIONS

Usually, when studying corrosion one is not so much concerned with the conditions for thermodynamic stability, but rather with the rate of attack and how it may be controlled.

The thermodynamic analysis of a reaction, based on the knowledge of initial and final states, is not enough to predict its reaction rate. In order to understand the kinetics of a given reaction, it is necessary to determine the reaction mechanism, which usually comprises several intermediate steps.

Corrosion reactions of metals in contact with an electrolyte are generally electrochemical in nature [55,57]. An electrochemical reaction differs from a chemical reaction in that at least one of the steps that make up the electrochemical over-all reaction must involve a charge (ion or electron) transfer.

Therefore, fundamental studies of electrochemical kinetics have applications in corrosion, although the occurrence of several (at least two) simultaneous reactions makes the application complex.

In this section, the principles of electrochemical kinetics will be briefly described.
SINGLE-ELECTRON CHARGE TRANSFER REACTIONS

Consider a general single-electron reaction occurring on a metal surface in an aqueous solution

\[ 0 + e^- \underset{\text{R}}{\overset{\text{R}}{\rightleftharpoons}} \]  \hspace{1cm} (1)

where the forward reaction is the reduction of an oxidized species 0, and the back reaction is the oxidation of the reduced species R. In a typical corrosion reaction, the reduced species is the metal (e.g., Fe) and the oxidized species is the corrosion product (e.g., Fe\(^{2+}\)).

The reaction rate, according to Faraday's law, is proportional to the total current through the electrode

\[ r = \frac{i}{nF} \] \hspace{1cm} (2)

where \( r \) is the rate of the heterogeneous reaction (e.g., moles \( \text{cm}^{-2} \cdot \text{s}^{-1} \)), \( n \) is the number of electrons transferred, \( i \) is the current density (A/cm\(^2\)), and \( F \) is the Faraday's constant \(^{\ast} \). In general, \( i \) has a cathodic, \( i_- \), and an anodic, \( i_+ \) component

\[ i = i_+ - i_- \] \hspace{1cm} (3)

where \( i_- \) is associated with the reduction reaction (negative by convention) and \( i_+ \) with the oxidation reaction.

If one considers the electrode process (1) to be an elementary reaction and the mass transport process to be fast, then the non-equilibrium current follows the Butler-Volmer equation [20,58]

\(^{\ast} \) See Appendix 1 for definition of symbols and their units.
\[ i = F k^o C_R \exp[(1-\beta)FE/RT] - F k^o C_0 \exp[-\beta FE/RT] \]  

(4)

where \( k^o_+ \) and \( k^o_- \) are the anodic and cathodic rate constants when the applied potential \( E \) is equal to 0 V (SCE); \( C_0 \) and \( C_R \) are the concentrations of the oxidized and reduced species; and \( \beta \) is the transfer coefficient \((0 < \beta < 1)\).

At the equilibrium potential \( E^o \), the anodic reaction rate is equal to the cathodic reaction rate

\[ F k^o C_R \exp[(1-\beta)FE^o/RT] = F k^o C_0 \exp[-\beta FE^o/RT] = i^o \]  

(5)

where \( i^o \) is called the exchange current density. If one now defines the activation overvoltage \( \eta \) as

\[ \eta = E - E^o \]  

(6)

then the following form of the Butler–Volmer equation is obtained from (4) and (5)

\[ i = i^o \{ \exp[(1-\beta)F\eta/RT] - \exp[-\beta F\eta/RT] \} \]  

(7)

This equation is valid only if a pure charge-transfer reaction is involved, and the surface concentrations are independent of current density and potential.

For \(|\eta| > 0.12 \text{ V} \) (high field approximation) one of the terms of equation (7) becomes negligible and the current shows an exponential dependence on overpotential. From the slope of a \( \log i \) vs. \( \eta \) plot (Tafel slope) the value of the transfer coefficient \( \beta \) can be found. For \( \eta < -0.12 \text{ V} \):
\[
\frac{\partial n}{\partial \log i} = 2.303 \frac{RT}{F\beta}
\]

(8)

where \(2.303RT/F\) is equal to \(0.058\) V at \(298^o\text{K}\). Experience shows that \(\beta \sim 0.5\) for elemental one-electron transfer reactions on metals electrodes, i.e., Tafel slope \(\sim 0.12\) V.

For \(|\eta| < 0.01\) V (low field approximation), equation (7) predicts a linear behavior of current on \(\eta\), in such a way that \(i^0\) can be calculated from the slope:

\[
\frac{\partial i}{\partial \eta} = i^0F/RT
\]

(9)

MULTISTEP ELECTROCHEMICAL REACTIONS UNDER ACTIVATION CONTROL

Given an over-all reaction composed of several intermediate steps, one of these steps is usually much slower than the others. In the steady state, all the partial reactions must proceed at the rate of the slowest reaction, called for that reason the rate-determining step (rds). The total current is, then

\[
i = ni_{\text{rds}}
\]

(10)

where \(n\) is the number of single-electron transfer steps in the over-all reaction, and \(i_{\text{rds}}\) is the partial current due to the slowest step. The existence of a unique rds process usually implies that other steps are virtually in equilibrium.
Consider for example the following multistep reaction

\[ \begin{align*}
0 + e^- & \rightleftharpoons P & K_a &= k_a^0 / k_{a+}^0 \quad (11a) \\
P + e^- & \rightleftharpoons Q & K_b &= k_b^0 / k_{b-}^0 \quad (11b) \\
Q + e^- & \rightarrow R & k_{Q-}^0, k_{Q+}^0 \quad (11c)
\end{align*} \]

with an over-all reaction

\[ 0 + 3e^- \rightarrow R \quad (11d) \]

in which reaction (11c) is the single-electron transfer rds preceded by two single-electron steps.

From equation (10), the total current \( i \) is proportional to the current of the rds reaction, and therefore can be expressed in terms of the Butler-Volmer relation:

\[ i = 3F(k_{c+}^0 C_R \exp[(1-\beta)FE/RT] - k_{c-}^0 C_Q \exp[-\beta FE/RT]) \quad (12) \]

in which the concentration of the intermediate \( Q \) is given by the preceding equilibrium steps. By equating forward and backward rates for, e.g., in the second step,

\[ Fk_{b+}^0 C_Q \exp[(1-\beta)FE/RT] = Fk_{b-}^0 C_P \exp[-\beta FE^0/RT] \quad (13) \]

then

\[ C_Q = k_b C_P \exp(-FE/RT) \quad (14) \]

* The rds is usually represented by a single arrow. Fast reactions are represented by double arrows to indicate quasi-equilibrium.
where $K_b$ is the equilibrium constant defined in equation (11b).

Similarly, for the first step

$$C_P = K_a C_0 \exp(-FE/RT)$$ (15)

Substituting equations (12) to (15) in (3), we obtain the following relation

$$i = 3F \left( k^0_{c+} C_R \exp[(1-\beta)FE/RT] - k^0_{c-} K_a K_b C_0 \exp[-(2+\beta)FE/RT] \right)$$ (16)

or

$$i = i^0 \{ \exp(a_+ F_\eta/RT) - \exp(-a_- F_\eta/RT) \}$$ (17)

where $a_+ = 1-\beta$ and $a_- = 2+\beta$.

The coefficients $a_+$ and $a_-$, also called transfer coefficients, play the same role in a multistep, $n$-electron transfer reaction as the factor $\beta$ does in one-electron transfer reaction (cf. equation 7). They determine the Tafel slope and are of primary importance in mechanistic interpretations. Their value generally depends on the following factors: 1) the number of single-electron transfer steps preceding and following the rds; 2) the number of times the rds is repeated for each over-all reaction (stoichiometry); and 3) whether or not the rds is a charge-transfer reaction [58].

The most general Butler-Volmer equation, valid for any multistep electrochemical reaction has the following form

$$i = nF \left( \frac{k^0}{c_{A'}^{a+} c_{B'}^{b-}} \exp(a_+ FE/RT) - k^0 c_{A}^{a+} c_{B}^{b-} \exp(a_- FE/RT) \right)$$ (18)
where \( A', B', \ldots \) are the products of charge transfer reactions involving \( A, B, \ldots \), respectively.

It follows from this equation that each reactant \( A, B, \ldots \) has an anodic and a cathodic electrochemical-reaction order, e.g., \( a', b', \ldots \), \( a, b, \ldots \), defined for \( E \gg E^0 \) as

\[
\left( \frac{\partial \log i^+}{\partial \log c_j} \right)_{E, C_{i+j}^+} = p_{j+} \tag{19a}
\]

and for \( E \ll E^0 \)

\[
\left( \frac{\partial \log i^-}{\partial \log c_j} \right)_{E, C_{i+j}^-} = p_{j-} \tag{19b}
\]

where \( p_{j+} \) and \( p_{j-} \) are, respectively, the anodic and cathodic electrochemical-reaction orders on the species \( j \). Note that in these equations the electrode potential \( E \), and not the overvoltage \( \eta \), must be maintained constant. Also, the potential value must be chosen far enough away from the equilibrium potential so that the Tafel law applies.

Usually determination of a reaction mechanism involves the experimental evaluation of the reaction orders \( p_j \) and the transfer coefficients \( \alpha \). These parameters are compared with those predicted by different reaction paths. The reaction path more consistent with the experimental results is then proposed as the probable mechanism.
ELECTROCHEMICAL REACTIONS UNDER TRANSPORT CONTROL.

The Butler–Volmer equations presented in the last section, e.g., equation (18), contain concentration terms which refer to surface \( C_s \) and not bulk \( C_b \) values. Only under certain conditions can these two concentrations be equal, e.g., when the current is zero.

Let's consider the following charge transfer reaction

\[
0 + ne^- \rightarrow R
\]

(20)

If a net current is flowing through the metal/solution interface, and the transport process is slow, then the material consumed in the reaction (20) is not fully replenished by transport from the bulk. Consequently, \( C_s^R \) tends to increase and, similarly, \( C_0^S \) to decrease. This change in surface concentration, from the bulk value at \( i = 0 \) to different values at finite currents, produces a concentration overvoltage \( \eta_c \), defined as

\[
\eta_c = E' - E^0
\]

(21)

where \( E' \) is the equilibrium potential at the new surface concentrations when \( i \neq 0 \). The concentration overvoltage is related to the equilibrium concentration of, e.g., the R species, by the Nernst equation [58]

\[
\eta_c = \frac{RT}{nF} \ln \left( \frac{C_s^R}{C_b^R} \right)
\]

(22)

Transport of a species within a solution can occur by three processes: i) convection, ii) diffusion and iii) charge migration. Convective mass transport is the result of physical displacement of the
solution caused by stirring. Diffusion is the transport of a species from a location of higher concentration to a location of lower concentration and occurs at a rate proportional to the concentration gradient. Migration is the transport of ionic species in response to an electrical potential gradient in the solution. The contribution of migration to the total rate of mass transport can be made negligible by addition of an inert electrolyte to the solution at a concentration much larger than that of the electroactive species.

In cases where the transport process is the slowest of all the steps (i.e., the rds) the reaction is said to be transport or diffusion controlled. In steady state, the rate of the reaction \( r \) will be equal to the flux of reactants at the electrode surface per unit area, which is given by Fick's law of diffusion. Thus,

\[
    r = D \left( \frac{\partial C}{\partial x} \right)_{x=0}
\]

where \( D \) is the diffusion constant in \( \text{cm}^2/\text{s} \), and \( x \) is the distance in \( \text{cm} \) measured from the surface electrode.

According to Nernst [59], a practically stationary liquid layer with linear concentration gradient can be assumed in front of the surface, regardless of whether the liquid is stirred or not. Using Nernst approach and equation (2), the diffusion controlled current \( i_d \) is given by

\[
    i_d = nFD \left( \frac{c^b}{\delta} - c^s \right)
\]

(24)
where $\delta$ is the effective thickness of the Nernst diffusion layer.

It follows from equation (24) that the maximum diffusion current corresponds to zero surface concentration ($C^* = 0$). Limiting conditions arise in the case of fast heterogeneous reactions where all of the substance transported to the surface can be assumed to be immediately transformed by the reaction. In this case, the limiting diffusion current $i_{d,1}$ is given by

$$i_{d,1} = \frac{nFDC}{\delta}$$ (25)

The thickness of the diffusion layer depends largely on the effectiveness of forced convection, e.g., stirring. For static electrodes with no forced convection, $\delta$ is roughly in the order of 0.05 cm, but it is not well defined and increases with the square root of time after imposing a potential or current step, reaching a maximum at long times [58]. Precise values for the thickness of the diffusion layer in systems of controlled hydrodynamics have been reported by Levich [60]. One of such systems, the rotating disc electrode, will be considered in next section.

REATIONS AT ROTATING DISC ELECTRODES

Figure 5a shows a typical rotating disc electrode (RDE) design. The electrode is constructed from a disc of the chosen material (e.g., iron) mounted on the end of a metallic shaft. The shaft and the disc are covered by a cylindrical shroud of inert material (e.g., Teflon).
FIGURE 5

Rotating Disc and Ring-Disc Electrode Assembly

(a) Rotating Disc Electrode

1:Shaft
2:Insulating Teflon Tube
3:Disc Electrode, e.g., Iron

(b) Rotating Ring-Disc Electrode

1:Shaft, Connected to Disc Electrode
2:Insulating Teflon Tube
3: Metallic Tube, Connected to Ring Electrode
4: Insulating Teflon Tube
5: Ring Electrode, e.g., Platinum
6: Disc Electrode, e.g., Iron
In use, the disc electrode is rotated at controlled angular velocity $\omega$ in an electrolyte solution about an axis perpendicular to and passing through the center of the disc surface. The liquid layer immediately adjacent to the disc surface adheres to it and takes part in the rotational motion. The layers not immediately adjacent to the disc must also rotate owing to the viscous forces. However, with increasing distances from the disc, the rotational motion becomes progressively attenuated. The centrifugal forces tend to throw elements of the rotating liquid toward the periphery of the disc. They are replaced by new elements of the liquid arriving from the bulk which in turn are entrained by the disc and transported toward its edges. To sum up, the disc acts as a pump, sucking solution toward it from the bulk and flinging it out centrifugally close to the disc surface [63].

The concentration profile is independent of the distance from the rotation axis, and $\delta$ is constant over the whole disc surface. This property, usually referred to as "uniform accessibility" of the surface, is a condition rarely encountered in other systems with forced convection. The thickness of the diffusion layer $\delta$, measured perpendicular to the electrode surface, is given by [60, 61]

$$\delta = 1.61 \omega^{-1/2} \nu^{-1/6} D^{1/3}$$

(26)

where $\nu$ is the kinematic viscosity and $\omega$ is the angular velocity.

This equation indicates that steady rotation defines a hydrodynamic diffusion layer which decreases with the angular velocity. When the convective diffusion takes place in water, for which $\nu/D \approx 10^3$, then $\delta$ is equal to 0.015 cm at 1 Hz, $5 \cdot 10^{-3}$ cm at 10 Hz, and $5 \cdot 10^{-4}$ at
$10^3$ Hz [61]. At sufficiently high velocities, the diffusion layer $\delta$ assumes a constant minimum thickness, such that the current is limited by charge transfer kinetics alone. At lower values of $\omega$, however, although $\delta$ is still defined, the reaction kinetics are under mixed control, limited by charge transfer at short times and by mass transfer at long times. Therefore, by studying current voltage relationships at different values of $\omega$, it is possible to characterize a metal dissolution process under various limiting conditions [62].

The expression for the transport controlled current can be obtained by substituting the value of $\delta$ from equation (26) into equation (25)

$$i_{d,1} = 0.62 nF\bar{c}^{1/6}D^{2/3}C^{b}O^{1/2}$$

(27)

This equation indicates that, for diffusion controlled reactions, plotting $i$ vs. $\omega^{1/2}$ should result in a straight line. From the slope of this plot, the bulk concentration of the diffusing species can be calculated, provided that its diffusion constant and the kinematic viscosity of the solution are known.

RECTIONS AT ROTATING RING-DISC ELECTRODES

Figure 5b presents a schematic diagram of a typical rotating ring-disc electrode (RRDE). It consists of three concentric parts: The central disc electrode ($R_1$ in radius), the ring electrode (internal radius $R_2$, external radius $R_3$) and a thin insulating separator between them (from $R_1$ to $R_2$). The working surface of both electrodes and the insulator lie in the same plane, forming a single flat surface.
Therefore, the general hydrodynamic picture does not differ from that discussed for the RDE.

The RRDE is a powerful analytical tool that can be used for electrochemical processes, including for distinguishing soluble and insoluble reaction products of passivation breakdown processes [60]. It utilizes force convection of the electrolyte to maintain a well-defined diffusion layer at the disc/electrolyte interface and to transport soluble components or intermediates to a concentric collector electrode (ring) where they can be electrochemically analyzed.

The total diffusion controlled disc current $I_{d,1}$ can be calculated from

$$I_{d,1} = n F A \frac{R_T^2}{R_1} i_{d,1}$$

(28)

where $i_{d,1}$ is given by the equation (27).

The ring current $I_{r,1}$ is influenced by the reactions occurring at the disc electrode which can increase or decrease the concentration of electroactive species in the radial flow stream.

If the disc electrode is set to pass a constant current which generates a constant flux of "intermediate", and the ring is set at a potential such that all intermediates that reach it are destroyed, then the ring current will be a fraction of the disc current due to the loss of some intermediate by diffusion into the bulk of solution [63]. This fraction $N_0$ is called "collection efficiency".

Thus we have, in general

$$\text{(disk)} \quad A \pm n_d \rightarrow B$$

(29a)
(ring) \hspace{1cm} B \pm n_x \rightarrow C \hspace{1cm} (29b)

then

\[ I_r = N_0 \frac{n_x}{n_d} I_d \hspace{1cm} (30) \]

where \( I_d \) and \( I_r \) are the absolute values of the electrical currents measured at the disc and ring electrodes, respectively.

An analytical expression for the theoretical collection efficiency \( N_0 \), was derived by Albery and Bruckenstein [64,65]:

\[ N_0 = 1 - F(a/\beta) + \beta^{2/3}[1 - f(a)] - \\
(1 + a + \beta)^{2/3}[1 - F((a/\beta)(1 + a + \beta))] \hspace{1cm} (31) \]

where \( a \) and \( \beta \) are constants which depend solely on the geometry of the electrode, i.e., on the disc radius \( R_1 \), and the internal \( R_2 \) and external \( R_3 \) ring radii.

\[ a = \left( \frac{R_2}{R_1} \right)^3 - 1 \hspace{1cm} (32) \]

\[ \beta = \left( \frac{R_3}{R_1} \right)^3 - \left( \frac{R_2}{R_1} \right)^3 \hspace{1cm} (33) \]

and \( F(x) \) is defined as

\[ F(x) = \frac{3^{1/2}}{4\pi} \ln \left( \frac{1 + x^{1/3}}{1 + x} \right) + \frac{3}{2\pi} \arctan \frac{2x^{1/3} - 1}{3^{1/2}} + \frac{1}{4} \hspace{1cm} (34) \]

It is general practice to obtain an experimental value for the collection efficiency by measuring \( I_{r,1} \) and \( I_{d,1} \) for a well known redox reaction (e.g., \( I^-/I_2 \)) and calculating \( N_0 \) from equation (30). The agreement between the theoretical and experimental collection efficiency
is generally excellent.

II.2 NUCLEATION AND GROWTH MODELS

The deposition of a new phase onto a surface under controlled potential conditions has been studied in great detail [66,67] and has been discussed in numerous books and reviews [68,69]. As a consequence, the theoretical interpretation of potentiostatic transients for electrocrystallization phenomena is well established. The application of this theory to anodic film nucleation and growth has also been studied extensively [70,71].

In the simplest case it is assumed that nuclei form at discrete centers and grow laterally across the surface. It is further assumed that the rate of growth (current) is proportional to the surface area $S$ onto which deposition occurs, and that the growth area may be modified by overlap with adjacent nuclei. The current flowing to a single nucleus may be written as

$$i = nFkS$$

where $k$ is the over-all rate constant for the growth process ($\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$) and the other symbols have their usual electrochemical meanings.

In the initial stages of the formation of a new phase, the individual centers grow independently of each other without overlapping. Therefore, it is necessary to include in the model the time dependence of the nuclei population $N$. If there is a uniform probability with time
of converting sites into nuclei, the nucleation law is first order [68]

\[ N = N_0 [1 - \exp(-At)] \]  \hspace{1cm} (36)

where \( N_0 \) is the total number of sites and \( A \) is the nucleation rate constant. For the initial time range, equation (36) gives two limiting cases of special interest. If \( A \) is large, then all the sites are converted to nuclei virtually instantaneously,

\[ N \sim N_0 \]  \hspace{1cm} (37)

but if \( A \) is small, the number of nuclei increases with time (progressive nucleation)

\[ N \sim AN_0 t \]  \hspace{1cm} (38)

Multiplying equation (35) by either equations (37) or (38) the following current-time transients are obtained:

**Instantaneous nucleation 1-D growth:**

\[ i = nFN_0 kS \]  \hspace{1cm} (39a)

**Progressive nucleation, 1-D growth:**

\[ i = nFAN_0 kS t \]  \hspace{1cm} (39b)

Equations (39) give the current flowing into a center which is growing in only one direction (1-D). For centers growing in two dimensions (2-D) or in three dimensions (3-D), the corresponding equations are:
Instantaneous nucleation, 2-D growth:

\[
i = \frac{2\pi n FM h^2 N_0}{\rho} t \quad (40a)
\]

Progressive nucleation, 2-D growth:

\[
i = \frac{2\pi n FM h^2 AN_0}{\rho} t^2 \quad (40b)
\]

Instantaneous nucleation, 3-D growth:

\[
i = \frac{2\pi n FM^2 k^3 N_0}{\rho^2} t^2 \quad (41a)
\]

Progressive nucleation, 3-D growth:

\[
i = \frac{2\pi n FM^2 k^3 AN_0}{\rho^2} t^3 \quad (41b)
\]

where \( h \) is the height of a cylindrical center. Similar equations can be deduced for more complicated geometries of the growing center.

It can be seen that the nature of the current-time transient (power of time) does not uniquely determine the law which applies, except in the cases (39a) and (41b). It is desirable, therefore, to deduce or confirm the nucleation law by microscopic study of the growth center geometry and the variation of its number with time. The slopes of the transients (39b), (40b) and (41b) give the product of two potential-dependent rate constants \( A \) and \( k \); in addition, \( N_0 \) may vary with potential.

At longer times, the current-time transients deviate from equations (39) to (41) for two reasons: i) in the case of a progressive nucleation there will be a change from the initial linear law (38) to the first
order relation (36); ii) in all cases, the centers will begin to overlap. The correct formulation of the problem following coalescence poses difficulties, specially when the progressive nucleation of centers is considered. It has recently been shown that one general equation can be applied for all cases of 2-D nucleation and crystal growth [72]. Depending on the value of the constant $A$, the initial part of the $i/t$ transient will follow a $t^n$ dependence, with $1 < n < 2$. The limiting cases remain the same as originally deduced [68]:

**Instantaneous nucleation, 2-D growth, with overlap:**

\[ i = \frac{2mnFMh^2N_0}{\rho} t \exp(-\pi M^2N_0k^2t^2/\rho^2) \quad (42a) \]

**Progressive nucleation, 2-D growth, with overlap:**

\[ i = \frac{2mnFMh^2AN_o}{\rho} t^2 \exp(-\pi M^2N_0k^2t^2/3\rho^2) \quad (42b) \]

Comparison of equations (42a) and (42b) with equations (40a) and (40b), respectively shows that the effect of the overlap is accounted for by the exponential terms in $t$.

The effect of overlap on the transient for 3-D growth (right circular cones) has been considered by Armstrong et al [73]

\[ i = nFk_2[1 - \exp(-\pi M^2k_1^2N_0At^2/3\rho^2)] \quad (43) \]

All these equations assume the charge transfer reaction to be rate-controlling. In many cases, however, growth of mature nuclei is
controlled by mass transfer of electrodepositing ions to the growing centers. The effect of transport controlled reactions on the nucleation and growth equations is difficult to quantify rigorously. Several simplifications have been proposed [74–78]. Because of the small size of the nuclei, their growth may be described in terms of localized spherical diffusion [77] rather than in terms of linear diffusion to a plane [79]. The initial current of growth of hemispheric nuclei, not considering overlapping, is then:

**Instantaneous nucleation, 3-D growth with diffusion control:**

\[
i = \frac{nF\pi(2DCb)^{3/2}M^{1/2}N_o}{\rho^{1/2}} t^{1/2}
\]  

(44a)

**Progressive nucleation, 3-D growth with diffusion control:**

\[
i = \frac{2nF\pi(2DCb)^{3/2}M^{1/2}AN_o}{3\rho^{1/2}} t^{3/2}
\]  

(44b)

In some cases, the current transients show a transition from a \(i-t^{3/2}\) to a \(i-t^{1/2}\) relationship, indicating that a progressive nucleation occurs at the early stages of the transients [77].

Taking into account overlapping of hemispheric centers, the nucleation and growth current is [78]:

**Instantaneous nucleation, 3-D growth with diffusion control and overlap:**

\[
i = \frac{nF\pi^{1/2}C_b}{\pi^{1/2}} t^{-1/2} \left[1 - \exp(-N_0nk'Dt)\right]
\]  

(45a)

**Progressive nucleation, 3-D growth with diffusion control and overlap:**
\[ i = \frac{\pi b}{4N_{b}D} t^{-1/2} [1 - \exp(-AN_{e}nk'Dt^2/2)] \]  

(45b)

where \( k' \) and \( k'' \) are defined as

\[ k' = (8\pi C_b M/\rho)^{1/2} \]  

(46a)

\[ k'' = \frac{4}{3} k' \]  

(46b)

This model has been shown to apply not only to electrodeposition of metals, but also in some processes of anodic film formation, as for instance when the compound deposited is a good electronic conductor [78]. Other authors have reported empirical equations for instantaneous nucleation and three-dimensional growth that have the same form as equation (45a) [80].

II.3 PASSIVITY AND ITS BREAKDOWN

NATURE OF PASSIVITY

The phenomena of localized or pitting corrosion on iron is generally related to the process of passivity breakdown due to some aggressive ions. Therefore, this process can not be explained without a clear understanding of the nature of passivity.

The nature of the passive metal surface is subject of controversy. Two main models have been proposed: i) passivity is due to an adsorbed monolayer of oxygen or oxygen-containing compounds, and ii) passivity is due to the formation of a three-dimensional oxide film on the metal surface. Those supporting the idea of an adsorbed monolayer based their
pitting mechanisms on the idea of competitive adsorption between the passivating and the aggressive species on the metal surface. Those in favour of a passive three-dimensional oxide film tried to find a way to undermine that film.

One of the fundamental difficulties in understanding the nature of passivity is that the kinetics of the electrode process, mainly of the anodic process, is a function of many variables, including the nature of the metal, the conditions of its surface, the nature and concentration of the electrolyte, and, finally, the time during which these variables change [81].

It is now generally accepted that neither model can explain all the properties of passive metals. Attempts at reconciliation of these two competing theories have pointed out that an adsorbed oxygen atom or oxygen-containing molecule is prerequisite to oxide film formation [82]. This controversy may be, in final instance, one of terminology instead of one of physics, since the distinction between a chemisorbed oxygen layer and a thin non-stoichiometrical oxide phase is practically impossible for the following two reasons: i) an oxide film which is only one or several cell units thick may have properties which differ from those of compact oxides; ii) the properties of a chemisorbed oxygen layer may be similar to the those of an oxide film [56].

Even though the nature of the initial process of passivation is still in discussion, it is now clear that a three-dimensional oxide film does form in time. The structure of the anodic oxide film formed on iron in borate buffer has been studied by a number of workers [83–98]. The thickness of the passive layer has been shown to increase steadily
with potential and with time of passivation. However, its exact composition is still unknown.

Through the years, a number of models for the passive film have been proposed. Two of the most widely accepted models are: i) a two-phase model consisting of an inner Fe₃O₄ and an outer Fe₂O₃ layer [86-89]; and ii) a single barrier phase of Fe₂O₃ covered by a layer of hydrous iron(III) oxide deposited from the solution [90-93]. The electronic properties of the iron(III) phase are consistent with a γ-Fe₂O₃ [12,13,98].

There is a drastic change in structure and stoichiometry between the initial film formed at potentials close to the active-passive transition and that formed at potentials positive to the Flade potential. Bockris et al [95], using ellipsometric and coulometric techniques, proposed that the initial passivation is due to coverage with Fe(OH)₂, which later converts to Fe₂O₃; this transformation is not complete until +0.5 V from the peak (near Eᶠ in the borate buffer). The presence of significant amount of Fe²⁺ ions in the inner layer of the surface film formed on iron passivated in borate solutions at E < Eᶠ has also been reported by Seo and Sato [96], using Auger electron spectroscopy; however, these results were ascribed to the presence of a Fe₃O₄ phase at E < Eᶠ and a Fe₂O₃ at higher potentials. Konno and Nagayama [97], using x-ray photoelectron spectroscopy, found that at E < Eᶠ the film is more porous and accommodates a great amount of adsorbed water; at higher potentials, water is adsorbed only at the outer surface.
For this investigation, the surface will be considered to be covered by a three-dimensional oxide film, Fe₂O₃, which stoichiometry and structure may, in general, vary with potential and time of passivation. Therefore, any mechanism of pitting corrosion must explain how such a film is undermined by the aggressive anions.

**CHARACTERISTIC ELECTROCHEMICAL PARAMETERS OF PITTING PROCESSES**

The various electrochemical parameters usually related to the passivity breakdown process (e.g., pitting) are schematically represented in Figure 6. Most of the discussion will be based on pitting corrosion, since it is one of the most common processes of localized corrosion. However, similar parameters can also be defined for other localized corrosion reactions (e.g., crevice corrosion) which are also initiated by a passivity breakdown process.

**Pitting Potential (Eₚ)**

This is the potential below which no pitting is observed. Above this potential, pitting would start almost immediately or after a short induction time. Many authors have studied the effect of temperature, alloy, and solution composition on Eₚ and have related this parameter to the susceptibility of the metal to localized corrosion. The more positive Eₚ is, the less susceptible to pitting corrosion [99].

Many techniques (e.g., potentiostatic, potentiodynamic, galvanostatic, galvanostaircase, "scratching method") have been devised to show that this potential is not an artifact of the experimental
FIGURE 6

Representation of Electrochemical Parameters Related to Pitting Corrosion.

(a) Pitting Potential, $E_p$.
(b) Repassivation Potential, $E_r$ (Arrows indicate direction of polarization).
(c) Inhibition Potential, $E_{inh}$.
(d) Induction Time, $\tau$ (Arrows indicate Injection of the Aggressive Solution).
technique. Several reviews have discussed the advantages and disadvantages of each method [99,100]. Steady state techniques are generally more accurate because time is an important factor in pitting nucleation. On the other hand, dynamic experiments are faster and less cumbersome and are, consequently, more commonly used in corrosion studies for comparative purposes. In potentiodynamic experiments, $E_p$ is defined as the potential at which the passive current sharply increases (Figure 6a).

**Repassivation Potential** ($E_r$)

This characteristic potential was first described by Pourbaix [101] who reported that pits, which started to grow at potentials above $E_p$, continued to grow even though the potential was dropped below $E_p$. These pits would only stop growing when the potential became lower than a certain value called repassivation potential (cf, Figure 6b). The value of $E_r$ is believed to be related to the degree of occlusion of the pit, e.g., the deeper the pit, the lower $E_r$ [102]. It has also been found that the difference between the pitting potential and the repassivation potential is a measure of the susceptibility of the metal to crevice corrosion, i.e., the higher the difference, the higher the susceptibility [103].
Inhibition Potential ($E_i$)

This potential was first described by Schwenk [104] for stainless steels in chloride solutions containing nitrates. In these solutions, the intensity of pitting increased with potential, for $E > E_p$; eventually, a potential was reached above which pits repassivated, i.e., the current decreased (cf. Figure 6c). This potential was called inhibition potential, $E_i$, and has been reported for iron in several other halide containing systems [105-107].

Induction Time ($\tau$)

Engell and Stolica [108] and later Hoar and Jacob [109] devised a technique to measure the kinetics of passivity breakdown of iron and stainless steels by halide ions. In this technique, the metal electrode is held potentiostatically in the passive region, a specific concentration of halide is injected, and the induction time $\tau$ preceding a sharp rise in current is recorded (cf. Figure 6d). The rise in the current was correlated with the breakdown of passivity and the initiation of pitting.

From the effect of anion concentration on the induction time, the order of reaction $n$, i.e., number of halide ions associated with dissolution of a single metal atom, can be calculated as follows [108]:

$$\frac{\partial \log 1/\tau}{\partial \log C_j} = n$$

(47)

where $C_j$ is the concentration of the aggressive anion $j$ (e.g., $Cl^-$, $S^-$).
This equation is similar to that defined for electrochemical-reaction orders $p_j$ [cf. equation (19)] where $1/\tau$ is taken as the rate of pit initiation, i.e., the number of events per unit time.

The activation energy $E_a$ for pitting initiation can be calculated from the effect of temperature on $\tau$ [109]. However, there has been no general agreement so far about the actual meaning of $E_a$ and $n$ calculated in this way [110].

**PITTING THEORIES**

Many theories, some of them conflicting and even exclusive, have been proposed to explain the pitting phenomena. While the assumption of initial adsorption of the aggressive anion on the passive film surface is common to almost all passivity breakdown mechanisms, the further action of these ions is still unclear.

It is important to notice that most of the experimental work has been carried out in halide-containing solutions. Even though the mechanisms proposed for these solutions have been generalized to pitting corrosion in other media, they may not be applicable to the case of sulfide anions. Contrary to the halide ions, sulfide anions can be easily oxidized and produce deposits (e.g., FeS) on the surface.

The different pitting theories can be compiled in four groups: i) ion migration through the passive film; ii) flaws in the oxide film; iii) competitive ion adsorption (followed by oxide dissolution); and iv) localized acidification.
Ion Migration Mechanisms

Early literature on passive films assumed that the oxide film acted as a static barrier that isolated metal from the solution (Figure 7a). In order for pitting to occur, a reaction must take place to bring the metal and the solution into contact. One possible way was for the aggressive anions to migrate into passive film, contaminate it, and change its properties. The anodic current could then increase in the contaminated zones, inducing pitting corrosion.

Contamination of the oxide film has been confirmed in several cases using impedance [111] and ellipsometric techniques [112,113], but the results of other surface analysis have been conflicting [114,115]. A recent communication [116] has suggested that these inconsistencies arise from the time after depassivation at which the observations were made; i.e., the chloride concentration inside the film reaches a maximum around breakdown time, decreasing for longer exposure.

Vetter and Strehblow [117] pointed out that a migration of polyatomic aggressive anions such as $SO_4^{2-}$, $ClO_4^-$ or $SCN^-$ (which have also been found to produce pitting in some cases) through a solid layer was not conceivable. Besides, theoretical calculations have revealed that the time required for $Cl^-$ to penetrate through a film is much longer than the $\tau$ measured experimentally [118].

Recent measurements have shown that films grown in aggressive solutions are contaminated with the anion even below $E_p$, demonstrating that contamination of the passive film is not a sufficient condition for pitting to occur [119,120]. Furthermore, passivating the metal in the
FIGURE 7

Schematic Representation of Different Passivity Breakdown Theories.

(a) Penetration Mechanism.
(b) Film Breaking Mechanism
(c) Ion Adsorption/Oxide Dissolution Theory.
(a) METAL OXIDE ELECTROLYTE

Me → Me^{2+} → Me^{2+} (Corrosion)

H₂O
O²⁻ Cl⁻ S²⁻ SO₄²⁻ (Penetration)

(b) (Repassivation)

OH⁻ SH⁻ (Competition) (Pitting)

(c) (Adsorption) (Dissolution) (Pitting)
aggressive solution can increase its resistance to pitting corrosion, compared to the metal passivated in the absence of the aggressive ion, i.e., contamination of the passive film can sometimes inhibit pitting [121].

**Flaws in the Oxide Film**

Wood et al [122] proposed that pitting starts at flaws in the oxide film. Noise analysis of passive metals at constant potential suggests that there is a dynamic balance between film rupture and self repair [123] (Figure 7b). Theoretical reasons to expect this type of behaviour have been give by Fromhold [124] and by Sato [125] who related the high electrical field across the film, $10^6 - 10^7 \text{ V cm}^{-1}$, to the formation of a compressive stress large enough to produce mechanical deformation or breakdown of the film. According to Sato, surface tension stabilizes the anodic film but its effect decreases with increasing film thickness. There is, therefore, a critical thickness above which mechanical deformation occurs. Sato proposed that the adsorption of aggressive anions decreases surface tension and, consequently, decreases the critical thickness.

Repassivation process has been shown to occur when the passive layer is locally cracked by either straining metal experiments or by surface scratching at a potential below $E_p$. These experiments suggest that even though flaw formation can be a necessary condition for pit initiation, it is not sufficient [110].
Ion Adsorption–Oxide Dissolution Theory

This theory, described by Hoar and Jacobs [109], suggests that nucleation of a pit can be started by the adsorption of the aggressive anions at energetically preferred places on the passive film surface. To overcome the repulsive force of the anions, the adsorption should lead to an exchange of OH$^-$ or O$^2-$ of the passive oxide by the aggressive anion [109]. The corresponding compound would have a greater dissolution velocity than the oxide, resulting in a partial or complete removal of the passive layer at these places. If the passive film becomes thinner, the metal dissolution rate increases locally due to the higher field strength (cf. Figure 7c).

Localized Acidification Mechanism

One of the earliest theories for electrochemical depassivation was the one originally proposed by Hoar [126], who explained the activating effect of Cl$^-$ not by selective adsorption on the surface, but by considering the influence of a non-depositing ion such as Cl$^-$ on the pH of the electrolyte next to the anode. Migration of Cl$^-$ instead of OH$^-$ would decrease the pH of the electrolyte adjacent to the anode and increase the Cl$^-$ concentration until soluble Fe(II) becomes stable and breakdown occurs.

A thermodynamic explanation of the pitting potential, based on the E/pH diagrams was first given by Pourbaix and coworkers [127]. This theory was later modified by Galvele et al introducing an electrochemical kinetic explanation for the pitting potential [110].
The key point in this mechanism is that there is a pH drop on the dissolving metal surface, and this pH drop is a necessary condition to sustain the pitting process. According to Galvele and co-workers, the corrosion potential $E_c^+$ of the metal in the acidified pit-like solution, is the minimum potential at which pitting can be sustained. In general, $E_p$ should be slightly greater than $E_c^+$ due to the reaction of protons with other reducible anions or with weak acid anions, diffusion to the bulk of the solution, etc [110].

II.4 PRINCIPLES OF ELECTROCHEMICAL PHOTORESPONSE

The composition and structure of passive films can be determined by numerous surface analysis techniques, such as Auger spectroscopy, electron microprobe, energy dispersion x-ray diffraction, etc.; however, most of these techniques require that the sample be taken out of the electrolyte and subjected to vacuum. The structural properties of the film can change under these conditions and, consequently, in situ techniques can give a more accurate information. Since passive films on iron and other metals have semiconductor properties, techniques based on photoresponse, traditionally used in semiconductor characterization, have been recently implemented in passivity studies [128-134]. The principles of photoelectrochemical response in single crystal semiconductors are very well known, and will be briefly presented in this section. The application of this theory to thin, polycrystalline (or amorphous) passive films presents, however, some complications which have not yet been completely solved.
The conduction properties of a solid phase have a considerable effect on the electrode behavior [135]. The essence of electrical conductivity in solids is that charges (i.e., electrons) must be able to move under an applied electrical field. For an electron to move, there must be a partially vacant energy band available.

A qualitative description of a semiconductor/electrolyte system is given in Figure 8. The energy states of the individual atoms degenerate in two bands when the atoms are grouped together to form the solid. The lower energy band, resulting from the overlap of filled valence orbitals, is called valence band (VB); the energy at the top of the VB is \( U_v \). The upper band, formed by the partially filled or empty orbitals, is called conduction band (CB); the energy at the bottom of CB is \( U_c \). The VB is separated from the CB by an energy gap \( U_g = U_c - U_v \). In a semiconductor, \( U_g \) is larger than the thermal energy of the electrons, \( kT \).

The Fermi level \( U_F \), i.e., the chemical potential of the electrons, is located between the two bands. In a statistical sense, \( U_F \) is the energy level which has equal probability of being filled or empty.

When the semiconductor surface is irradiated with a light of quantum energy \( h\omega > U_g \), an electron may be promoted from the VB to the CV, leaving behind an unoccupied energy state, or hole. Holes \( (h^+) \) can be treated as if they were positively charged particles. If an electrical field is applied across the interface, the electron/hole pairs will separate and an electric current will flow. Otherwise, \( e^-/h^+ \) recombination will occur with a corresponding release of energy as heat.
FIGURE 8

Schematic Representation of an n-Type Film/ Electrolyte Interface Under Illumination.
An intrinsic semiconductor (e.g., Si) has a small number of electrons in the conduction band, in equilibrium with an equal number of holes in the valence band. The number of carriers ($e^-$ or $h^+$) can be increased (and become majority carriers) by adding specific impurities, i.e., doping the semiconductor. Depending on whether electrons or holes are the majority carriers, semiconductors are usually classified as n-type or p-type, respectively. Passive films on iron behave as an n-type semiconductor [128-131,136].

When a semiconductor surface is in contact with vacuum, its band structure is constant from the bulk to the surface, i.e., the bands are flat. However, the band energies near the surface are disturbed by the existence of an electrical field in the electrolyte double layer, producing "band bending" [58]. Near the surface, electrons and holes are not present in equal numbers; this region of the semiconductor is called the "space charge" region. Four basic conditions can be found in the charge region interface, depending on the redox potential:

1) Accumulation layer, where the excess charge is of the same sign as the majority carriers of the bulk.

2) Flat band, where there is no excess charge in the semiconductor, and the energy bands are flat from the bulk to the electrolyte.

3) Depletion layer, where the excess charge is opposite in sign to the majority carriers in the bulk.

4) Inversion layer, where the minority carriers in the bulk become the majority carrier at the surface.
Figure 8 shows a typical interface of an n-type semiconductor under illumination and anodic polarization. In a potentiostatic photoelectrochemical experiment, the Fermi level of the oxide is constant since it is set by the applied potential. The absorption of photons results in the generation of electron-hole pairs, separated by the electric field in the depletion region. The charges formed in each band move to opposite directions by the applied field; under anodic polarization, the electrons in the conduction band move towards the bulk of the semiconductor, whereas the holes generated in the valence band move towards the surface and are trapped at the interface. The electrons are transferred via the external circuit to the metallic cathode, i.e., platinum, where a reduction reaction (e.g., hydrogen evolution) can take place. In order to complete the electrical circuit, and allow for the current to flow, suitable electron donors must be present in the solution to "receive" the holes at the semiconductor surface. The net result is, e.g., photoassisted water splitting, according to the following reactions

\[
\text{photoanode:} \quad 2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{O}_2 + 4\text{H}^+ \quad (48)
\]

\[
\text{counterelectrode:} \quad 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (49)
\]

If the metallic cathode is large enough, the photoresponse of the cell is determined by the kinetics of reaction (48) and the behavior of the electron-hole pair generated in the semiconductor. Note that the net effect of the photoexcitation in an n-type semiconductor is to increase the number of holes in the depletion layer, in relation to the
equilibrium value in the dark. Therefore, the anodic current increases.

If the reaction kinetics at the interface is neglected, the total photocurrent \( i^* \) flowing through the semiconductor can be expressed, according to Butler's model [137] as

\[
i^* = c \Phi (E-E_{fb})^{1/2} N_D^{-1/2} (E-V_g)^{m/2}/N_D^{1/2}
\]

(50)

where the equation has been simplified to show only a constant \( c \) and the parameters which play most important role in determining the current behavior were identified. These parameters are: the photon flux \( \Phi \) (proportional to light intensity), the flat-band potential \( E_{fb} \), the concentration of donors \( N_D \), the band gap \( U_g \) and the light frequency \( \Phi \). The exponent \( m \) depends on whether the transition is direct \( (m = 1) \) or indirect \( (m = 4) \) [138].

This equation predicts a square-root dependence of the photocurrent on the applied potential, and suggests a simple method to determine \( E_{fb} \) as the potential at which the photocurrent tends to zero. The value obtained in this way, also called "onset" potential, usually agrees within 0.2 V with the values obtained by capacitance methods using Mott-Schottky plots [137]. The magnitude of \( E_{fb} \) is an important quantity because it determines the relative Fermi levels of the semiconductor and electrolyte and, therefore, the amount of bending at the interface. At potentials positive to \( E_{fb} \), the bands are "bent up" and the photocurrent is anodic. Conversely, at \( E < E_{fb} \), the bands are bent down and the photocurrent is cathodic.
Equation (50) also indicates a method for determining the band gap: when $h\nu \rightarrow U_g$, then $i^* \rightarrow 0$. Therefore, the value of $U_g$ can be directly found, or extrapolated from, the spectral response of the semiconductor at constant potential.

Also a linear relationship between the photocurrent and the light intensity (number of photons) is expected. At higher light intensities, however, the reaction kinetics will eventually limit the photocurrent. In this case, the Butler-Volmer equations, e.g. equation (17), can be applied.

Thin semiconductor films on metallic electrodes may differ from these models based on three dimensional single crystal semiconductors. Such possible differences are [139]:

1. The film thickness is less than the penetration depth of the light.
2. The film is amorphous instead of crystalline
3. The film has high impurity concentration.
4. Photoinduced processes result from excitation in either phase, the film and the underlying metal.

The quantitative effect of each possibility is not fully understood at the present. However, qualitatively, it is clear from the first possibility, that the photocurrent should increase with the film thickness until it becomes larger than the penetration depth of the light. This has been observed experimentally in numerous occasions [13, 128].
III. EXPERIMENTAL

Reagents

The electrolyte solutions were all prepared with high conductivity water having a resistivity > 2 \times 10^7 \text{ ohms-cm}. All chemicals were reagent grade or better.

The buffer stock solution used in all experiments was 0.15 M in $\text{H}_3\text{BO}_3 + 0.0375 \text{ M in Na}_2\text{B}_4\text{O}_7\cdot10\text{H}_2\text{O}$. A stock solution of 1 M sodium sulfide was prepared from crystalline Na$_2$S (Alfa Products) and the borate buffer. Solutions containing 0.1, 0.01 and 0.001 M Na$_2$S were also prepared from these stock solutions.

The final concentration of the working solution was obtained by diluting a known volume of a sulfide solution with the borate buffer. The final pH was adjusted (if necessary) with a carbonate free NaOH solution.

All experiments were carried out at the constant pH of 8.4. At this pH, the dissolved sulfide is present almost entirely as hydrosulfide ions (HS$^-\). The borate buffer system was chosen because iron exhibits essentially ideal passive behaviour in this solution over the entire accessible range, in the absence of "agressive" ions such as chlorides or sulfides. The passive range extends over 1.2 volts, thus allowing the application of relatively large voltage changes to the electrode without having to compensate for side reactions. Studies of the anodic films formed in this solution have been carried out by many researchers and the
components of this buffer have been found not to participate as reactants or intermediates in any electrode reaction nor to incorporate into the passive film during its formation and growth [84,88,89,94,97]. At high anodic potential, however, some boron may be incorporated to the outmost layer due to the oxidation of ferrous borate complex ions [FeB(OH)₄]⁺ dissolved in the solution [96].

No supporting electrolyte was added to the borate buffer to maintain constant ionic strength during passivity breakdown experiments, since the presence of "inert" anions can cause unpredictable effects in the corrosion behavior.

Electrode Construction

Iron specimens were machined in discs from a polycrystalline rod of Zone Refined Iron *. Three different designs were used: Vertical electrodes (for stationary experiments), rotating disc electrodes, and ring-disc electrodes.

The diameter of the discs used in the vertical electrodes were either 1.00 or 0.50 cms. Larger electrodes were preferred for most experiments in order to have a large area to edge ratio. On the other hand, small diameter discs were used in photoelectrochemical measurements in order to assure uniform coverage by the light.

The working electrode assembly is shown in Figure 9. A nickel wire was soldered to one of the flat faces of the disc. The electrode was

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* Impurities in ppm: C 3.5, O 2.5, N 1.0, Al 2.0, Cu 10.0, Ni 1.00, S 1.00, Ca 5.0
Stationary Working Electrode and
Photoselectrochemical Cell

2: Reference Electrode, SCE.
3: Quartz Window.
4: Luggin Capillary.
5: Gas Inlet, Nitrogen.
6: Fritted Glass.
7: Auxiliary Electrode, Platinum Gauze.
prepared by placing the specimen inside a holder with the contact wire extending out of the holder through a glass tube. Epoxide resin was used to cover the samples sides and the contact wire. Therefore, only one face of the iron specimen, epoxy and glass are in contact with the solution.

The exposed electrode surface was then mechanically abraded using #120, #180, #220, #360, #400 and #600 silicon carbide paper in succession. A mirror finish was then achieved by wet polishing with 0.05 μ Gamma polishing alumina. The electrode was thoroughly washed and ultrasonically cleaned in water after every sanding step and after the final polish. The electrode was then washed with absolute ethanol, rinsed with conductivity water, and then dried.

Metallographic examination of the electrode thus treated revealed a smooth and mechanically uniform surface structure with an intact metal-epoxy seal. The electrodes could be conveniently reused by repolishing the surface.

The rotating disc electrode (RDE) assemble is shown in Figure 5a. The cylindrical electrodes, 0.80 cm in diameter, were machined from the same iron batch used in the other experiments but instead of using epoxide resin to fill the sides, the metal electrode was pressed into a Teflon cylinder of the same inside diameter. This method, in common use in corrosion studies, proved not to be suitable for this study since the iron-Teflon seal was not tight enough to prevent crevice corrosion. Therefore, a procedure similar to the one described by Delnick [12] was used. The electrode was gently heated, and powdered linear polyethylene (low density) was sprinkled onto its surface. When the polyethylene
became molten, the electrode was pressed through the Teflon cylinder, extruding polyethylene from the iron-Teflon crevice. A polyethylene washer was thus formed upon cooling. The excess polyethylene was removed by sanding and the electrode polished and treated as described above. The electrode thus prepared showed a perfect iron-polyethylene seal with no crevices visible even at 1000 x magnification. Similar electrodes showed no signs of corrosion at the iron-polyethylene contact after five months in a borate buffer solution containing an excess of 0.5 M NaN₃ [12].

The rotating ring-disc electrode assembly (RRDE) is shown in Figure 5b and was described in section II.1. It consists of two concentric electrodes, disc and ring, located in the same plane and separated by a narrow insulator. The dimensions are \( R_1 = 0.300 \) cm, \( R_2 = 0.411 \) cm, and \( R_3 = 0.556 \) cm.

Since the corrosion experiments require separate preliminary treatment of the disc (iron) and the ring (platinum), a detachable system was used in which the disc and the ring could be separately treated and mounted together immediately before measurements. The disc was made and treated in the same way as described above for the RDE whereas the platinum ring was polished with the 0.05 μ alumina, degreased in absolute alcohol, and rinsed with water. A Pt/Pt ring-disc electrode was also used in some experiments. In this case the electrode was non-detachable, which permitted a thinner disc to ring gap.

The fresh iron electrodes were cathodically polarized for 2 minutes at \(-1.2 \) V (vigorous hydrogen evolution) in the working solution (in situ) before each experiment, in order to remove any reducible surface
films. It is assumed that this pretreatment produces a virtually oxide-free surface since, thermodynamically, air formed oxides can be removed at potentials slightly anodic to the hydrogen evolution reaction. Ellipsometric data for iron [91] and measurements of the charge associated with reduction of the film [88] support this assumption. Before beginning the experiment the electrode was left for at least 4 minutes at the initial potential in order to allow for hydrogen diffusion out of the electrode surface.

**Electrochemical Cell**

The electrochemical cell used for photoelectrochemical experiments consisted of a conventional three-compartment Pyrex design containing an optical quartz window, as shown in Figure 9. The compartments were separated by fine fritted glass to prevent mixing of soluble species between compartments. The main compartment contained the working electrode inlet, a gas inlet tube and a Luggin capillary probe, the latter to minimize ohmic drop between the working and reference electrodes. The reference electrode consisted of a saturated calomel electrode (SCE), to which all potentials are referred. The counter electrode consisted of a platinum gauze, which was cleaned in concentrated HNO₃, washed with conductivity water and rinsed in working solution before each use.

For other static tests, a similar three compartment cell but without quartz window was used.
In rotating electrode experiments, a three compartment cell (Figure 10) was specially designed to seal the cell from the ambient atmosphere and to allow precise positioning of the Luggin capillary.

The various methods which could be used for sealing the cell from the ambient atmosphere, have been extensively studied [61]. The hydraulic seal used ensures a good seal and excludes contamination of the solution. The seal consists of two parts made out of Teflon: The first one is attached tightly to the electrode rod using Teflon tape, and the second is filled with water and connected to the cell through a ground joint. The system can be used for rotation speeds up to about 6,000 rpm. At higher speeds, centrifugal forces spill water out of the jar, disturbing the hermeticity of the seal. The maximum speed can be increased easily by adding vertical ribs on the internal wall of the seal jar in order to slow down the liquid movement.

Excess nitrogen pressure was constantly maintained in the cell during the experiments to prevent leakage of the ambient atmosphere into the cell. During rotating measurements, however, the gas was not bubbled through the solution so as not to disturb the hydrodynamics of the system; instead, the nitrogen was diverted over the solution level by using a three way stopcock.

The Luggin probe was introduced into the cell using a round joint, which gave three degrees of freedom to the tip. Precise positioning of the probe is important in order to minimize ohmic drop in the electrolyte (IR drop). This is more critical in RRDE, since an IR drop common to the ring and disc systems, produces the so called pseudo-collection effect [139,140] For RDE experiments, the best
FIGURE 10

Electrochemical Cell for Rotating Electrodes.

1: Auxiliary Electrode, Platinum Gauze.
2: Rotating Disc or Ring-Disc Electrode.
3: Luggin Capillary.
4: Reference Electrode, SCE.
5: Hydraulic Seal, Teflon Stopper.
6: Hydraulic Seal, Teflon Cap Attached to the Shaft.
position of the probe is usually perpendicular to the center of the disc and close to the electrode (0.2–0.5 mm) [61]. For RRDE experiments, on the other hand, the optimal position of the tip had to be found by trial and error and it was usually near the gap between the disc and the ring.

All glassware was washed using chromic acid solution (K₂Cr₂O₇ – H₂SO₄) followed by thorough rinsing, firstly with conductivity water and finally with the working solution. The electrochemical cell was then filled with previously degassed working solution and further purged with purified nitrogen for at least 3 hours.

The nitrogen purification train was designed to saturate the flowing gas with the working solution, and to remove traces of O₂ and CO₂ from the prepurified nitrogen gas, since these could affect the experimental conditions. The train consisted of a Pyrex glass column filled with copper turnings, heated to ~350°C by a heating mantle, and several consecutive washing bottles containing conductivity water, NaOH solution, and working solution.

**Instrumentation**

The current through the electrochemical cell was measured as a function of the electrode potential by using a standard potentiostat/galvanostat instrument*. The potential (or the current) could be changed manually or automatically using a function generator.

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* See Appendix 2 for a list of the instruments used.
The experimental method to measure photocurrents (Figure 11) employs a phase sensitive amplification system. A 1000 W Xe light source was focused onto a grating monochromator (590 grooves/mm) having an approximate band pass of 6 nm. A cut off filter (L.P. 300 or 470 nm) was used to eliminate higher order diffraction patterns from the output of the monochromator. The working electrode was positioned approximately 1 cm from an optical quartz window through which the monochromated light was focused onto the electrode surface with the system under potentiostatic control. A mechanical chopper placed between the monochromator and the quartz window provided the lock-in amplifier with a reference signal (f=13.8 Hz). The corresponding periodic component of the electrode current was then selectively amplified and displayed on an X-Y recorded. The periodic light pulses minimized heat buildup at the electrode/solution interface. Spectral responses were taken by automatically scanning the wavelength at 25 nm/min.

For RRDE experiments, the disc potential (or current) and the ring potential were independently controlled by the use of a commercial double potentiostat, which could also measure both ring and disc currents, as well as potentials, directly. No interaction was found between the ring and disc signals except when there was an uncompensated ohmic drop common to both electrodes (common IR drop effect). In this case the current flowing through one circuit will produce a loss in potential control of the other circuit, and vice versa. This effect, called by Shabrang and Bruckenstain [139, 140] "pseudocollection" and "inverse pseudocollection" effects, can be of great importance if the
FIGURE 11

Photocurrent Detection System.
common resistance is large or if large currents are encountered. A small pseudocollection effect was found if the reference electrode was not positioned correctly. A rather large effect (several hundreds millivolts) was sometimes found when a leak developed between the ring and the Teflon sleeve, letting the solution penetrate by capillarity and short circuit the ring and disc. The independence of both circuits was checked and corrected before each experiment.

The data output was usually recorded using X-Y, X-Y-Y' or X-t recorders, although for fast transients, either a signal averager or a storage oscilloscope was used. For some experiments, a microcomputer was interfaced in real time, to control the experiment and to acquire and process the data.

Procedure

In potentiostatic experiments, the electrode potential was quickly changed (< 0.01 s) from the cathodic potential used to reduce the air formed oxides to the desired anodic potential in the passive region. The film was allowed to grow for a fixed amount of time (1 hour unless otherwise specified) in buffer solution, and then a known volume of the concentrated sulfide solution was added with a glass syringe. The increase of the anodic current with time (chronoamperometry) was simultaneously recorded on an X-Y recorder and transmitted to a digital computer for further data processing.

In potentiodynamic experiments, the electrode potential was scanned in the anodic direction from the initial potential, -1.00 V, to the
final potential (e.g., +1.10 V) at a rate of 1.0 mV/s. Prior to the potential scan, the electrode was maintained at the initial potential until steady currents were obtained.

In most of the RRDE experiments, the ring was potentiostatically controlled, unless otherwise noted, at -0.70 V in order to analyze the Fe(III) going to solution. At potentials cathodic to -0.60 V, the reduction reaction of Fe(III) to Fe(II) was found to be diffusion limited, i.e., the reduction current was potential independent; however, there was some background current due to the reduction of water at the platinum electrode (H deposition), which increased with negative potentials.

Sometimes, the ring was potentiostated at a more noble potential (e.g., +0.70 V) in order to oxidize the Fe(II) produced on the disc to Fe(III). When sulfide ions were present, potentials in the diffusion limiting oxidation of Fe(II) could not be chosen because the oxidation of sulfide would produce considerable interference. In this case, the collection efficiency would be much less than the theoretical and would be potential dependent.

In galvanostatic RRDE experiments, the disc electrode was first polarized at a constant current of -1 mA for 2 min and then, unless otherwise specified, the current was stepped directly (<0.01 s) to an anodic value. In some cases, the electrode was allowed to rest at zero current for ~10 seconds before the anodic step in order to obtain the background ring current. In others, a potential step was applied from the cathodic region to the passive region to prevent active dissolution, then the control was changed to galvanostatic and the current step
applied. In order to obtain the ring current due to oxidation of Fe(II) to Fe(III), $I_{r+}$, and the cathodic current due to reduction of Fe(III) to Fe(II), $I_{r-}$, two parallel experiments were performed using identical conditions with exception of the ring potentials. This also served to check the reproducibility of the disc chronopotentiometric curves, which was usually excellent.

After each experiment, the electrode was quickly rinsed in conductivity water and ethanol, and then dried to be observed under a stereomicroscope. The number, location and morphology of the pits were noted. When necessary, an optical metallographic microscope was used to study the pits under higher magnification (up to 1000X). In some cases, surface deposits were analyzed using an analytical electron microprobe and a scanning electron microscope.

All values of current have been normalized using the corresponding geometric area.
IV RESULTS

IV.1 POTENTIODYNAMIC EXPERIMENTS

SULFIDE FREE SOLUTION

Figure 12 shows typical anodic polarization curves for iron in borate buffer containing various supporting electrolytes at pH 8.4.

This system presents an ideal active-passive behaviour in the absence of aggressive ions (curve A) with an active-to-passive peak at ca. –0.60 V and small passive currents.

Most of the studies reported in the literature regarding iron passivation have been performed in solutions containing supporting electrolytes such as nitrates, sulfates or perchlorates. However, those results have been found to depend on the nature and concentration of the "inert" anion. A great deal of attention has been given to this matter lately, but the available results are still considered controversial.

Some authors have reported inhibiting influence of sulfate, perchlorate and nitrate anions in the passivity breakdown process [100,105,107], whereas others have found these ions to be "agressive", i.e. to induce localized corrosion [106]. In view of these differences, some experiments were performed to determine which supporting electrolyte, if any, should be used.

Curves B and C in Figure 12 show the effect of the addition of NO₃⁻ and SO₄⁻ on the active to passive transition. The amount of charge necessary to passivate the electrode and the background passive current
Anodic Polarization of Iron in Borate Buffer Containing Different Supporting Electrolytes.

Sweep rate = 1 mV/s.

Curve A: Borate Buffer Only
Curve B: Borate Buffer + 0.5 M NaNO₃
Curve C: Borate Buffer + 0.5 M Na₂SO₄
increase when the "inert" electrolyte, is added to the pure borate. A similar effect in the polarization curve was also found for the addition of perchlorate ions into sodium hydroxide solutions.

Microscopic examination showed localized corrosion on the electrode surface after polarization experiments in sulfate and perchlorate solutions. The effect of nitrate anions in the passivation process, on the other hand, was not found to be pronounced and no localized corrosion was detected after polarization experiments. The relative aggressiveness of the anions at the concentrations studied was found to be $SO_4 > ClO_4 >> NO_3$.

Therefore, it was decided that none of these anions would be used in this study since they may affect the kinetics of the passivation breakdown process in an unpredictable way.

The cathodic current in Figure 12, curve A, at $E < -0.70$ V corresponds to reduction of water

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

The interpretation of the anodic curve, on the other hand, depends on the model adopted for the passivation process. Several reaction schemes have been postulated which can account for the observed anodic behaviour assuming either the formation of oxides or hydroxide films [85,95,141].

One of the schemes in agreement with our experimental results involves active dissolution of iron at potentials more negative than $-0.60$ V, peak (I):
\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{E}^0 = -0.86 \text{ V} \quad (52) \]

where the equilibrium potential \( \text{E}^0 \) was calculated at pH 8.4.

The \( \text{Fe}^{2+} \) ions either diffuse into the bulk of the solution or precipitate onto the surface as \( \text{Fe(OH)}_2 \), which would initiate an oxide film. The formation of this film is thermodynamically favored at the working pH [141]. Ellipsometric measurements indicate that the film formed before peak (I) is a 3-dimensional ferrous oxide phase, probably \( \text{Fe(OH)}_2 \), which begins to transform to ferric oxide at this peak. This transformation is complete at \( \sim 0.50 \text{ V} \) positive from peak (I) where the film is composed of \( \gamma\text{-Fe}_2\text{O}_3 \) [95]. Therefore, one may write the over-all reaction at anodic potentials as

\[ 2\text{Fe} + 3\text{H}_2\text{O} \rightarrow \gamma\text{-Fe}_2\text{O}_3 + 6\text{H}^+ + 6e^- \quad \text{E}^0 = -0.75 \text{ V} \quad (53) \]

The small residual currents \( i_{\text{pas}} \) in the passive region reflect a kinetic equilibrium between oxide formation, equation (53), and oxide dissolution. The over-all equation for the oxide dissolution process in basic media is

\[ \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Fe}^{3+} + 6\text{OH}^- \quad (54) \]

No transpassive dissolution is observed in the absence of aggressive ions, and the increase in current at \( \sim 0.80 \text{ V} \) is associated with the oxidation of water to yield oxygen:

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \quad (55) \]
Equations (52) to (55) are considered to be the only possible over-all reactions for iron in borate buffer in the absence of sulfides. A detailed discussion of these reactions will follow presentation of the results from rotating electrode experiments.

SULFIDE CONTAINING SOLUTION

Figure 13 presents typical anodic polarization curves, showing the influence of sulfide anions in the passivation process. Four major changes can be noted in the potentiodynamic curves when sulfide is added: peak (I) at ca. -0.60 V, corresponding to the active to passive transition, becomes a shoulder which tends to disappear at higher sulfide concentration; two peaks are formed at ca. -0.65 V, peak (II), and at ca. -0.20 V, peak (III); and the passive background current increases.

Due to the complexity of the system Fe-S-H₂O, the assignment of reactions for the different regions of the polarization diagram is controversial and will be discussed in more detail in section V.

Figure 14 shows the dependence of the anodic currents at peaks (II) and (III) on the the sulfide concentration at constant pH. The current at peak (III), \( i_{(III)} \) showed a higher order dependence on the aggressive anion concentration than the current at peak (II), \( i_{(II)} \). Empirically,

\[
\log i_{(III)} = 1.7 + 0.90 \log C_{Na₂S} \quad (56)
\]

\[
\log i_{(II)} = -1.3 + 0.27 \log C_{Na₂S} \quad (57)
\]

Severe pitting occurs on the electrodes polarized in solutions containing more than \( 10^{-3} \) M \( Na₂S \). During anodic polarization, a black
FIGURE 13

Effect of Sulfide Concentration on the Anodic Polarization of Iron in Borate Buffer.

Sweep Rate = 1 mV/s.

Curve 0: \( C_{Na_2S} = 0 \)
Curve 1: \( C_{Na_2S} = 10^{-5} \text{ M} \)
Curve 2: \( C_{Na_2S} = 10^{-4} \text{ M} \)
Curve 3: \( C_{Na_2S} = 10^{-3} \text{ M} \)
Curve 4: \( C_{Na_2S} = 10^{-2} \text{ M} \)
Dependence of Current Maxima at Peaks (II) and (III) of Figure 13 on Sulfide Concentration.
film began to form at ca. -0.75 V. This deposit was very thick but non-adherent.

**Surface Analysis**

In order to get more information to interpret the polarization curve in sulfide solutions, the following series of experiments were performed. The iron electrode was scanned potentiodynamically in the borate buffer containing 10^{-2} M Na_2 S following the same experimental conditions as before. The only difference was in that the potential scan was stopped at an anodic limit \( E_a \) and left in potentiostatic control for 25 min. For each experiment, a new solution and a new electrode were used. The electrode thus polarized was carefully rinsed in water and alcohol, dried and stored in a dessicator. The surface of the electrode was then studied, within few hours, under a scanning electron microscope (SEM) and the corrosion products analyzed using an analytical electron microprobe (AEM).

The major drawbacks of the AEM technique for our study were the fact that it could not measure oxygen and that the electron beam could penetrate into the iron substrate, thus increasing the minimum detection limit. Therefore, it would not be possible to discriminate between different oxide concentrations, or to detect very thin uniform films. However, very small deposits on the surface were detected without any substantial interference from the metallic substrate.

When the potentiodynamic scan stopped at \( E_a = -0.60 \) V, i.e., maximum of peak (I), the formation of the black film was just becoming
visible at a few spots. The anodic current increased under potentiostatic conditions from \( \sim 0.3 \text{ mA/cm}^2 \) to a maximum of \( \sim 0.5 \text{ mA/cm}^2 \) in 2 min. After 25 min, the anodic current returned to its initial value and approximately 90% of the electrode was covered by the black film. This indicates that the presence of this film (later identified as ferrous sulfide) does not passivate the metal even though the surface becomes almost completely covered by it. The ferrous sulfide film, formed under these conditions, did not peel off on washing and rinsing. Analysis of the surface by SEM and AEM showed two distinctive areas: Most of the electrode was covered with a "flaky", dry looking film for which the elemental composition was consistent with FeS, i.e., about 1:1 ratio S:Fe. The other area showed a "clean" iron (oxide) surface with less than 5% S. This area did not show any deposits and is believed to be covered by a sulfide-contaminated oxide film. No pitting corrosion was found.

Studies performed using X-ray diffraction, and Auger, at this pH have found mackinawite (tetragonal \( \text{Fe}_{1+x} \text{S} \)) to be the most probable ferrous sulfide formed under these experimental conditions [35,36].

The corrosion potential, \( E_c \), of iron in borate solution was found to be in the passive region, between \(-0.30\) to \(-0.40\) V. Sulfide addition shifted the corrosion potential towards active potentials, e.g. \( E_c \) ca. \(-0.8\) V at \(10^{-2}\) M \( \text{Na}_2\text{S} \). Therefore, at open circuit, iron should be expected to corrode actively producing mackinawite. In fact, this is the most common product found under natural corrosion conditions [31-34,43].
At $E_a = -0.20$ V, maximum of peak (III), the electrode surface appeared completely covered by the black film. Under potentiostatic conditions, the current decreased steadily with time from 0.82 to 0.09 mA/cm$^2$. The black film peeled off almost completely during the rinsing step. AEM analysis of the surface showed negligible amounts of sulfur except for some circular patches and very small amorphous deposits. These tiny deposits were found to be almost pure sulfur, whereas the patches were consistent with a FeS composition. No clear evidence of pyrite was found.

During the anodic potentiodynamic scan, the black film stopped growing after peak (III). At $E_a = + 0.20$ V, the current decreased slowly with time, from 0.26 to 0.16 mA/cm$^2$, showing some electrochemical noise. This suggests a competition between passivation process and active dissolution, i.e., pitting corrosion. AEM analysis of the surface showed a "clean" surface with negligible concentration of sulfur, except for some deposits of elemental S. Some shallow pits were found. The S:Fe ratio inside the pits was found to be ~1.8. This ratio, which is in between pyrite and mackinawite, can be interpreted either as a mixture of these two phases or as a mixture of mackinawite and sulfur.

AEM analysis of a sample polarized at $E_a = 0.80$ V showed some circular patches with sulfur concentration near the rims that matched closely to those from a standard pyrite sample. These deposits were amorphous and did not have the characteristic habit of pyrite, i.e., cube or pentagonal dodecahedron [53]. It has been suggested that, in some cases, framboidal pyrite (non-crystalline) is a necessary precursor.
to the euhedral (crystalline) form [142].

Therefore, even though AEM analysis is not completely conclusive in the sense that it can not positively identify different iron sulfide or oxide phases, the results of these experiments strongly indicate that peak (II) is not related to the formation of pyrite. This phase could be found only at high anodic potentials. The formation of elemental sulfur was unequivocally identified on the surface of electrodes polarized at potentials more positive than peak (III) and (possibly) inside pits at these anodic potentials. The general composition of the black sulfide film, as well as the major component of corrosion products inside pits, was consistent with a ferrous sulfide. Even though this experimental technique is not accurate enough to assure the stoichiometry, there is sufficient evidence in the literature to assume this film to be mackinawite [36,37].

It is important to note that no pitting potential, as defined in the section II.3 (Figure 6a) for potentiodynamic experiments, was found. However, potentiodynamic curves with similar general shape to the ones presented in Figure 13 have been reported for iron and stainless steels in chloride solutions containing "inert" anions [104-107]. The potential at which the anodic current begins to rise has been interpreted as pitting potential $E_p$, and the potential over which the metal repassivates, as inhibition potential $E_{inh}$ (cf. Figure 6c). Using these definitions in our system, the pitting potential would increase in the negative direction with sulfide concentration from ca. $-0.30$ V to ca. $0.43$, whereas the inhibition potential would increase in the noble direction from ca. $-0.03$ V. The significance of these two parameter $E_p$
and \( E_{inh} \), defined in this way is controversial and will be discussed in section V.3.

IV.2 GALVANOSTATIC RRDE EXPERIMENTS

SULFIDE FREE SOLUTION

Figure 15 shows a typical transient response of the disc potential and ring currents to an anodic current step at the iron disc in the pure borate buffer solution. The current step was chosen high enough to drive the electrode potential from the rest value to oxygen evolution. The chronopotentiometric curve presents three well defined sections, which can be described qualitatively as follow:

In region A, from the time the step is applied to a first arrest at ca. \(-0.60\) V, active dissolution of iron occurs. This potential arrest is associated with the active to passive transition, peak (I) in the corresponding potentiodynamic curve (cf. Figure 12). The anodic ring current, \( I_{r^+} \), increased in this region, presenting a peak at \(-3\) sec., at the same time the inflection in the disc potential appeared. This peak is associated to the maximum fraction of the anodic current used for active dissolution of the iron to Fe(II). The cathodic ring current, \( I_{r^-} \), did not show any increase, indicating that the only soluble species generated in the active dissolution of iron was Fe(II).

Region B represents the range where the electrode becomes passive and the oxide film grows. The chronopotentiometric curve is characterized by a linear increase of the potential with time [143-145].
Typical RRDR Galvanostatic Transient in Pure Borate Solution.

\[ i_d = 0.71 \text{ mA} \cdot \text{cm}^{-2} \]
\[ E_{r^+} = +0.70 \text{ V} \]
\[ E_{r^-} = -0.70 \text{ V} \]
The anodic ring current decreased sharply after the potential arrest indicating a negligible active dissolution of the iron at more noble potentials, i.e., the metal became passive. This section showed an increase in $I_{\text{an}}$, reaching a plateau shortly before the oxygen evolution started; this plateau is associated to the fraction of Fe(III) generated at the disc which was dissolved and reduced on the ring.

In region C, the potential reached the steady state corresponding to oxygen evolution. The anodic ring current did not show any increase in this region, indicating that the iron remained passive. On the other hand, the cathodic ring current increased beyond the first current plateau as soon as the oxygen evolution potential was reached at the disc. This rise in current was due to the reduction of the oxygen produced on the disc.

In order to interpret the ring curves quantitatively, the collection efficiency was determined experimentally.

**Collection Efficiency and Oxygen Evolution**

The theoretical collection efficiency $N_0$ for the Fe/Pt RRDE (iron disc/platinum ring) can be calculated using the values of R1, R2, and R3 measured with a traveling microscope (0.300, 0.411 and 0.556 cm respectively). From equations (31) to (34), $N_0$ was found to be 0.390.

In order to determine the value of $N_0$ experimentally, the difference between the two cathodic ring current plateaus in Figure 15, related to the reduction of the oxygen generated at the disc, was used.
Oxygen ionization is a complex electrochemical process involving both parallel and consecutive steps. It has been studied in great detail, specially at platinum electrodes [61]. In alkaline solution, the reduction reaction on a platinum electrode generally proceeds in two stages:

\[(\text{ring}) \quad O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad (59a)\]

followed by

\[(\text{ring}) \quad HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad (59b)\]

or

\[(\text{ring}) \quad HO_2^- + H_2O \rightarrow H_2O_2 + OH^- \quad (59c)\]

whereas the oxygen evolution on the passive iron can be expressed as

\[(\text{disc}) \quad 4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad (55)\]

These equations indicate that four electrons would be used in the oxygen evolution on the disc, i.e., $n_d = 4$, but that either four or two electrons could be used in its reduction, depending on whether the electrochemical reaction (59b) or the chemical reaction (59c) follows the initial step (59a). It was found, in agreement with results of Heusler and Fisher [144], that only two electrons were used in the oxygen reduction on the ring, i.e., the only electrochemical reaction that took place was (59a) and $n_r = 2$.

The average value of collection efficiency calculated using these experimental results with equation (30) was $N_0 = 0.35$, slightly smaller than the geometrical value 0.39. The experimental value was used in all
calculations involving Fe(III) reduction to Fe(II).

**Anodic Film Formation and Growth**

The total disc current $I_d$ in section B of the curve (Figure 15) is

\[ I_d = I_f + I_a + I_s \]  \hspace{1cm} (60)

where $I_a$ is the current due to active dissolution of iron, reaction (52); $I_f$ is the current due to film formation, reaction (53); and $I_s$ is the current due to oxide dissolution, i.e., combination of reactions (53) and (54).

The total applied current $I_d$ was constant throughout the experiment (0.71 ma/cm²). The portion of the total current used for active dissolution was obtained by potentiostatic controlling the ring at anodic potentials high enough to oxidize the Fe(II) ions going into the solution to Fe(III). From the anodic ring current, $I_{r^+}$, $I_a$ can be calculated using equation (30), where $n_d = 2$ and $n_r = 1$. Similarly, the current due to oxide dissolution was obtained by reducing the Fe(III) ions to Fe(II) on the ring controlled at negative potentials, $I_{r^-}$, i.e. $n_d = 3$ and $n_r = 1$.

The potential arrest (inflection) in the $E_d$ vs. t curve and the maximum in the $I_{r^+}$ vs. t curve indicate the beginning of the passivation process. If one considers that the electrode is not completely passive until the iron(II) dissolution current has become negligible ($t \sim 8$ s, $E_d \sim 0$ V), then the total charge $Q_d$ needed to passivate the electrode completely can be calculated to be $\sim 5.7$ mC/cm².
The amount of charge used in active dissolution, \( Q_a \) and the amount used in ferric oxide dissolution \( Q_s \) can be calculated integrating the proper \( I_r \) vs. \( t \) curve

\[
Q_a = \frac{2}{N_0} \int_0^t I_{r+} \, dt \tag{61}
\]

\[
Q_s = \frac{2}{N_0} \int_0^t I_{r-} \, dt \tag{62}
\]

Using the upper limit \( t = 8 \, \text{s} \) in equations (61) and (62), \( Q_a \) and \( Q_s \) were found to be \( \sim 25\% \) and \( \sim 5\% \) of \( Q_d \), respectively. Therefore, only \( \sim 70\% \) of the total charge needed for complete passivation was used to form the passive film, i.e. \( Q_f \sim 4 \, \text{mC/cm}^2 \).

The potential at which the disc current became negligible, i.e. \( E_d \sim 0 \, \text{V} \), coincided with the value of Flade potential, \( E_F \) for iron in borate buffer. Sato et al [96] found, using Auger Electron Spectroscopy, that at potentials positive to \( E_F \) the composition of the passive film was consistent with a ferric oxide phase. At potentials lower than \( E_F \), on the other hand, they found a dual layer of \( \text{Fe}_3\text{O}_4 \) and \( \text{Fe}_2\text{O}_3 \).

If one considers that at \( E_d \sim 0 \, \text{V} \), the charge \( Q_f \) was used to form ferric oxide, following the overall reaction (53), then the thickness of the oxide layer can estimated from Faraday's law, equation (63) to be \( \sim 22 \, \text{Å} \). Thus

\[
L = \frac{Q_f M}{F n \rho} \tag{63}
\]

where the film molecular weight \( M \) and density \( \rho \) were taken to be those
of the bulk $\gamma$-$\text{Fe}_2\text{O}_3$, i.e. 159.7 gr/mol and 5.1 gr/cm$^3$ respectively [88]. The film thickness thus calculated was very close, considering the different experimental conditions, to the results reported for iron passivated at $E = 0$ V using cathodic coulometric and ellipsometric measurements [90,91].

The minimum thickness found for a complete coverage of ferric oxide, is also in agreement with the results of Bockris et al [95]. They found that the ferrous oxide formed at low anodic potentials completely converted to ferric oxide at $\sim 0.5$ V positive to the peak potential, and calculated the oxide thickness to be $\sim 20$ Å.

The linear dependence of $E_d$ with time (and total charge) suggests that the anodic film grows linearly with anodic potentials, as found by Sato et al under potentiostatic conditions [90,91]. After correcting for iron and oxide dissolution the increase in thickness with potential was found to be $\sim 19$ Å/V, for potentials between 0 and 0.9 V. This value is slightly smaller than the ones reported under potentiostatic conditions [cf. equation (69)], since under galvanostatic conditions, the film is not allowed to reach the steady state thickness.

SULFIDE SOLUTIONS

Similar experiments to the ones just described were performed in sulfide containing solutions. However, the active-passive transition current in these solutions is too high (cf. Figure 13) and, therefore, most of the chronopotentiometric curves only shows the first section described above, i.e., the potentials reached a plateau at values
slightly more cathodic than the corresponding active-to-passive peak potential. The iron surface was rapidly covered by black Fe(II) sulfide and no Fe(III) could be detected at the ring. At higher anodic currents, the peak potential was eventually reached and the rest of the curve could be observed.

Figure 16 presents the results of a typical galvanostatic charge curve in the borate buffer containing 0.01 M Na_2S solution. This curve also exhibits three separate sections.

Section A' corresponds to the active dissolution of iron and formation of black ferrous sulfide. It presents a flat plateau at \( E_d \) ca. -0.65 V for quite a long time indicating that a large charge is needed to passivate the metal (~750 mC/cm\(^2\) compared to ~6 mC/cm\(^2\) in sulfide-free buffer). The fraction of the applied current used for iron dissolution, as measured by the anodic ring current \( I_{\text{ring}} \), decreased with time. This indicates that the iron surface was becoming passivated by the FeS and/or Fe(OH)_2.

The formation of the ferrous sulfide scale at pH 8.4 can occur, thermodynamically, at potentials about 0.3 V more active than the formation of Fe(OH)_2 [14,31]. This fact was also confirmed on potentiodynamic experiments, where the black iron sulfide was shown to appear cathodic to the active-to-passive peak associated with the formation of Fe(OH)_2. The ferrous sulfide film is poorly adherent and not likely to be passivating. Therefore, passivity in sulfide solutions probably involves adsorption competition between the OH\(^-\) and the HS\(^-\) for the surface, where a Fe(OH)_2 film is formed either displacing the FeS or forming a mixed phase.
FIGURE 16

Typical RRDR Galvanostatic Transient in Sulfide-Containing Borate Buffer.

\[
\begin{align*}
C_{Na_2S} &= 10^{-2} \text{ M} \\
I_d &= 2.8 \text{ mA cm}^{-2} \\
E_r^- &= -0.70 \text{ V}
\end{align*}
\]
The anodic film growth, section B', presents a potential arrest from ca. -0.37 to ca. 0.3 V. At these potentials the anodic ring current begins to oscillate, indicating fast cycles of active-passive transitions, i.e., pitting nucleation. Even though this type of oscillation in ring current has not been studied in depth, similar current oscillations have been reported in passivity breakdown of iron in chloride solutions, and have been ascribed to the onset of pitting corrosion [145]. The anodic ring current continues oscillating until the disc potential reaches the final plateau. Microscopic study of the surface after the experiment showed small diameter deep pits under the black deposits all over the sample.

The steady state potential in section C' appears to be due not to oxygen evolution but to the oxidation of sulfide. Sulfide adsorption has been shown to increase oxygen evolution overpotential beyond the sulfide oxidation potential on other solid electrodes [146]. It is supported in this case by the cathodic ring current, which does not present any increase due to oxygen reduction (as with the sulfide-free buffer).

IV.3 POTENTIOSTATIC EXPERIMENTS

Figure 17 presents a typical chronoamperometric curve for an iron electrode, under the potentiostatic conditions described in section III. The anodic current decays exponentially after the potentiostatic step is applied from the cathodic region to the passive region. After one hour at constant potential in the borate solution, the passive current had
FIGURE 17

Typical Current Transient Following a Potentiostatic Step in Borate Buffer and a Sulfide Injection

The Arrow Indicates the Moment of Sulfide Injection

\[ t_{\text{pas}} = 1\text{hr} \]

\[ E_{\text{inj}} = 0.30 \text{ V} \]

\[ E_{\text{pas}} = 0.30 \text{ V} \]

\[ C_{\text{Na}_2\text{S}} = 10^{-2} \text{ M} \]
usually decayed to values lower than ~ 0.1 \( \mu \text{A} \). This background current did not decrease much after one hour of passivation.

The low value of the passive current and its dependence with time were found useful for screening "unsuitable" samples. The working electrodes prepared as mentioned in section III, generally presented excellent crevice corrosion resistance and could be safely repolished and reused. However, after high metal dissolution, the iron-epoxide junction may lose its tightness and allow crevice corrosion to occur. In this case, the current decay with time is slower and the passive current obtained after one hour is substantially higher (> 2 \( \mu \text{A} \)).

Following sulfide injection and after a short induction time, the chronoamperometric curve usually exhibits a two-stepped rise to a maximum and then decays to a steady state value.

The first rising section of the curve (region i), was found to be associated with the formation of a sulfide phase on the surface. No localized corrosion was observed if the experiment was stopped before the onset of the second rise. Microscopic examination showed only the presence of dark circular patches throughout the surface with no visible pitting underneath. SEM and AEM studies showed these spots to consist of small deposits of FeS. Similar patches have been produced in other sulfide containing basic solutions and have been identified as mackinawite [37]. These patches always precede pitting, but if the sulfide concentration is too low, sulfide patches are formed but no localized corrosion is found. In this latter case, the current transient curve only exhibits the first plateau, with no onset of pitting after several hours of exposure. Therefore, the formation of
iron sulfide patches is a necessary but not sufficient condition for the pitting process to occur.

The presence of a current plateau preceding the onset of active pitting at constant potential has been reported for passivity breakdown of stainless steel and aluminum by chlorides [99,147]. In the latter case, the formation of an aluminum chloride compound on the surface was postulated as the initiation step in the pitting process.

The second rising section of the curve (region p) is characterized by a sharp increase in the anodic current, which is generally accompanied with electrochemical noise. This current usually passes through a maximum $I_{p,m}$ before stabilizing. This region was shown to be associated with the pitting process itself. Higher maximum currents correlated with more and/or deeper pits.

The morphology and location of the pits were studied under an optical microscope after each experiment. If $I_{p,m}$ was low, the surface showed only circular shaped patches. Small pits were found to nucleate beneath the outside edge of the sulfide spots in such a way that, after the surface was slightly polished with alumina, the pits delineated the original patch perimeter. Conversely, if $I_{p,m}$ was high, deposits shaped as a “volcano” were formed on the surface. After removing these deposits, intensive pitting corrosion was found underneath. All the individual pits that had nucleated beneath a patch coalesced, given the impression of a macroscopic pit. The deepest part of this pit was near the edge of the deposit. The center the deposit generally remained at the same level as the outside surface, i.e., practically uncorroded. The major component inside pits was identified as FeS.
Pitting corrosion was located preferentially close to the lower edge of stationary (vertical) electrodes. On the other hand, pits were generally found to nucleate at random on rotating (horizontal) electrodes, although at higher angular velocities they tended to concentrate near the center.

Two experimental parameters were chosen to characterize the potentiostatic curves: The current maximum at each section, $I_m$, and their induction times $\tau$ (time before onset of current). Since there are several parallel reactions occurring on the surface at the same time, the effect of sulfide addition on the anodic currents were studied using currents increments, i.e.

$$\Delta I_i = I_i - I_{pas}$$

$$\Delta I_p = I_p - I_{i,m}$$

where $I_{pas}$ is the background passive current before the sulfide addition, $I_i$ is the current at the first process, and $I_p$ the current at the pitting process.

The effect of sulfide concentration, passivation potential, and passivation time on both the induction time and current maximum were investigated using vertical electrodes in stagnant solutions. Hydrodynamic effects were studied using rotating disc and rotating ring/disc electrodes.
EFFECT OF SULFIDE CONCENTRATION.

Figure 18 shows the dependence of induction times on sulfide concentration, with electrode potential as a parameter also. If one assumes that $1/\tau$ is a measure of the rate of initiation of the passivity breakdown [109], then the reaction order for initiating the first process $n_1$ and for initiating the pitting process $n_p$ can be directly calculated from the slope of the logarithmic plot. From equation (47) it follows that

$$\frac{\partial \log \tau_1}{\partial \log C_{Na_2S}} = -n_1$$
(66)

$$\frac{\partial \log \tau_p}{\partial \log C_{Na_2S}} = -n_p$$
(67)

from which $n_1$ and $n_p$ were calculated to be ca. 1 and 2 respectively. These results suggest that the first process is associated with the formation of a surface compound with one sulfide atom, possibly FeS. The pitting process initiation, however, would involve two sulfide atoms.

Figure 19 shows the dependence of the current maximum associated with the first process, $I_{i,m}$, on sulfide concentration, with potential as a parameter. $I_{i,m}$ shows a linear dependence with the square root of sulfide concentration at low anodic potentials, up to ~ 0.5 V, plot (a), and linear with the sulfide concentration at higher anodic potentials, plot (b). This change in the over-all reaction order indicates that a
FIGURE 18

Dependence of Initial and Pitting Induction Times on Sulfide Concentration Under Potentiostatic Conditions.

$t_{pas} = 1 \text{ hr}$

$E_{inj} = E_{pas}$

<table>
<thead>
<tr>
<th>Initial</th>
<th>Pitting</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>(■)</td>
<td>(□)</td>
<td>$-0.20 \text{ V}$</td>
</tr>
<tr>
<td>( )</td>
<td>(+)</td>
<td>$+0.20 \text{ V}$</td>
</tr>
<tr>
<td>(●)</td>
<td>(○)</td>
<td>$+0.80 \text{ V}$</td>
</tr>
</tbody>
</table>
FIGURE 19

Dependence of Initial Current Maximum on Sulfide Concentration Under Potentiostatic Conditions.

\[ C_{\text{Na}_2\text{S}} = 10^{-2} \text{ M} \]

\[ t_{\text{pas}} = 1 \text{ hr} \]

\[ E_{\text{inj}} = E_{\text{pas}} \]

Plot (a): \[ \Delta I_{i,m} \text{ vs. } C_{\text{Na}_2\text{S}}^{1/2} \]

(+) \[ E = + 0.20 \text{ V} \]

(□) \[ E = - 0.20 \text{ V} \]

Plot (b): \[ \Delta I_{i,m} \text{ vs. } C_{\text{Na}_2\text{S}} \]

(○) \[ E = + 0.80 \text{ V} \]
change on the mechanism may take place at high anodic potentials, and/or that a different reaction product may be formed.

Figure 20 shows the dependence of the current maximum associated with the pitting process, $\Delta I_{p,m}$, on sulfide concentration under the same experimental conditions of Figure 19. The slope is in all cases ca. 2, indicating that the over-all reaction order for the pitting process does not change with potential.

EFFECT OF ELECTRODE POTENTIAL

Figure 21 shows the dependence of the initial (Curve A) and pitting (Curve B) induction times on the applied potential. The electrodes were passivated for one hour before the sulfide addition, keeping constant potential throughout the experiment.

The induction time of the initial process is, within experimental error, independent of potential. The dispersion is mainly due to a non-uniform sulfide concentration in the electrochemical cell for the first seconds after sulfide injection. This non-uniform distribution strongly affects the values of $\tau_i$, which were in all cases under 10 s.

The pitting induction time, $\tau_p$, on the other hand, decreases with increasing potentials passing through a minimum at $\approx 0.20$ V. The magnitude of the potential dependence for $E < 0.20$ V (slopes ca. $-0.9$ dec/V) is smaller than for $E > 0.20$ V (slopes ca. 2 dec/V). These results indicate that the rate of pitting initiation increases slightly with potential, reaching a maximum at $\approx 0.20$ V. For higher potentials, the initiation rate decreases, suggesting a competition between
FIGURE 20

Dependence of Pitting Current Maximum on Sulfide Concentration Under Potentiostatic Conditions.

\[ t_{\text{pas}} = 1 \text{ hr} \]
\[ E_{\text{inj}} = E_{\text{pas}} \]

(o) \[ E = +0.80 \text{ V} \]
(⊕) \[ E = +0.20 \text{ V} \]
(□) \[ E = -0.20 \text{ V} \]
FIGURE 21

Dependence of Initial (A) and Pitting (B) Induction Times on Applied Potential.

\[ t_{\text{pas}} = 1 \text{ hr} \]
\[ E_{\text{inj}} = E_{\text{pas}} \]
\[ C_{\text{Na}_2\text{S}} = 10^{-2} \text{ M} \]

Curve A: \[ \tau_i \text{ vs. } E \] (○)

Curve B: \[ \tau_p \text{ vs. } E \] (△)
passivity breakdown and repassivation processes. This dependence does not follow the empirical relationship generally reported for pitting corrosion by halides [144]

\[ \log \tau = \frac{U}{AE} \] (68)

where \( AE = E - E_p \) and \( U \) is a constant.

Figure 22 shows the dependence of the initial (Curve A) and Pitting (Curve B) current maxima on the applied potential. The current maximum associated with the first process, \( AI_{i,m} \), is nearly potential independent for \( E < \sim 0.30 \text{ V} \), which suggests a diffusion controlled reaction. At higher anodic potentials, \( AI_{i,m} \) increases exponentially with potential, with a Tafel slope of \( \sim 0.11 \text{ V/dec} \). This indicates the onset of a new reaction on the surface.

Curve B in Figure 22 shows larger dispersion due not only to the stochastic nature of the pitting process but also to the effect of the solution agitation, not accurately controlled in these experiments. The current maximum associated with the pitting process, \( AI_{p,m} \), also shows a maximum between 0.20 and 0.30 V, decreasing sharply at higher potentials.

The sharp reduction of the pitting current and the increase in its induction time (cf. Curves B in Figures 22 and 21) coincides with the onset of a new reaction on the surface (Curve A in Figure 22). These results suggest a competition between the the passivation and the breakdown process. The effect of high anodic potentials on the passivation (or repassivation) process is higher than on the pitting process.
FIGURE 22

Dependence of initial (A) and Pitting (B)

Current Maxima on Applied Potential.

\[ t_{\text{pas}} = 1 \text{ hr} \]
\[ E_{\text{inj}} = E_{\text{pas}} \]
\[ C_{\text{Na}_2S} = 10^{-2} \text{ M} \]

Curve A: \[ \Delta I_{i,m} \text{ vs. } E (O) \]
Curve B: \[ \Delta I_{p,m} \text{ vs. } E (+) \]
The potential dependence of the passivity breakdown process can be caused by different factors. These could not be separated based on previous experimental conditions since the passive film properties and the heterogeneous reactions at the surface changed simultaneously with increasing applied potential. The following factors should be considered: i) the thickness of the oxide film increases at a rate of \( \sim 23 \, \text{Å/V} \) [93]; ii) the composition of the passive film changes [89, 96, 97]; iii) the rate of sulfide oxidation increases; or iv) a new sulfur-containing phase is formed.

In order to determine whether the potential dependence of the passivity breakdown is associated to the potential at which the passive film is grown, or is due to the potential at which the sulfide is injected, the experiments described below were performed.

**Effect of Injection Potential**

Figure 23 shows typical potentiostatic current transients following sulfide injection. The electrodes were previously passivated at \( E_{\text{pas}} = 0.80 \, \text{V} \) for 1 hr and the potential quickly stepped to the desired value of \( E_{\text{inj}} \). The sulfide solution was added after the new steady state current was reached. Under these experimental conditions, the thickness and composition of the passive layer remains nearly the same for all the experiments [13]. The chronoamperometric curves showed only an initial increase, proportional to the square root of time, which reached a maximum before stabilizing.
FIGURE 23

Effect of Injection Potential on the Current Transient After Sulfide Injection Under Potentiostatic Conditions.

\[ t_{\text{pas}} = 1\text{hr} \]
\[ E_{\text{pas}} = 0.80 \text{ V} \]
\[ C_{\text{Na}_2\text{S}} = 10^{-2} \text{ M} \]

Curve A: \[ E_{\text{inj}} = 0.40 \text{ V} \]
Curve B: \[ E_{\text{inj}} = 0.00 \text{ V} \]
Curve C: \[ E_{\text{inj}} = -0.20 \text{ V} \]
The induction time $\tau_i$ increased slightly with $E_{\text{inj}}$ and were ~ 2 times greater than those measured at the same potential but under the conditions of $E_{\text{pas}} = E_{\text{inj}}$. This suggests that more time is necessary to break through the oxide film when it has been grown at higher potentials.

The maximum current $I_{i,m}$ showed no appreciable dependence on injection potential between -0.20 V and 0.40 V. Their magnitudes, however, were ~ 3 times higher than those measured at the same injection potentials but under the condition $E_{\text{pas}} = E_{\text{inj}}$. It is difficult to rationalize the higher reaction rates measured on thicker oxide films if ion penetration through the oxide film is assumed. Therefore, a different explanation must be obtained.

The fact that higher currents in the initial process are associated with a reduction of the pitting tendency suggests that a different sulfur-containing phase with passivating properties is formed on the surface under these conditions. At these anodic potentials, several oxidation reactions are thermodynamically possible for the system Fe-S-H$_2$O (cf. section V.1). Either precipitation of elemental sulfur or formation of pyrite, FeS$_2$, could induce repassivation of the surface.

**Effect of Passivation Potential**

The effect of the film growth potential on the passivity breakdown is illustrated in Figure 24. After passivation at different constant potentials (e.g., $E_{\text{pas}} = 0.80$ V), for one hour, the potential was changed as quickly as possible to $E_{\text{inj}}$ (e.g., 0.20 V) and sulfide was
FIGURE 24

Effect of Passivation Potential on the Current Transient After Sulfide Injection Under Potentiostatic Conditions.

\[ t_{\text{pas}} = 1\text{hr} \]
\[ E_{\text{inj}} = 0.20 \text{ V} \]
\[ C_{\text{Na}_2\text{S}} = 10^{-2} \text{ M} \]

Curve A: \[ E_{\text{pas}} = 0.20 \text{ V} \]
Curve B: \[ E_{\text{pas}} = 0.80 \text{ V} \]
injected then. Passivating the iron electrode at higher potentials (e.g., 0.30 V compared to 0.20 V) resulted in a twentyfold increase in \( \tau_p \), and a one order of magnitude decrease in \( I_{p,m} \) (note the difference in the scale for the curves). In addition, \( \tau_i \) doubled.

Similar results have been reported in the case of pitting corrosion of iron in chloride solutions, and ascribed, according to the ion penetration model, to an increase in the film thickness [148,149]. However, a functional relationship between the thickness and the induction time has not been established. Since different potentials were used to change the film thickness, variations in film composition could also be a factor (as shown in our results).

It seems that the most important factor in the process leading to passivity breakdown of iron by sulfides is the growth potential, which in turn determines the composition and thickness of the passive layer. The injection potential seems to have more effect on the pitting process itself, where higher anodic potentials tend to increase pitting. Highly positive potentials, however, favor the formation of a different surface phase which repassivates the electrode.

**EFFECT OF PASSIVATION TIME**

Figure 25 shows typical chronoamperometric curves obtained under the same conditions except for the passivation time: \( t_{\text{pas}} = 1 \) hr (Curve A) and \( t_{\text{pas}} = 14 \) hr (Curve B). The main effects of longer passivation times were i) an increase in the pitting induction time and ii) a decrease in pitting current. The pitting induction time \( \tau_p \) increased ~
FIGURE 25

Effect of Passivation Time on the Current Transient After Sulfide Injection Under Potentiostatic Conditions.

\[ E_{\text{pas}} = E_{\text{inj}} = 0.20 \text{ V} \]
\[ C_{\text{Na}_2\text{S}} = 10^{-2} \text{ M} \]

Curve A: \[ t_{\text{pas}} = 1 \text{ hr} \]
Curve B: \[ t_{\text{pas}} = 14 \text{ hr} \]
30 times, whereas \( i_{p,m} \) decreased \( \sim 3 \) times. On the other hand, \( \tau_i \) and \( i_{i,m} \) were practically independent of the passivation time.

Table I presents calculated passive film thicknesses of iron in borate buffer for different values of \( E_{\text{pas}} \) and \( t_{\text{pas}} \). The following empirical equation was used to estimate the change of thickness with potential [89-91]

\[
L = 9 + 24 (E_{\text{pas}} + 0.75)
\] (69)

where \( L \) is the thickness of the passive film in Å after 1 hr polarization in the borate buffer pH 8.4 at constant potential \( E_{\text{pas}} \). The increase in the oxide film thickness after \( t_{\text{pas}} = 1 \) hr was estimated in \( \sim 0.2 \) Å/hr [13]. In some cases, however, thicker oxides can be formed by oxidation and deposition of the ferrous ion dissolved during active dissolution. This is not considered to be the case in the borate buffer where active dissolution is very small.

If one assumes that the only effect of the increased passivation time is to increase the passive film thickness, then the increase in pitting resistance could qualitatively be interpreted as a proof for the mechanism of ion penetration. However, the thickness difference between the film grown for \( t_{\text{pas}} = 1 \) hr and the one grown for \( t_{\text{pas}} = 14 \) hr was estimated in only 9% (cf. Table I). This suggests that the effect of such an increased pitting resistance at \( E_{\text{pas}} = 0.20 \) V with passivation time can not be attributed solely to an increase in thickness.

Table I also shows that the thickness of the oxide film grown for \( t_{\text{pas}} = 16 \) hr at \( E_{\text{pas}} = 0.60 \) V is \( \sim 10 \) Å smaller than the film grown for \( t_{\text{pas}} = 1 \) hr at \( E_{\text{pas}} = 0.80 \) V. If we consider \( \tau_p \) to be the time
TABLE I

Passive Film Thickness of Iron in
Borate Buffer, pH 8.4.

<table>
<thead>
<tr>
<th>$E_{\text{pas}}$ (V)</th>
<th>$t_{\text{pas}}$ (hr)</th>
<th>L (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>1</td>
<td>32</td>
</tr>
<tr>
<td>0.20</td>
<td>14</td>
<td>35</td>
</tr>
<tr>
<td>0.60</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>0.60</td>
<td>16</td>
<td>43</td>
</tr>
<tr>
<td>0.80</td>
<td>1</td>
<td>45</td>
</tr>
</tbody>
</table>
necessary to "penetrate" the oxide barrier, then \( v_p \) should be much larger for \( E_{\text{pas}} = 0.80 \). Results in Figure 25 and 24 show, on the contrary, that the pitting induction time was \( \sim 200 \) s longer for \( E_{\text{pas}} = 0.20 \) V. This result suggests that the penetration theory is not applicable in this case.

**EFFECT OF ANGULAR VELOCITY**

The experiments in this section were performed using both RDE and RRDE. The iron disc electrodes were passivated in the pure buffer solution for 1 hr before the injection of the deoxygenated sulfide solution. The angular velocity was maintained constant during each experiment.

The current transient after sulfide injection presented the same general features described for stationary electrodes (cf. Figure 27). For low anodic potentials (e.g., \( E = 0.20 \) V), the transient followed a \( i-t^{1/2} \) relationship, similar to the one shown in Figure 23. When using RRDE, the ring was potentiostatically controlled to measure an increase in either the \( \text{Fe}^{3+} \) or the \( \text{Fe}^{2+} \) dissolution. However, at the potentials necessary to measure \( \text{Fe}^{2+} \) (e.g., \( 0.70 \) V), the sulfide ions are oxidized at the ring, inducing faradaic currents of, typically, one order of magnitude higher than the disc currents. The measurement of the \( \text{Fe}^{3+} \), on the other hand, was affected by its chemical reaction with the sulfide in solution, and also by the change in the background hydrogen evolution current. The latter is due to the dependence of the hydrogen overvoltage on sulfide concentration. Therefore, ring current
transients were not conclusive and will not be presented.

The effect of rotation speed on the passivity breakdown is rather complex because it affects the various processes involved, e.g. iron sulfide formation, pit nucleation and growth, and repassivation, in different ways.

At very low velocities (quasi-stagnant solution) there was no noticeable increase in passivation current even 2 hours after sulfide injection. No signs of localized corrosion or formation of iron sulfide nuclei were detected on the electrode under 1000X magnification. If under steady state conditions, the rotation speed was increased, the anodic current was found to increase but in a highly irreversible way, i.e., the current did not return to the original steady state when returned to the low velocity.

Figure 26 shows the dependence of first plateau current $I_{i,\infty}$ on the rotation speed. In the range of angular velocities used, $I_{i,\infty}$ was shown to be proportional to the square root of the angular velocity, which suggests a diffusion control reaction [cf. equation (27)].

The small value of the slope of the $I_i$ vs. $\omega^{1/4}$ line, i.e. 0.39 $\mu A \cdot cm^{-2} \cdot s^{3/4}$, indicates that either the diffusion constant or the concentration of the limiting species is very small. The diffusion constant of ionic species in aqueous solutions, however, is usually in the range of $10^{-5}$ to $10^{-6}$ cm$^2$/s, e.g. $D_{Fe^{2+}} = 5.7$ to $8.5 \cdot 10^{-6}$ cm$^2$/s [150]. Using an average value of $D = 6 \cdot 10^{-6}$ cm$^2$/s, and $\omega = 10^{-2}$ cm$^2$/s, then the concentration of the limiting species can be estimated from equation (27) to be in the order of $2 \cdot 10^{-5}$ M, assuming a 2 electron transfer.
FIGURE 26

Dependence of First Plateau Current
on Rotation Speed

\[ t_{\text{pas}} = 1\text{hr} \]
\[ E_{\text{pas}} = 0.20 \text{ V} \]
\[ E_{\text{inj}} = E_{\text{pas}} \]
\[ C_{\text{Na}_2\text{S}} = 10^{-2} \text{ M} \]
The activity of the different sulfide species in the solution can be calculated from the following equilibria [52]

\[ \begin{align*}
    H_2S & \rightleftharpoons HS^- + H^+ & K \sim 1 \cdot 10^{-7} \\
    HS^- & \rightleftharpoons S^{2-} + H^+ & K \sim 1 \cdot 10^{-14}
\end{align*} \] (70a) (70b)

At the working pH 8.4, and for total sulfide concentration of $10^{-2}$ M, the concentration of the different sulfide species in the bulk of the solution are

\[ \begin{align*}
    c_{HS}^b & \sim 1 \cdot 10^{-2} \text{ M} \\
    c_{S^2}^b & \sim 4 \cdot 10^{-4} \text{ M} \\
    c_{S^2}^b & \sim 2 \cdot 10^{-8} \text{ M}
\end{align*} \]

where activity coefficients have been assumed to be unity.

Consequently, the first reaction leading to passivity breakdown is not controlled by diffusion of any of the sulfide species from the bulk of the solution.

Dissolution of metals, however, can also be transport-controlled by species diffusing away from the electrode. In this case, equations (24)-(27) can be easily modified to obtain the following equation

\[ i_d = 0.62 nF \gamma^{-1/6} D^{2/3} \omega^{1/2} (c^S - c^b) \] (71)

where the limiting current $i_{d,1}$ is found when the concentration of the dissolving compound at the surface is equal to its solubility at the given pH and temperature, and the bulk concentration of the dissolving compound is negligible.
Similar results have been reported by Tewary et al. [151-153] for carbon steel corrosion in high pressure hydrogen sulfide solutions at pH 3-5. These authors explained the linear dependence of the rate of uniform dissolution of iron discs with respect to the square root of the angular velocity by assuming an equilibrium between the breakdown rate and the rate of development of the corrosion products. They measured the solubility of the different iron sulfides, and concluded that the corrosion was most probably controlled by the dissolution of mackinawite and transport of FeSH\(^+\). Extrapolation of their dissolution data to pH 8.4 was considered, however, unreliable. The dependence of solubility on pH was performed maintaining constant pressure of H\(_2\)S, but the effect of increasing the total amount of dissolved sulfide species (H\(_2\)S + HS\(^-\) + S\(^-\)) with the pH was not considered [152,153].

The pitting current maximum \(I_{p,m^*}\) on the other hand, was affected in the opposite way, i.e., the current maximum decreased as the rotation speed increased. Correspondingly, the number and depth of pits also decreased with \(\omega\).

The steady state current \(I_{p,\infty}\) was found to increase with the rotation speed. This velocity dependence of the steady state current, however, was not proportional to the square root of the angular velocity \(\omega\). Furthermore, the current changes were slightly higher on going from low \(\omega\) to high \(\omega\) than on going in the opposite direction. Therefore, the steady state reaction is not controlled by solution diffusion and it is more probably controlled by diffusion through corrosion deposits which can be removed by the electrode rotation.
IV.4 PHOTOELECTROCHEMICAL EXPERIMENTS.

One of the most important parameters affecting the breakdown of passivity on iron in sulfide-containing borate buffer was shown in previous sections to be related to the properties of the passive film. The following experiments were performed to obtain more information about the changes occurring in this film during the passivity breakdown.

A potentiostatic technique similar to the ones used in the last section was used. The main difference was that the photocurrent response was measured simultaneously with the total anodic current.

No interference is expected to occur between the photoelectrochemical process (which involves very small currents) and the passivity breakdown process.

SEMICONDUCTOR PROPERTIES OF PASSIVE FILMS

Experiments performed in this laboratory have demonstrated that the passive films of iron in borate solutions exhibit semiconductor properties [12,13]. When illuminated with light with energy greater than the band gap, $E_g$, passive films on iron generate photocurrents which have sizable magnitude considering their thickness. The photocurrent response, $I^*$, has been investigated as a function of pH, electrode potential and buffer composition [13]. In general, the spectral response curves for all solutions and electrode potentials are identical except for magnitude. This observation tends to support the oxide film theory rather than the absorption theory of passivity.
The dependence of the photocurrents on light energy in the visible region \((I^* \text{ vs } \lambda)\) is seen in Figure 27. The visible spectral response curves are not corrected for light attenuation by the monochromator system, source intensity, or solution absorbance. The shape of the curves is jointly determined by the efficiency of the monochromator grating and the absorbance of the oxide film. The maximum of the curve appears at \(\lambda \sim 400\) nm. The sharp drop of the photoresponse at higher energies (lower \(\lambda\)) is due to the long pass (L.P.) filter used, which absorbs light of lower wavelength. The solid curve was obtained using a 300 nm L.P. filter, whereas the discontinuous plot was done with a 470 nm L.P. filter. These filters were used to eliminate higher order diffractions from the monochromator, which could introduce false peaks, e.g. peaks at \(\lambda > 575\) nm (solid line). The actual photocurrent response at higher wavelength (discontinuous line) decreases to zero at \(\sim 630\) nm. This value, i.e. the minimum energy required to observe a photocurrent response, corresponds to a bandgap energy, \(E_g \sim 2.0\) eV. This result is in excellent agreement with reported values for anodically grown iron oxides, \(E_g = 2.0\) eV [13], for thermally grown iron oxides, \(E_g = 2.0\) eV [154], and for polycrystalline \(\alpha-\text{Fe}_2\text{O}_3\), \(E_g \sim 1.7-2.0\) eV [155].

In order to find out whether the photocurrent was cathodic or anodic, the total current was measured directly, without using a lock-in amplifier, chopping the light manually at regular intervals. In this way, the photocurrents were found to be anodic, which corresponds to the normal behaviour of a n-type semiconductor biased at potentials positive to its flat-band potential.
FIGURE 27


\[ t_{\text{pas}} = 1 \text{ hr} \]
\[ E_{\text{pas}} = 0.80 \text{ V} \]

Solid line: Filter = 300 nm, L.P.

Broken line: Filter = 470 nm, L.P.
Fe₂O₃ is an n-type semiconductor. The least controversial, but not universally accepted, data concerning this semiconductor are the flat-band potential and the bandgap. Taking the flat-band potential to be ca. +0.4 V vs. RHE [156] or (equivalent) ca. −0.3 V vs. SCE in the borate buffer (pH 8.4), then the application of a potential of 0.60 or 0.80 V SCE should give rise to an anodic photocurrent on absorption of light of energy larger than the bandgap. The faradaic process associated with this anodic current in the sulfide free buffer is evolution of O₂ according to

$$2h^+ + 20H^- \rightarrow \frac{1}{2}O_2 + H_2O$$

(72)

Figure 28 shows the effect of the passivation time on the spectral response. The magnitude of the photocurrents increased with $t_{pas}$, keeping the shape of the curve unchanged. In fact, recording the photocurrent response with time following the step from cathodic to passive potentials, it was found that most of the increase in the photocurrent occurred at the initial times of passivation, when the thickness of the film increased faster. However, the difference in thickness between the film grown at $E_{pas} = 0.20$ V for $t_{pas} = 1$ hr and the one grown for $t_{pas} = 16$ hr was estimated to be only $\sim 3 \text{ Å}$, i.e. $\sim 8$ % (cf. Table I). It is difficult to rationalize a $\sim 80$ % increase in photoresponse caused by the increase in $t_{pas}$, if the thickness only is considered. Therefore, other reasons for the photoreponse increase must be found.
Effect of Passivation Time in the Spectral Photoresponse of Passive iron in Borate Buffer.

\[ E_{\text{pas}} = 0.60 \text{ V} \]
\[ \text{L.P. Filter} = 300 \text{ nm} \]

Curve A: \[ t_{\text{pas}} = 1 \text{ hr} \]
Curve B: \[ t_{\text{pas}} = 16 \text{ hr} \]
The effect of the passivation potential can be studied by comparing Figures 28 and 27. The magnitude of the photocurrents increased with anodic potentials, leaving the spectrum unchanged. This effect could be due either to a slightly thicker oxide layer in the passive film grown at 0.80 V (see Table I) or to larger rate constants.

If the kinetics of the photoelectrochemical reaction (72) is very slow on the iron oxide surface, then the photocurrent would show an exponential dependence on the applied potential [cf. equation (17)]. Conversely, if the photoelectrochemical reaction is controlled by the hole production, then the photocurrent would show a square root dependence on the applied potential [cf. equation (50)]. In consequence, the increase of photoresponse with potential could be due to an increase in the faradaic process instead of an increase on the oxide thickness.

In order to separate these two effects, i.e. oxide thickness and faradaic process, the following procedure was used. The electrode was passivated for $t_{\text{pas}} = 16 \text{ hr at } E_{\text{pas}} = 0.60 \text{ V}$ prior to the application of a voltage pulse to the potential of measurement. The photocurrent was quickly determined ($\sim 10 \text{ s}$) and the potential was then instantaneously returned to $E_{\text{pas}}$ until steady state conditions were reached. The purpose of this procedure was to maintain constant oxide thickness during the measurements. This was checked by comparing both the total anodic current and the photocurrent after the pulses with their original values.
The potential dependence of the photocurrent at constant film thickness can be seen in Figure 29. The onset potential, defined as the potential just anodic to which photocurrent can be observed, was found to be \(\sim 0.1 \text{ V}\). Even though the onset potential is generally very close to the flat-band potential for ideal semiconductors, it was found to be too anodic in this case. This discrepancy can be explained by the low faradaic reaction rate, which makes the determination of the currents at potentials close to the flat-band potential very difficult. Besides, the change of sign in the photocurrent at potentials negative to \(E_{fb}\) could not be corroborated since, due to the low magnitude of the current \(10^{-9} \text{ A}\), a lock-in amplifier had to be used. Similar discrepancies have been reported on polycrystalline \(\alpha-\text{Fe}_{2}\text{O}_{3}\) electrodes in basic solutions [156].

Between 0.25 V and 0.55 V, the photocurrent showed an exponential increase with potential (Tafel slope \(\sim 0.21 \text{ V/dec.}\)) indicating a faradaically controlled reaction. At higher anodic potentials, the curve began to flatten up, suggesting that transport phenomena became significant.

A photocurrent of \(\sim 0.60 \mu\text{A/cm}^2\) can be obtained from extrapolation of Figure 29 to \(E = 0.80 \text{ V}\). This value is significantly higher than the one obtained from the electrode at \(E_{pas} = 0.80 \text{ V}, t_{pas} = 1 \text{ hr}, \text{i.e.,}\) \(0.31 \mu\text{A/cm}^2\) for \(\lambda = 400 \text{ nm}\) in Figure 27. This strongly suggests that the oxide thickness is not the only parameter affecting the photoresponse.
**FIGURE 29**

Potential Dependence of Passive Iron

Photocurrent in Borate Buffer.

\[ E_{\text{pas}} = 0.60 \text{ V} \]
\[ t_{\text{pas}} = 16 \text{ hr} \]
\[ \lambda = 400 \text{ nm} \]
It seems logical to consider that the oxide film formed during longer time may have fewer defects or more crystalline properties. This would increase the photoelectrochemical properties of the semiconducting film. Equation (50) shows that the photocurrent is inversely proportional to the square root of the donor concentration $N_D$. In Fe$_2$O$_3$ semiconductors, $N_D$ is related to the concentration of Fe$^{2+}$ in the lattice or, more generally, to its non-stoichiometry [136].

Therefore, photoelectrochemical results are consistent with a decrease in the non-stoichiometry of the oxide film with time of passivation.

EFFECT OF SULFIDE ADDITION

Figure 30 shows the electrode (dark) current and photocurrent transients after sulfide injection under potentiostatic conditions. Following a short induction time of nearly the same magnitude, both the total electrode current, $I$, and the photocurrent, $I_{\lambda=400 \text{ nm}}^\ast$, increased in a similar way to a plateau. Since no pitting was found on the electrode surface after the experiment, the total electrode current plateau was associated to the first process described in Figure 17, i.e. $I = I_i$. The fact that the induction times for both the initial process and the photoelectrochemical reaction were nearly identical indicates that $\tau_i$ is not associated with ion penetration of the oxide film, since photoelectrochemical reactions generally occur on the oxide covered surface.
FIGURE 30

Electrode Current (A) and Photocurrent (B)

Transient After Sulfide Injection Under

Potentiostatic Conditions.

\[ E_{\text{pas}} = E_{\text{inj}} = 0.80 \text{ V} \]
\[ t_{\text{pas}} = 1 \text{ hr} \]
\[ \lambda = 400 \text{ nm} \]
\[ C_{\text{Na}_2\text{S}} = 5 \cdot 10^{-3} \text{ M} \]
Some of the pitting theories derived for chloride environments, assume that the addition of an aggressive anion (e.g. chloride) chemically dissolves the oxide film, decreasing its thickness until breakdown occurs [143-145]. If this were considered to be the case, and taking into account that the photoresponse of a thin oxide film generally increases with thickness, then the magnitude of the photoresponse should be expected to decrease. Therefore, the results in Figure 30 indicates that general thinning of the iron oxide does not occur.

The effect of sulfide concentration in the photocurrent spectral response is shown in Figure 31. The magnitude of the photocurrent increased with the sulfide concentration, but the shape of the curve remained unchanged. The onset of pitting corresponded to an increase in the photoresponse noise, but no effect on its magnitude was detected. These results strongly suggest that the chemical environment of cations in the passive films is identical before and after the addition of sulfides into the electrolyte. This finding tends to rule out the possibility that ionic penetration of the sulfides through the passive film is the cause of passivity breakdown.

The dependence of the photocurrents on the sulfide concentration can be seen in Figure 32. At both 0.60 and 0.80 V, the photoresponse increased linearly with the sulfide concentration, but the slope for $E_{\text{pas}} = 0.60$ V was much larger than for $E_{\text{pas}} = 0.80$ V. The photocurrent values shown for $E_{\text{pas}} = 0.80$ V, correspond to maximum values, since the photocurrent decayed slowly to a steady state. The higher the concentration, the slower the decay. This effect was not seen at 0.60 V, where the photocurrents reached a plateau that remained steady for
FIGURE 31


\[ E_{pas} = 0.60 \text{ V} \]
\[ t_{pas} = 16 \text{ hr} \]
\[ \text{L.P. Filter} = 300 \text{ nm} \]

Curve A: \[ C_{Na_2S} = 1.0 \text{ M} \]
Curve B: \[ C_{Na_2S} = 1.5 \text{ M} \]
Curve C: \[ C_{Na_2S} = 2.0 \text{ M} \]
Curve D: \[ C_{Na_2S} = 2.5 \text{ M} \]
Curve E: \[ C_{Na_2S} = 3.0 \text{ M} \]
FIGURE 32

Dependence of Photocurrents on
Sulfide Concentration
Under Potentiostatic Conditions.

\[ \lambda = 400 \text{ nm} \]

Curve A
\[ E_{\text{pas}} = 0.80 \text{ V} \]
\[ t_{\text{pas}} = 1 \text{ hr} \]

Curve B
\[ E_{\text{pas}} = 0.60 \text{ V} \]
\[ t_{\text{pas}} = 16 \text{ hr} \]
long time.

Figure 33 shows the dependence of the dark current on the sulfide concentration during same experiment as in Figure 32. At $E_{\text{pas}} = 0.80 \text{ V}$, the dark current is about two orders of magnitude higher than the photocurrent, and increases linearly with sulfide concentration. On the other hand, at $E_{\text{pas}} = 0.60 \text{ V}$, dark currents are much smaller and increase parabolically with the sulfide concentration. The change in the reaction order from $p = 2$ at $E_{\text{pas}} = 0.60 \text{ V}$ to $p = 1$ at $E_{\text{pas}} = 0.80 \text{ V}$ is consistent with the dark current reaction changing from activation-control to diffusion-control.

The increase in the photoresponse with the sulfide addition can be rationalized by considering that the presence of sulfide ions in solution provides an alternative reaction for holes reaching the surface by their ability to be oxidized to sulfur or sulfate. Figure 34 shows that the addition of sulfide shifts the photocurrent onset potential from ca. 0.1 V to $\sim -0.1 \text{ V}$. The photooxidation reaction is activation controlled for $E < 0.55 \text{ V}$. At highly positive potentials, the photocurrent is limited by the concentration of sulfide available at the surface. The lower dependence of the photocurrent at $E = 0.80 \text{ V}$ on $C_{\text{Na}_2\text{S}}$ can then be explained by smaller concentration available on the surface due to its reaction in the dark, which is several orders of magnitude higher.
FIGURE 33

Dependence of Steady State Dark Currents on Sulfide Concentration Under Same Conditions as in Figure 32.

Curve A
\[ E_{\text{pas}} = 0.80 \text{ V} \]
\[ t_{\text{pas}} = 1 \text{ hr} \]

Curve B
\[ E_{\text{pas}} = 0.60 \text{ V} \]
\[ t_{\text{pas}} = 16 \text{ hr} \]
FIGURE 34

Potential Dependence of Passive Iron
Photocurrent in Sulfide Solution

\[ E_{\text{pas}} = 0.60 \text{ V} \]
\[ t_{\text{pas}} = 16 \text{ hr} \]
\[ \lambda = 400 \text{ nm} \]
\[ C_{\text{Na}_2\text{S}} = 10^{-3} \text{ M} \]
V. DISCUSSION

V.1 ELECTROCHEMICAL BEHAVIOR OF IRON IN ALKALINE SULFIDE SOLUTIONS

The complexity of the system Fe-S-H₂O and the fact that the thermodynamically most stable substances are sometimes kinetically unfavored, make the assignments of specific reactions to the different regions of the polarization diagram controversial. Polarization curves similar to the ones shown in Figure 13 have been reported by several authors [36-40,43-48]. Major discrepancies arise in the assignment of reactions for peak (II) and peak(III) even when interpretations were based solely on thermodynamical considerations (E/pH diagrams).

The rest potential of iron in sulfide-borate solution has been considered as the mixed potential between the cathodic decomposition of water

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad E^0 = -0.74 \text{ V}^* \]  

(73)

and the anodic oxidation of the metal by the HS⁻ ion [44]

\[ \text{Fe} + \text{SH}^- \rightarrow \text{FeS} + \text{H}^+ + 2e^- \quad E^0 = -1.00 \text{ V} \]  

(74)

The mixed potential established by these two reactions is -0.87 V, in excellent agreement with the experimental value, i.e., -0.89 V (Curve 4, Figure 13).

*The equilibrium potentials shown, \( E^0 \) (V vs. SCE), were calculated for pH = 8.4 and total sulfide concentration of 10⁻² M. Concentration of any other soluble species was assumed to be 10⁻⁶ M unless otherwise specified.
The active-to-passive transition at high sulfide concentrations, peak (II), has been related to the partial coverage of the surface by pyrite formed by electro-oxidation of the ferrous sulfide [43,44]

$$\text{FeS} + \text{SH}^- \rightarrow \text{FeS}_2 + \text{H}^+ + 2e^- \quad E^o = -0.85 \text{ V}$$

(75)

Peak (III) has been interpreted in the past as the oxidation of sulfide to yield sulfur (or polysulfide) [45]

$$\text{SH}^- \rightarrow \text{S} + \text{H}^+ + 2e^- \quad E^o = -0.49 \text{ V}$$

(76)

$$2\text{SH}^- \rightarrow \text{S}_2^= + 2e^- \quad E^o = -0.38 \text{ V}$$

(77)

or as the oxidation of pyrite to either sulfur or sulfate [44]

$$2\text{FeS}_2 + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 4\text{S} + 6\text{H}^+ + 6e^- \quad E^o = -0.22 \text{ V}$$

(78)

$$2\text{FeS}_2 + 19\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 4\text{SO}_4^= + 38\text{H}^+ + 30e^- \quad E^o = -0.52 \text{ V}$$

(79)

Direct oxidation of sulfide to sulfate was not considered because it generally requires high overvoltages [157] and occurs at significant rates only at potentials at which sulfur can also be a product. On noble metals, for example, the production of sulfate from sulfide is only marginal before the onset of O\textsubscript{2} evolution [146].

Reaction (79) is thermodynamically favored over reaction (78). However, as mentioned before, reactions yielding sulfate are usually very slow and require high overvoltages. In fact, electrochemical studies on natural occurring pyrite have found that its main oxidation
product is S at E < 0.30, whereas at higher potentials, increasing amounts of $\text{SO}_4^{2-}$ are produced [49]. Sulfur is unstable in presence of alkaline solutions, in which it tends to disproportionate to give $\text{HS}^-$, $\text{S}^-$ (or $\text{S}_x^-$) and $\text{SO}_4^{2-}$. In practice, however, this reaction is very slow and take place only in hot very alkaline media [14].

On this basis, the main reaction products for iron in alkaline sulfide media at potentials greater than $\sim 0$ V would be ferric oxide and sulfur, reaction (78), which would tend to passivate the electrode. At higher potentials and/or higher sulfide concentration, the amount of sulfate produced through reaction (79) increases. Formation of sulfate increases the local acidity at the surface in the ratio of 38 moles $\text{H}^+$ per mole of $\text{Fe}_2\text{O}_3$ produced. The chemical dissolution rate of ferric oxide would also increase leading to rapid anodic dissolution and inducing localized corrosion (pitting).

This interpretation of the polarization diagram, although thermodynamically correct presents several flaws:

1. The main corrosion product of iron in natural occurring sulfide-containing solutions at room temperature is mackinawite [31-34,38,44] even when the corrosion potential falls within the stability range of pyrite.

2. X-ray diffraction studies of corrosion products of iron on alkaline sulfide solutions have shown that mackinawite is the main product of localized corrosion, even at high anodic potentials [35].
3. Conversion of mackinawite (Fe$_{1+x}$S) or pyrrhotite (Fe$_{1-x}$S) to pyrite (FeS$_2$) is a very slow process even at 100° C, and occurs through a dissolution-reprecipitation mechanism rather than through a solid state transformation [49]. In fact, natural pyrite-producing reactions are known to be particularly slow [49]. Therefore, reaction (75), having an overvoltage of ~ 0.2 V seems to be unlikely.

4. AEM analysis of the iron electrode surface polarized at potentials negative to peak (III) showed ferrous sulfide and sulfur deposits, but no pyrite (cf. section IV.1)

Taking these facts into consideration, the electrochemical behavior of iron in sulfide borate buffer solution can be best interpreted as follows:

Peaks (I) and (II) are associated with two competing reactions, i.e. the formation of Fe(OH)$_2$ and FeS respectively. As the sulfide concentration increases at constant pH, the ratio HS$^-$/OH$^-$ also increases and the formation of Fe(OH)$_2$ is inhibited.

Since at potentials negative to peak (II) the metal is in the active dissolution region, the ferrous sulfide film could be in principle formed by either direct oxidation of the substrate, reaction (74), or by precipitation of the Fe(II) ions dissolved from reaction (52):

$$\text{Fe}^{2+} + \text{HS}^- \rightarrow \text{FeS} + \text{H}^+$$  \hspace{1cm} (80)
Thermodynamical considerations, as well as the current dependence of peak (II) with sulfide concentration [equation (57)] favor direct oxidation reaction (74).

The mackinawite film is porous and poorly adhesive and is unlikely to reduce the dissolution rate of iron significantly. In fact, holding the electrode at the potential of peak (II) did not result in passivation even though the surface was covered with mackinawite. Therefore, the initial passivation at peak (II) is most probably due to the partial displacement of the ferrous sulfide on the surface by ferrous oxide. Both the current needed to passivate the electrode and the passive current increase with sulfide concentration suggesting the formation of a mixed oxide/sulfide, which is not as protective as the "pure" oxide [48]. AEM analysis support this interpretation, since the atomic concentration of sulfur in the film-covered surface was ~ 50 % (i.e., FeS) whereas in the "clean" area, less than 5 % (i.e., possibly mixed oxide/sulfide).

At potentials positive to peak (I), the passive layer is gradually oxidized to Fe$_2$O$_3$ as it is in sulfide-free solutions. But, as shown in Figure 16, this oxidation is not completed until ~ 0 V. Therefore, at potentials between peak (I) and peak (III) there is still some iron dissolution as Fe(II), which forms ferrous sulfide in the solution and re-precipitates on the surface. The mackinawite film formed through this mechanism is expected to be very fine and nonadherent. Results from potentiostatic experiments at potentials between peak (II) and peak (III), e.g. -0.40 V, corroborated this expectation: No black film was found to adhere to the surface. Instead, a black powder precipitated
near the surface and diffused away. In this case, the oxide film was formed prior to the ferrous sulfide formation.

Peak (III) is associated either with the formation of sulfur at defects in the passive film by direct oxidation of bisulfide ion (reaction (76)), or with the oxidation of the remaining ferrous sulfide:

\[ 2\text{FeS} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 2\text{S} + 6\text{H}^+ + 6\text{e}^- \quad E^0 = -0.34 \text{ V} \quad (81) \]

Reaction (81) is kinetically more favorable than the production of pyrite (reaction (75)). In fact, the main oxidation products of pyrrhotite (Fe\(_{1-x}\)S) in alkaline solutions are sulfur and ferric oxide, which tend to cover the surface and decrease the reaction rate [49]. AEM analysis of an iron electrode polarized at these potentials confirmed that sulfur was deposited over a matrix of iron oxide.

At more positive potentials, the current in the passive range is due to Fe\(^{3+}\) dissolution. Fe\(^{3+}\) can oxidize HS\(^-\) in the solution through a mechanism such as

\[ \text{Fe} \quad \overset{\text{Fe}^{3+} + 3\text{e}^-}{\leftrightarrow} \quad (82a) \]

\[ 2\text{Fe}^{3+} + 3\text{HS}^- \overset{\text{Fe}_2\text{S}_3 + 3\text{H}^+}{\leftrightarrow} \quad (82b) \]

\[ \text{Fe}_2\text{S}_3 \overset{\text{FeS}_2 + \text{FeS}}{\leftrightarrow} \quad (82c) \]

which would explain the composition of the deposits found after polarization at 0.20 V. Although Fe\(_2\)S\(_3\) is not known to form naturally, it can be produced easily by heating iron fillings with sulfide or by absorption of H\(_2\)S onto ferric oxide [53]. This compound is metastable and easily disproportionates to form a mixture of ferrous sulfide and ferrous disulfide (reaction 82c). Its domain of stability in the E/pH
diagram is completely included into that of the pyrite [52].

V.2 PROCESS LEADING TO PASSIVATION BREAKDOWN

Pitting of iron in sulfide containing borate solutions is always preceded by the formation of iron sulfide patches (mackinawite and in some cases pyrite) on the surface. In order to understand the process of passivity breakdown, one must first understands the kinetics of iron sulfide formation.

Two different situations can be considered: The iron surface can initially be bare (oxide-free) or it can be covered by a passive film. For the first case, the discussion will be based on the results from anodic polarization experiments in the sulfide containing solutions. At the beginning of these experiments, the iron electrode can be considered oxide-free by virtue of the cathodic polarization pretreatment. The second case will be discussed on the basis of potentiostatic experiments in which a passive oxide film was grown prior to injection of sulfide ions into the solution.

FERROUS SULFIDE FORMATION ON INITIALLY OXIDE-FREE SURFACES

Potentiodynamic and galvanostatic data suggest that passivation in neutral sulfide solutions is preceded by the active dissolution of the metal as Fe(II) and the formation of a ferrous sulfide film. These results can be rationalized on the basis of competitive adsorption processes at the iron surface and alternative electro-oxidation reactions involving the different adsorbed species [39]. Since HS\textsuperscript{-} ions
form approximately a chemisorb monolayer on iron [158], their accelerative effect on the dissolution rate can be due to the formation of a surface catalyst, similar to that formed by OH\(^-\) ions [159].

The adsorption equilibria at the metal surface involving \( \text{H}_2\text{O}, \text{OH}^- \) and HS\(^-\) can thus be represented as

\[
\begin{align*}
\text{Fe(} \text{H}_2\text{O)_{ad} + OH^-} & \rightleftharpoons \text{Fe(OH)}^-_{\text{ad}} + \text{H}_2\text{O} \quad (83a) \\
\text{Fe(OH}^-_{\text{ad}} + \text{HS}^- & \rightleftharpoons \text{Fe(HS}^-_{\text{ad}} + \text{H}_2\text{O} \quad (83b)
\end{align*}
\]

The surface covered by OH\(^-\) can then form an oxide layer as follows

\[
\begin{align*}
\text{Fe(OH}^-_{\text{ad}} & \rightleftharpoons \text{Fe(OH)} + e^- \\
\text{Fe(OH)} & \rightleftharpoons \text{Fe(OH)}^+ + e^- \\
\text{Fe(OH)}^+ + \text{OH}^- & \rightleftharpoons \text{Fe(OH)}_2 \quad (84c) \\
\text{Fe(OH)}_2 & \rightarrow \text{Passive oxide layer} \quad (84d)
\end{align*}
\]

Reactions (84) comprise the pathway corresponding to electrodissolution and passivation of iron in alkaline solutions in the absence of sulfide [160]. The sulfide covered metal can be electro-oxidized to form a mackinawite film:

\[
\begin{align*}
\text{Fe(HS}^-_{\text{ad}} & \rightleftharpoons \text{Fe(SH)} + e^- \\
\text{Fe(SH)} & \rightleftharpoons \text{FeSH}^+ + e^- \\
\text{FeSH}^+ + \text{HS}^- & \rightleftharpoons \text{FeS} + \text{H}_2\text{S} \quad (85c) \\
\text{FeS} & \rightarrow \text{Mackinawite} \quad (85d)
\end{align*}
\]
The intermediate species FeSH\(^+\) may also be responsible for active metal dissolution:

\[(\text{FeSH}^+)_{\text{ad}} \leftrightarrow (\text{FeSH}^+)_{\text{s}}\]  \hspace{1cm} (86a)

\[(\text{FeSH}^+)_{\text{s}} \leftrightarrow \text{Fe}^{2+} + \text{HS}^-\]  \hspace{1cm} (86b)

where the dissolved ions are probably hydrated.

The presence of FeSH\(^+\) species has been proposed in numerous electrochemical studies of iron in aqueous sulfide solutions [35,37,39,151,158] but the existence of such species has not been confirmed experimentally by any other technique. However, absorption spectra of dissolved iron from carbon steel in aqueous H\(_2\)S solutions showed a shift in the Fe\(^{2+}\) peak, which has been interpreted as an evidence of FeSH\(^+\) existence [151].

If the dissolution of FeSH\(^+\) [reaction (86b)] leads to local supersaturation, then precipitation of an unadherent mackinawite film or different polymorphs of FeS or FeS\(_2\) (at higher potentials) occurs.

IRON SULFIDE FORMATION ON PASSIVE IRON

The breakdown of passivity is related to the formation of iron sulfide patches on the iron surface. Analysis of Figures 19 and 22 suggests the existence of two potential regions in relation to the initial process leading to pitting corrosion. At E < ~ 0.5 V, the first current plateau is independent of potential and shows a reaction order of ~ 1/2 with respect to sulfide concentration. Mackinawite and some elemental sulfur are the major component of the patches. At E > ~ 0.5
V, the current plateau becomes potential dependent, increasing with a Tafel slope of $\sim 0.11$ V/dec. At these potentials, the order of reaction on sulfide concentration increases to 1. These factors indicate the onset of a second reaction. Corrosion products at $E > 0.5$ V show higher concentration of elemental sulfur and probably FeS$_2$ (framboidal pyrite). The presence of pyrite (instead of mackinawite) is probably one of the causes for the decrease in pitting tendency at higher potentials. The solubility of pyrite is several orders of magnitude lower than that of the mackinawite and its "passivating" properties are better [153]. Therefore, formation of pyrite will tend to repassivate the electrode.

**Nucleation and Growth of Iron Sulfide on Passive Electrodes**

The electrochemical formation of iron sulfide patches on passive iron occurs through a nucleation and growth process before the onset of pitting. Further information about the mechanism of mackinawite formation can be obtained analysing the current transients after sulfide injection on the basis of the theoretical equations derived from different nucleation and growth models (cf. section II.2).

The total current following sulfide injection can be considered to be, in general, a sum of three major contributions

$$i = i_{\text{pas}} + i_{p} + i_{i}$$  \hspace{1cm} (87)

where the current $i_{i}$ is related to the formation of the sulfide film; the passivation current $i_{\text{pas}}$ was constant and subtracted from the total current; and the pitting current $i_{p}$ was neglected by working at times
prior to the onset of pitting, or at conditions where no pitting occurs. Therefore, the total change in measured current after the sulfide injection and prior to the onset of pitting will be considered to be due to the nucleation and growth of an iron sulfide film.

Nucleation is considered to occur on weak spots of the oxide film (see next section). In general, growth of anodic films after nucleation can be controlled by three steps: i) dissolution of the metal, ii) growth of the new phase, or iii) a resistance to current flow elsewhere. Each step gives rise to a different current-time behaviour [70]: If metal dissolution is the rate-determining step, the current decreases exponentially with time at constant potential. If film growth is controlling, the current-time curve at constant E exhibits a maximum. If external circuit is the rds, the initial current is constant until the film is continuous and then decreased sharply. Observation of the i/t transients (e.g., Figure 24) rules out both metal dissolution and resistance control of the reaction.

As mentioned before, two different sulfide films can be formed depending on the potential range. Consequently, different nucleation and growth mechanisms may apply. The nature of the i/t transient (power of time) for $t \to 0$ is critical in order to determine the nucleation and growth law. Figure 35 presents a double logarithmic plot of current transients typical of the two potentials ranges. The slope of the best fitting line is in each case different: $\sim 1/2$ at $E < 0.50 \text{ V}$ (e.g., $-0.20 \text{ V}$) and $\sim 2$ at $E > 0.50 \text{ V}$ (e.g., $0.80 \text{ V}$). Different models should, therefore, apply to these two ranges of potentials, and those will be considered separately.
FIGURE 35

Current Transient (log i vs. log t)

for the Iron Sulfide Formation

Typical of Two Potential Ranges.

\[ t_{\text{pas}} = 1\text{hr} \]
\[ C_{\text{Na}_2\text{S}} = 10^{-2} \text{ M} \]
\[ E_{\text{pas}} = E_{\text{inj}} \]

Curve A: \[ E = -0.20 \text{ V} \]
Curve B: \[ E = 0.80 \text{ V} \]

Numbers shown in figure correspond to slopes.
Formation of FeS Patches, E < 0.5 V

At potentials between -0.60 V and 0.50 V the \( i/t^{1/2} \) relationship found for short times (cf. Curve A in Figure 35) does not fit any of the nucleation and growth models developed for charge transfer controlled reactions [equations (35) to (43)] but does fit a diffusion controlled growth, e.g. equation (44). Rotating electrode experiments show a diffusion controlled reaction clearly and support this conclusion. The circular patches formed on the surface are composed of microscopic FeS particles of spherical shape. Therefore, the three dimensional growth model with spherical diffusion seems appropriate and equation (45a) or (45b) should be used. The same nucleation and growth law has been found to apply for the anodic film formation of \( \text{Cu}_2\text{S} \) on Cu from sulfide solutions [78].

Equation (45a) can be written as

\[
i = c \ t^{-1/2} \left[ 1 - \exp(-at) \right] \tag{88a}
\]

where \( a \) and \( c \) are constants defined as

\[
a = N_0 \pi (8\pi C_b M / \rho)^{1/2} D \tag{88b}
\]

\[
c = n F D^{1/2} C_b / \pi^{1/2} \tag{88c}
\]

For short times \( 1 - \exp(-at) \sim at \) and

\[
i \sim ac \ t^{1/2} \tag{89a}
\]

where \( ac \) is proportional to \( N_0 \) [cf. equation (44a)]:

\[
ac = n F \pi (2DC_b)^{3/2} M^{1/2} N_0 / \rho^{1/2} \tag{89b}
\]
Therefore the slope $1/2$ in the double logarithmic plot at $t \rightarrow 0$ is indicative of an instantaneous nucleation, equation (45a). Instantaneous nucleation actually means that the velocity of nuclei formation is too fast to be measured under the experimental conditions and, consequently, the total number of nuclei seems to be constant [cf. equations (88) and (89)].

Figure 36 presents typical plots $i$ vs. $t^{1/2}$ for electrodes passivated at $E_{\text{pas}} = E_{\text{inj}} < 0.50$ V. The good linearity at short times confirms the model and allows the product $ac$ to be calculated from the slope $\partial i/\partial t^{1/2}$. From this value, the number of nucleation sites can be estimated. For example, from curve B ($E = 0.40$ V), $ac = 0.43 \mu A \cdot cm^{-2} \cdot s^{-1/2}$. Assuming a density value for the sulfide film equal to that of bulk FeS, i.e., $\rho = 4.7$ gr $\cdot cm^{-3}$ [161], $c^b = 10^{-5}$ mol $(Na_2S) \cdot cm^{-3}$ and $D = 6 \cdot 10^{-6}$ cm$^2 \cdot s^{-1}$, then $N_0 \sim 1.4 \cdot 10^2$ sites $\cdot cm^{-2}$. This value seems too low compared with typical nucleation density for metal deposition ($10^6$ sites $\cdot cm^{-2}$). On the other hand, if the diffusion of a dissolving species with a surface concentration of $\sim 10^{-8}$ mol $\cdot cm^{-3}$ (as calculated by RDE experiments) is considered to be the limiting step, then $N_0 \sim 4 \cdot 10^6$ cm$^{-2}$. This value is in the same order of magnitude as the number of "weak" spots identified by Kruger using decoration techniques [162]. Therefore, the results from transient analysis are consistent with those of rotating electrodes in that the controlling diffusion species is not the hydrosulfide ion.

Figure 37 compares a typical experimental curve with a theoretical curve calculated using equation (89a). At short times a fair fit was
FIGURE 36

Typical $i$ vs. $t^{1/2}$ Plots for Mackinawite Formation at Potentials Negative to 0.5 V.

$$C_{Na_2S} = 10^{-2} \text{ M}$$
$$t_{pas} = 1\text{hr}$$
$$E_{pas} = E_{inj}$$

Curve A: $E = -0.20 \text{ V}$
Curve B: $E = 0.40 \text{ V}$

Numbers shown in figure correspond to slopes in $\mu A \cdot cm^{-2} \cdot s^{-1/2}$
FIGURE 37

Typical Current Transient after
Sulfide Injection at \( E < 0.5 \) V, Showing
Experimental and Theoretical Curves.

Broken line : Experimental Curve

\[
C_{Na_2S} = 10^{-2} \text{ M}
\]

\[
t_{pas} = 1\text{ hr}
\]

\[
E_{pas} = E_{inj} = -0.20 \text{ V}
\]

Solid line : Theoretical Curve

Equation (89)

\[
a = 2.5 \cdot 10^{-2} \text{ s}^{-1}
\]

\[
c = 35 \mu\text{A} \cdot \text{cm}^{-2} \cdot \text{s}^{-1/2}
\]
found, but at longer times, the experimental current increased over the theoretical due to the onset of pitting corrosion.

Two reasons suggest that the number of active sites $N_o$ calculated from equation (45a) should be considered, at the present time, as an order of magnitude estimate:

(i) In rotating electrode experiments, the slope of the $i-t^{1/2}$ curve was strongly dependent on the angular velocity (cf. Figure 38). The slope was found to follow a relationship of the type

$$\frac{\delta i}{\delta t^{1/2}} = b [\exp(a\omega) - 1]$$

(90)

where $a$ and $b$ are empirical constants. Equation (45a) cannot explain the exponential dependence of the slope $\delta i/\delta t^{1/2}$ on the angular velocity $\omega$. The existence of a diffusion layer, dependent on the hydrodynamics of the solution, was not considered in the deduction of this diffusion-controlled growth law.

(ii) The situation encountered in the passivity breakdown experiments is different from that normally encountered during the nucleation and growth of anodic films. In the latter, the nucleation sites are "active" sites (e.g. kinks) on the surface. The material required by the growing centers is then provided by reaction at the uncovered surface, and the peak in the current is due to the overlap of growing centers and the consequent elimination of free uncovered area. In the present case, the nucleation sites are pores or defects in the oxide film which can be attacked by the hydrosulfide ions. The area not covered by sulfide is covered by oxide and is not a source of material
FIGURE 38

Dependence of the $i$ vs. $t^{1/2}$ Slope on Rotation Speed, for $E_{\text{inj}} < 0.5 \text{ V}$

$c_{\text{Na}_2\text{S}} = 10^{-2} \text{ M}$
$t_{\text{pas}} = 1\text{ hr}$
$E_{\text{pas}} = E_{\text{inj}}$
$E_{\text{inj}} = 0.20 \text{ V}$
for the growing process. Therefore, the supply of Fe(II) must come from a highly reactive area at the growing edge, where the oxide is being dissolved and displaced by the mackinawite.

At constant sulfide concentration and hydrodynamic conditions, however, the initial slope of the transient curve can be considered to be proportional to the number of nucleation sites. This relation will be helpful in comparing the relative effects that different experimental parameters may have on $N_0$.

The dependence of $N_0$ on the injection potential, at constant passivation potential, is obtained from Figure 23. The slopes of the linear portion of the curves are in all cases $0.18 \pm 0.01 \mu A \cdot cm^{-2} \cdot s^{-1/2}$. Therefore, the number of sites available for nucleation is independent of the injection potential (at constant $E_{\text{pas}}$) in the range of potentials studied.

On the other hand, comparing the slopes of Figure 23 with those of Figure 36 suggests that the effect of passivating the electrode at more positive potentials can be related to a decrease in the number of nucleation sites. Figure 39 shows the linear dependence of $N_0$ on passivation potential. Assuming equation (89b) holds, the number of nucleation sites can be estimated to decrease with passivation potential at a rate of $\sim 6 \cdot 10^6$ sites $\cdot$ cm$^{-2} \cdot$ V$^{-1}$. 
FIGURE 39

Dependence of the $i$ vs. $t^{1/2}$ slope on Passivation Potential, for $E_{\text{inj}} < 0.5$ V

$C_{\text{Na}_2\text{S}} = 10^{-2}$ M

$t_{\text{pas}} = 1$ hr

$N_0$ was calculated from equation (89b)
Formation of $\text{FeS}_2$ patches, $E > 0.5 \, \text{V}$ -

For potentials more positive than $\sim 0.5 \, \text{V}$, the current transients shows a second order dependence on time (cf. Curve B in Figure 35). In this case, the nucleation law is not uniquely determined, since either an equation of the type (40b) or (41a) can be applied. However, SEM study of the deposit morphology indicates that a three dimensional growth is more appropriated. Therefore, the nucleation law in this case is considered to be an instantaneous nucleation with 3-D growth under activation control.

Figure 40 presents a typical $I$ vs. $t^2$ plot, showing the good linearity at short times. From equation (41a) the slope of the curve is proportional to the number of nuclei $N_0$ and the growth rate constant $k$:

\[
\frac{\partial I}{\partial t^2} = 2\pi n \rho^2 k N_0 / \rho^2
\]  

(91)

In general, both $k$ and $N_0$ can vary with potential. Figure 41 shows the dependence of the initial slope of the $i/t^2$ on the applied potential: It increases at a rate of $\sim 0.05 \, \text{V/dec}$. This is approximately half of the Tafel slope found for the plateau currents at $E > 0.70 \, \text{V}$ (cf. Figure 22), i.e., $\frac{\partial E}{\partial \log i} \sim 0.11 \, \text{V/dec}$. Therefore, although there is not enough information at the present to separate the potential dependence of $N_0$ from that of $k$, comparison of the potential dependence of the $i/t^2$ slope and the steady state current suggests that $N_0$ also increases with potential.
FIGURE 40

Typical $i$ vs. $t^2$ Plots for Iron Sulfide Formation at Potentials Positive to 0.5 V.

$C_{Na_2S} = 10^{-2}$ M

$t_{pas} = 1$ hr

$E_{pas} = E_{inj} = 0.60$ V
FIGURE 41

Dependence of the $i$ vs. $t^2$ Slope

on Potential, for $E > 0.5$ V.

$C_{Na_2S} = 10^{-2}$ M

$t_{pas} = 1$ hr

$E_{inj} = E_{pas}$
Mechanism of Mackinawite Formation

Photoelectrochemical results are consistent with the semiconductor model of the passive film. That is, the iron surface is covered by a three dimensional layer of $\gamma$-Fe$_2$O$_3$, with electronic properties of an n-type semiconductor. Anodic reactions are inhibited on n-type semiconductors and, therefore, any mechanism for the nucleation and growth of mackinawite should include a model for the penetration or dissolution of the passive film. Three models can account for the nucleation of mackinawite on passive electrodes (cf. Figure 7).

1. Penetration of sulfide ions through the passive film:

   This mechanism was ruled out on basis of the photoelectrochemical results. The induction times for the photoresponse are identical to those of the mackinawite formation. The fact that photoelectrochemical reactions occur on the oxide surface, strongly indicates that the first induction time is not related to sulfide penetration through the film. The solid state diffusion or migration through a finite (e.g., 40 Å thick) should take much longer times [118]. Besides, the fact that the photoresponse spectrum did not change upon sulfide addition suggests that the chemical environment of the oxide film does not change substantially.

2. Chemical dissolution of the passive film:

   This mechanism is analogous to that of passivity breakdown by chlorides. The nucleation of the iron sulfide is considered to start by adsorption of hydrosulfide ions at prefered sites
on the oxide surface. This adsorption would lead to the
formation of an iron sulfide compound with greater dissolution
velocity than the oxide. In this way, local dissolution of the
oxide could be possible, increasing the electrical field
through the oxide and, therefore, the metal dissolution. This
model is consistent with the short induction time found for the
mackinawite formation and its coincidence with the
photoelectrochemical induction time.

3. Electrooxidation of iron substrate at oxide flaws.

The dynamic model of passive film considers a continuous
formation and breakdown of the oxide film. This model would
give direct access for hydrosulfide ions to electrooxidize the
bare metal, inducing a local increase in the current, even in
the absence of permanent defects. There would be a competition
between the OH\(^-\) and the HS\(^-\) for the bare metal surface inside
the pores, similar to that proposed for oxide-free surfaces
[reactions (83) to (86)]. If the OH\(^-\) is adsorbed,
repassivation would occur, but if HS\(^-\) is adsorbed the formation
of a nonprotective iron sulfide film would be favored.

A clear decision between the hydrosulfide adsorption-oxide
dissolution or the film breaking-direct oxidation mechanism does not
seem feasible at the present. It is possible to dissolve ferric oxide
chemically in neutral buffered solutions (pH 6-8) to produce ferrous
sulfide and sulfur [163], although this reaction in more alkaline
solutions (pH 11.5) has been reported to be negligible [39].
One of the major pieces of evidence for the local dissolution theory comes from RRDE studies in chloride solutions [143-145]. The cathodic ring current (proportional to concentration of Fe$^{3+}$) was found to increase just after the chloride injection even though the total current did not. Similar experiments on sulfide solutions were not conclusive due to interference of sulfide reactions at the ring and, possibly, to the reduction of Fe$^{3+}$ by the sulfide in solution.

Photoelectrochemical results indicated that general thinning of the passive film does not occur under our experimental conditions. However, it could be argued that the dissolution might be limited to patches (< 1% of total area) and therefore no changes in the photocurrent would be noticed.

The number of nucleation sites for the mackinawite formation decreases and its induction time increases with potentials and time of passivation. These results are consistent with the film breaking model. Passivating the electrode at higher anodic potentials or for longer times produces a thicker, more compact oxide layer with fewer defects; consequently, the number of sites available for nucleation decreases. However, these results do not rule out the adsorption-dissolution model because the production or reduction of defects in the film can also affect film surfaces and thereby influence the adsorption of damaging anions at that surface [162]. Besides, passivating at higher potentials could decrease the solubility of the passive film or reduce the number of the "weak" spots at the surface.
The film breaking model, followed by reactions (83) to (86), is consistent with the first order dependence of the reaction initiation on sulfide concentration (cf. Figure 18). On the other hand, oxide sulfidation through a dissolution-reprecipitation mechanism has been found to have a 3/2 dependence on sulfide concentration [163]. A different mechanism, however, can be proposed with the adsorption of a HS\(^-\) anion on the surface as the rate determining step. In this way, a first order dependence would be obtained.

Formation of iron sulfide, e.g., reaction (85) leads to lowering the pH at the surface. Once a nucleus of iron sulfide is formed, it can easily spread over the surface due to the dissolution of the adjacent oxide film at the lower pH formed by the surface reaction.

The current at the first plateau depends on rotation speed, indicating that a diffusion process in solution is involved. The calculated concentration of the diffusing species was much lower than that of the HS\(^-\). This suggested that the current was limited by diffusion of a corrosion product away from the surface.

To explain the velocity dependence of iron dissolution in acidic H\(_2\)S media, a mechanism has been proposed in which the rate-determining step (rds) is considered to be the dissolution of mackinawite film and diffusion of FeSH\(^+\) [151]. No reliable data for dissolution of iron sulfides in our range of pH was found in order to corroborate this hypothesis. Moreover, the fractional order on sulfide concentration would be difficult to explain on this basis.
A mechanism more consistent with our results would consider as rate-determining steps the dissolution of the iron oxide at the growing edge of the sulfide patches, followed by the transport of the sulfidation products to the bulk of the solution. The morphology of deposits and the nucleation and growth studies are consistent with this mechanism:

\[
\begin{align*}
\text{Fe} & \rightleftharpoons \text{Fe}^{3+} + 3\text{e}^- & (92a) \\
\text{Fe}^{3+} + \text{HS}^- & \rightleftharpoons \text{FeSH}^{2+} & (92b) \\
2\text{FeSH}^{2+} + \text{HS}^- & \rightleftharpoons 2\text{FeSH}^+ + \text{S} + \text{H}^+ & (92c) \\
\text{FeSH}^+ & \rightleftharpoons \text{Fe}^{2+} + \text{HS}^- & (92d) \\
(\text{Fe}^{2+})_s & \rightarrow (\text{Fe}^{2+})_b & (92e)
\end{align*}
\]

Reaction (92a) actually corresponds to the net corrosion process which compensates for the oxide dissolution. It should therefore include three one-electron transfer reactions [similar to reactions (84)] to produce ferric oxide, followed by the dissolution of the oxide:

\[
\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \rightleftharpoons 2\text{Fe}^{3+} + 6\text{OH}^- 
\]

The oxide dissolution reaction (92a') can be assumed to be in fast equilibrium in basic solutions, but would be displaced to the right following local acidification due to sulfide discharge reactions, e.g., (85). The formation of mackinawite would follow step (92d) by a reaction such as

\[
\text{Fe}^{2+} + \text{HS}^- \rightleftharpoons \text{FeS} + \text{H}^+ 
\]
Taking the diffusion reaction (92c) as the rate determining step, then the limiting current [cf. equation (71)] could be expressed as

$$i_i = 0.62 \ nF^{1/6} D^{2/3} \omega^{1/2} C_{Fe^{2+}}^s$$

(93)

where bulk concentration $C_{Fe^{2+}}^b$ has been neglected.

Assuming that all reactions, (92a'), (92b), (92c), and (92d) preceding the rds are in fast equilibrium, the surface concentration of $Fe^{2+}$ can be expressed in terms of their respective equilibrium constants, $K_a$, $K_b$, $K_c$, and $K_d$:

$$C_{Fe^{2+}}^s \sim [Fe^{2+}] = \frac{K_d (K_a, K_c)^{1/2} K_{[BS^-]}^{1/2}}{K_{w}^{1/2} [OH^-]^{5/2}}$$

(94)

where the terms in square brackets represent the activities of the dissolved species at the surface and $K_w$ is the dissociation constant of water. For simplicity, the $Fe^{2+}$ activity was assumed to be equal to its concentration, which is reasonable for low concentrations.

From equations (93) and (94) the dependence of the current plateau on concentration is

$$\frac{\partial i_i}{\partial [BS^-]} = 0.5$$

(95)

in agreement with the experimental reaction order. The dependence of $i_i$ on angular velocity is:
$$\frac{\partial i_i}{\partial \omega^2} = 0.39 \cdot 10^{-6} \text{ A cm}^{-2} \text{s}^{1/2}$$ (96)

from which the surface concentration of Fe$^{2+}$ was calculated to be \(\sim 10^{-5} \text{ M}\). This concentration is smaller than the maximum solubility of Fe$^{2+}$ in sulfide free solutions at pH 8.4 [161], but higher than that of FeS. This apparent supersaturation in FeSH$^{+}$ is due to the localized acidification.

**Mechanism of Pyrite Formation.**

The mechanism of pyrite formation is not clear at the present. It is probably formed not by direct reaction in the solid state but rather by a dissolution-reprecipitation mechanism. This is basically the same mechanism generally proposed for the formation of pyrite in nature [163] and is consistent with the morphology of the deposits found in this study.

Neither the initiation order of reaction on sulfide concentration nor the induction times \(\tau_i\) changed when potential increased over 0.5 V. This indicates that the same nucleation mechanism would apply for both mackinawite and pyrite formation. Therefore, a model for the formation of pyrite is proposed that has the same first two steps (92a and 92b) followed by an electrooxidation reaction and precipitation of pyrite:

$$\text{Fe} \rightleftharpoons \text{Fe}^{3+} + 3e^-$$ (97a)

$$\text{Fe}^{3+} + \text{HS}^- \rightleftharpoons \text{FeSH}^{2+}$$ (97b)

$$\text{FeSH}^{2+} \rightarrow \text{Fe}^{2+} + S + \text{H}^+ + e^-$$ (97c)
\[ S + HS^- \rightleftharpoons S_2^- + H^+ \]  \hspace{1cm} (97d)
\[ \text{Fe}^{2+} + S_2^- \rightleftharpoons \text{FeS}_2 \]  \hspace{1cm} (97e)

Reaction path (92) is in competition with reactions (97), so that pyrite, mackinawite and sulfur can be found in the final product. The main difference between these two reaction paths is in that in the formation of pyrite more sulfur is formed by direct sulfide oxidation (97c). The sulfur would then dissolve in excess $\text{HS}^-$ producing polysulfides* which may react with dissolved Fe(II) to produce more sulfur, FeS and/or FeS$_2$. At higher pH, dissolution of oxide film has been reported to produce a soluble ferric sulfide complex following a mechanism [36]:

\[ \text{Fe}^{3+} + 2\text{SH}^- \rightleftharpoons \text{Fe(SH)}_2^- \]  \hspace{1cm} (98a)
\[ \text{Fe(SH)}_2^- + 2\text{OH}^- \rightarrow \text{FeS}_2^- + 2\text{H}_2\text{O} \]  \hspace{1cm} (98b)

where the ferric sulfide complex then forms a colloidal NaFeS$_2$. However, the characteristic green color of this colloidal compound was not found in our experiments. Besides, the experimental reaction order and Tafel slopes could not be explained by this model either.

Considering reaction (97c) as rds, and the reactions preceding it in fast equilibrium, the expression for the steady state current would be, using the Butler-Volmer relation (4):

\[ i = Fk^0K_b[\text{Fe}^{3+}][\text{HS}^-] \exp((1-\beta)FE/RT) \]  \hspace{1cm} (99)

* The $S_2^-$ ions will be in equilibrium with other polysulfide species and will probably be protonated under the present conditions.
where the back reaction has been neglected ($\eta > 0.05 \text{ V}$). From this equation, the order of reaction on [HS$^-\text{}]$ would be

$$p_i = \frac{\partial i}{\partial [\text{HS}^-]} = 1$$ (100)

and the Tafel slope

$$\frac{\partial E}{\partial \log i} = \frac{(1-\beta)F}{RT}$$ (101)

which are consistent with the experimental values of $n_i = 1$ and $\frac{\partial E}{\partial \log i} \sim 0.11 \text{ V/dec (i.e., } \beta \sim 0.45).$

V.3 LOCALIZED CORROSION

Localized corrosion of passive iron in alkaline sulfide solutions will be discussed in terms of the potentials range where it may occur, mechanism of pit initiation, and kinetics of pit growth.

PITTING POTENTIAL

The discussion of the polarization curves (section V.1) did not include any of the "characteristic" potentials usually related to pitting corrosion, such as pitting potential, repassivation potential and inhibition potential. As mentioned in the section I, the current increase at peak(III) has been interpreted in the past as corresponding to the onset of pitting corrosion [36,39,40]. In this sense, the
potential at which current begins to rise at peak (III) would correspond
to the pitting potential and the potential over which metal
repasses, as inhibition potential.

Pitting may be considered a stochastic process related, in general,
to applied potential and time. Since these two parameters are changed
simultaneously in a potentiodynamic polarization experiment,
interpretation of these curves regarding pitting potentials may be
misleading [99,100,104].

Galvanostatic or galvanodynamic experiments have been reported to
give more accurate values of pitting potentials in halide solutions
[100,164]. Use of these two techniques for iron in sulfide solutions
indicated that there was no pitting potential associated with this
system. Under galvanostatic conditions, for example, pitting corrosion
should occur at the steady potential $E_p$. Figure 16 shows that, after
the application of a galvanostatic step, the electrode potential
increases until the sulfide oxidation or oxygen evolution controls the
potential, at $E > 1.10$ V. The onset of pitting corrosion can be noticed
at the ring electrode as an increase in the electrochemical noise
between $-0.4$ and $0.3$ V, but the disc potential does not stabilize in
this range.

It could be argued that $E_p$ is in the active-to-passive region, in
which case the pitting potential would be difficult to measure. In
fact, pitting potentials between $-0.70$ and $-0.60$ V have been reported
by Salvarezza et al [40] for iron in sulfide solutions (pH 8.0).
However, their experimental technique differed from ours in that no
previous passivation in sulfide-free solution was done. Under those
conditions, there is not an uniform coverage of the electrode surface by the oxide film in the potential range where pitting potentials were observed. Consequently, the corrosion mechanism can be different to that of passivity breakdown studied in this work.

Potentiostatic experiments on passivated iron corroborated that pitting can occur at any potential positive to the active-to-passive transition peak. Therefore, there is no well defined pitting potential in this system.

PIT INITIATION

One of the most important aspects of pitting corrosion is the mechanism of its initiation. The formation of iron sulfide patches on the surface was found to be a necessary (but not sufficient) condition for the development of pitting corrosion. Therefore, the kinetics of pit initiation is expected to be closely related to that of iron sulfide formation.

Microscopic analysis of pits clearly indicated that pitting corrosion in alkaline sulfide media initiates under the edge of iron sulfide patches, suggesting a mechanism similar to that of crevice corrosion [23]. The formation of iron sulfide, e.g., reaction path (92), produces a local decrease in the surface pH, mainly in the highly reactive area under the growing edges of the patches where the oxide is being dissolved and displaced by the sulfide. Also, the presence of a non-passivating iron sulfide film on the surface hampers the diffusion of oxidizers (e.g., OH⁻) needed to repassivate the metal. All these
factors contribute to creating favorable conditions for displacing the potential beneath the deposit beyond the range of passive potentials, and into that of active dissolution. This mechanism is similar to that of the development of crevice corrosion by differential concentration cells [165].

The pitting initiation process is strongly dependent on the thickness and composition of the passive layer, as shown by the dependence of pitting induction time on passivation potential and passivation time. The film breaking model assumes that the iron sulfide is formed directly on the bare iron surface at pores or defects. As the sulfide patches grow laterally, replacing the oxide film by the non-passivating sulfide, the acidity increases and conditions for pitting can be created. In this case, pitting initiation should be determined by the kinetics of iron sulfide formation and growth. However, the kinetics of ferrous sulfide formation was shown to be almost independent of the passivation potential and, therefore, can not explain the potential dependence of \( t_p \). On the other hand, the adsorption-dissolution nucleation mechanism is consistent with the existence of a passive layer beneath the sulfide patches. The three-dimensional growth of these patches would imply not only a lateral growth but also a dissolution of the oxide layer beneath the sulfide. In this case the initiation of pitting corrosion would not only be affected by the kinetics of sulfide growth but also by the thickness and composition of the passive layer. Therefore, these experimental facts favor the model of hydrosulfide adsorption-local oxide dissolution for the iron sulfide formation.
The minimum in the pitting induction time at $E_{\text{pas}} \sim 0.2$ V can be correlated with a change in composition of the passive layer. At potentials more negative than $\sim 0$ V, the oxide layer has many flaws and imperfections, accommodating considerably amount of adsorbed water, whereas at higher potentials, the oxide becomes highly compact and the water adsorbs only near the surface [97]. Consequently, at more positive potentials, lateral growth of the sulfide patches is favored and, therefore, resistance to passivity breakdown increases.

The increase in pitting resistance with passivation time is generally ascribed to an increment on the film thickness. The present results, however, can not be explained on that basis alone but, rather, on the basis of a decrease in the number of oxide defects with $t_{\text{pas}}$. This is supported by the photoelectrochemical results. The increase in photoresponse with $t_{\text{pas}}$ indicates an increment on the number of donors, which is consistent with a decrease in the non-stoichiometry of the oxide; that is, either the concentration of $\text{Fe}^{2+}$ in the oxide or the density of $O^{2-}$ vacancies decreases.

The reduction of the pitting tendency at more positive injection potentials is related to the precipitation of a different sulfur containing phase, such as pyrite, with better passivating properties than mackinawite.
PIT GROWTH

The rate of development of pits can be characterized by analyzing the current transients. The increase of the pitting current at constant potential follows the well known relation [108]

\[ \Delta i = a' (t - \tau_p)^b \]  

(102)

where \( a' \) is a constant, \( \Delta i \) is the increase in the current due to the corrosion process, i.e., \( \Delta i = i_p - i_i, \omega' \) and \( b \sim 1 \).

Equation (102) was originally derived by Engel [108] using a model of hemispheric pits. For hemispheric pits, \( b = 2 \) when the number of pits remains constant and \( b = 3 \) when it is proportional to time. This pitting model is similar to that of nucleation and 3-D growth of crystals [cf. equations (41a) and (41b)], where \( N_o \) would correspond to the total number of active sites and \( A \) the rate of nucleation of pits.

Many authors have confirmed the course of pitting corrosion according to equation (102). However, the exponent \( b \) has sometimes been found to be both greater than 3 and smaller than 2. This suggests that Engel's model of hemispheric pits is not valid for all cases of pitting corrosion. Depending on the shape of the pits, different models of pit growth have to be taken into consideration.

Equation (102) with \( b = 1 \) may fit either a progressive nucleation with 1-D growth model, equation (41b), or an instantaneous nucleation with 2-D growth, equation (42a). Pit morphology ruled out the later model. Pits nucleate at different times depending on the location. First pits nucleate at sites beneath the edge of the patches. Later,
old pits begin to overlap and new pits are formed closer to the center of the patches. At longer times, pitting corrosion has spread out and may cover the whole area beneath the deposits. In this way, deeper corrosion occur near the edge. This is a typical morphology of crevice corrosion.

The electrochemical behaviour of a metal in a crevice is caused only by the difference in access of the corrosive medium. If pitting corrosion is a peculiar kind of crevice corrosion, then it would stop if the pit and the rest of the surface were equally accessible to the electrolyte, e.g., by removal of corrosion products [166]. Similarly, pitting corrosion in rotating electrodes should be favored by low velocities. Higher velocities tend to remove surface products and increase the accessibility of passivators (e.g., OH⁻) to the pit site. Results from RDE experiments corroborated this expectation: The current maximum related to pitting corrosion decreased with increasing angular velocity.

Specimen position affects the pit process. Under the same experimental conditions, vertical electrodes consistently developed slightly more pitting corrosion than horizontal electrodes (exposed surface facing down). An opposite effect has been observed on stainless steel in chloride media [167]. This discrepancy is due to differences in the corresponding mechanisms. In the case of stainless steel, the pitting mechanism proposed is similar to that of electropolishing, whereas in this work the mechanism is that of crevice corrosion. On horizontal electrodes, gravity will tend to displace the corrosion products faster than on vertical electrodes. This would induce a
natural convection, thus increasing the \( \text{OH}^- \) access to the metal surface.

Active dissolution of iron (pitting) in sulfide environment yields an increase concentration of \( \text{Fe}^{2+} \). When the solubility product is exceeded, precipitation of mackinawite occurs, producing deposits, with a volcano shape, over the pit area. The decrease in pitting current after reaching the maximum is due to the partial coverage of the pits by corrosion products. An increase in the rotation speed after the steady state is reached facilitates the breakdown of these loose deposits and therefore increases the current. The fact that this steady state current is not limited by diffusion through the solution is backed by the irreversibility of the angular velocity dependance of the current and its not following the theoretical equation (27).

From the previous discussion, the mechanism of localized corrosion of iron in slightly alkaline solutions can be summarized as follows:

After the iron sulfide nuclei are formed on the oxide surface, they grow by dissolution of the adjacent oxide layer producing visible dark patches. The sulfide film is, more porous and less protective than the oxide film. The formation of the sulfide film increases the local acidity at the active growing edge, and decreases the diffusion rate of passivators (e.g., \( \text{OH}^- \)) to the surface beneath it. In places where the passive layer has been locally dissolved through, conditions may be created where crevice corrosion initiates by a process similar to that of differential concentration cells. In these areas, active iron(II) dissolution occurs and pitting corrosion spreads beneath the patches.
The experimental data is consistent with a mechanism of pitting growth similar to the path proposed for active metal dissolution and mackinawite formation [cf. reactions (83) to (86)]. The second order dependence of $i_{p,m}$ on hydrosulfide concentration suggests that reaction (85c) is the rate determining step.
VI. CONCLUSIONS

The electrochemical behavior of iron in alkaline sulfide solutions depends on whether or not a passive film is present on the electrode surface, prior to its contact with the sulfide ions.

In the absence of pre-grown passive films, iron in sulfide-containing borate buffer undergoes active corrosion at $E < -0.65$ V, covering the surface with an iron(II) sulfide layer (mackinawite). This film is not protective.

The active-passive transition is due to the partial coverage of the surface by a ferrous oxide (or hydroxide) phase, and not by transformation of mackinawite to pyrite. The mechanism of passivity is consistent with a model that includes a competitive adsorption process between the $\text{OH}^-$ and the $\text{SH}^-$ anions. At higher $\text{SH}^-/\text{OH}^-$ ratio, the formation of the passivating $\text{Fe(OH)}_2$ is inhibited and, therefore, complete passivation becomes more difficult to obtain.

A second peak at potentials above the active-passive transition is related to the transformation of the FeS present on the surface to $\text{Fe}_2\text{O}_3$ and S. At these potentials, sulfur can also be produced by direct oxidation of $\text{SH}^-$ at flaws in the passive film.

At higher potentials, the electrode surface is covered by a protective $\text{Fe}_2\text{O}_3$ phase. However, some localized corrosion can occur in places where the oxide film does not fully develop. Iron(II) disulfide (pyrite) can precipitate from the solution, probably by reaction of the
dissolved Fe$^{3+}$ with HS$^{-}$.

The process leading to the breakdown of passivity was identified as the formation of iron sulfide patches on the iron surface. At potentials lower than ~ 0.5 V, mackinawite is the main component of the sulfide patches. At higher potentials sulfur is produced and pyrite may also precipitate.

The mechanism of formation of mackinawite patches on passive iron is consistent with one of localized sulfide adsorption/oxide dissolution. The nucleation rate is controlled by the HS$^{-}$ adsorption process, in competition with the OH$^{-}$ adsorption. The rate of nucleation is so fast that all available active sites are "instantaneously" converted to nucleation sites. The number of nuclei decreases with increase potential and time of passivation. The growth rate is determined by the oxide dissolution at the growing edge of the patches, and diffusion of the Fe$^{2+}$ away from the surface. At higher potentials, the formation of mackinawite is in competition with the oxidation of HS$^{-}$ to sulfur, and precipitation of pyrite. This reaction is activated-controlled.

The kinetics of localized corrosion in sulfide-containing borate buffer is closely related to that of formation of the iron sulfide patches. Pitting corrosion begins under the edges of the growing patches, where the surface pH has dropped considerably and the oxide film has been locally undermined. In these areas, active iron(II) dissolution occurs and pitting corrosion spreads beneath the patches, following a mechanism similar to that of crevice corrosion.
The resistance of the passive film to breakdown is related not only to the thickness of the oxide film but, more important, to its composition and electronic properties.

The dependence of the pitting susceptibility on passivation potential is consistent with a change in the iron oxide composition and structural properties at potentials positive to the Flade potential. This change in properties is common to several of the existing models of passive film composition.

The increase in corrosion resistance with passivation time can be correlated with a gradual decrease in the non-stoichiometry of the oxide, as indicated by the photoresponse dependence on passivation time.

The transient study of the photoresponse and its dependence on light energy also complemented the more classical electrochemical techniques in identifying the probable mechanism of iron sulfide formation. Photoelectrochemical techniques are potentially useful in studies of passivity breakdown processes. However, most of these results are, at the present, qualitative in nature and more research is needed to quantify these findings and to correlate the properties of the oxide film with its resistance to breakdown.
## APPENDIX 1

### DEFINITION OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Nucleation rate constant</td>
<td>(s^{-1})</td>
</tr>
<tr>
<td>a</td>
<td>Empirical constant in equation (90)</td>
<td></td>
</tr>
<tr>
<td>(a')</td>
<td>Constant in equation (102)</td>
<td>(A \cdot cm^{-2})</td>
</tr>
<tr>
<td>b</td>
<td>Empirical constant in equation (90)</td>
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<tr>
<td>b'</td>
<td>Exponent in equation (102)</td>
<td></td>
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<tr>
<td>(C^j)</td>
<td>Concentration of the specie j</td>
<td>(mol \cdot cm^{-3})</td>
</tr>
<tr>
<td>(C^b_j)</td>
<td>Concentration of j in bulk of solution</td>
<td>(mol \cdot cm^{-3})</td>
</tr>
<tr>
<td>(C^s_j)</td>
<td>Concentration of j at the surface</td>
<td>(mol \cdot cm^{-3})</td>
</tr>
<tr>
<td>(D)</td>
<td>Diffusion constant</td>
<td>(cm^2 \cdot s^{-1})</td>
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<tr>
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<td>Electrode potential</td>
<td>V</td>
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<td>(E^0)</td>
<td>Reversible equilibrium potential</td>
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<tr>
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<td>Equilibrium potential when (i \neq 0)</td>
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<td>Anodic limit in a potentiodynamic scan</td>
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<td>(E_{c})</td>
<td>Corrosion potential</td>
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<td>(E_{c}^+)</td>
<td>Corrosion potential in pit-like solution</td>
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<tr>
<td>(E_{F})</td>
<td>Flade potential</td>
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<td>(E_{fb})</td>
<td>Flat band potential</td>
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</tr>
<tr>
<td>(E_{inh})</td>
<td>Inhibition potential</td>
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<tr>
<td>(E_{inj})</td>
<td>Potential at the time of sulfide injection</td>
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</tr>
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<td>(E_p)</td>
<td>Pitting potential</td>
<td>V</td>
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<tr>
<td>$E_{\text{pas}}$</td>
<td>Passivation potential</td>
<td>V</td>
</tr>
<tr>
<td>$E_r$</td>
<td>Repassivation potential</td>
<td>V</td>
</tr>
<tr>
<td>$e^-$</td>
<td>Electron</td>
<td></td>
</tr>
<tr>
<td>$e_0$</td>
<td>Charge of an electron ((1.602 \cdot 10^{-19}))</td>
<td>C</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday's Constant ((96480))</td>
<td>C \cdot \text{eq}^{-1}</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck's constant ((4.13 \cdot 10^{-15}))</td>
<td>eV \cdot s</td>
</tr>
<tr>
<td>$h^+$</td>
<td>Height of a 2-D growth center</td>
<td>cm</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
<td>A</td>
</tr>
<tr>
<td>$i$</td>
<td>Current density</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i^*$</td>
<td>Photocurrent</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i^0$</td>
<td>Exchange current</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i_a$</td>
<td>Current due to active dissolution</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i_{d,l}$</td>
<td>Limiting current on disc electrode</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i_d$</td>
<td>Total current on disc electrode</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i_f$</td>
<td>Current due to film formation</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i_i$</td>
<td>Initial current on potentiostatic experiments</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i_p$</td>
<td>Pitting Current on potentiostatic experiments</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i_{\text{pas}}$</td>
<td>Residual current in the passive region</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i_r$</td>
<td>Total current on ring electrode</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i_{r^+}$</td>
<td>Anodic current on ring electrode</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i_{r^-}$</td>
<td>Cathodic current on ring electrode</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i_s$</td>
<td>Current due to oxide dissolution</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>$i_t$</td>
<td>Total current</td>
<td>A \cdot \text{cm}^{-2}</td>
</tr>
<tr>
<td>K</td>
<td>Equilibrium constant</td>
<td></td>
</tr>
<tr>
<td>k</td>
<td>Over-all growth rate constant</td>
<td>mol \cdot \text{cm}^{-2} \cdot \text{s}^{-1}</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>$k^0$</td>
<td>Heterogeneous rate constant when $E = 0 \text{ V (SCE)}$</td>
<td>$\text{cm} \cdot \text{s}^{-1}$</td>
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<tr>
<td>$k'$</td>
<td>Constant defined in equation (46a)</td>
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<tr>
<td>$k''$</td>
<td>Constant defined in equation (46b)</td>
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</tr>
<tr>
<td>$L$</td>
<td>Film thickness</td>
<td>$\text{cm}$</td>
</tr>
<tr>
<td>$m$</td>
<td>Exponent in equation (50)</td>
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</tr>
<tr>
<td>$M$</td>
<td>Molecular weight</td>
<td>$\text{g} \cdot \text{mole}^{-1}$</td>
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<tr>
<td>$n$</td>
<td>Number of electrons transferred in a reaction</td>
<td></td>
</tr>
<tr>
<td>$n_i, n_p$</td>
<td>Reaction order of $i$ or $p$ process, defined in</td>
<td></td>
</tr>
<tr>
<td></td>
<td>equation (66) and (67)</td>
<td></td>
</tr>
<tr>
<td>$n_d$</td>
<td>Number of electrons transferred at disc</td>
<td></td>
</tr>
<tr>
<td>$n_r$</td>
<td>Number of electrons transferred at ring</td>
<td></td>
</tr>
<tr>
<td>$N$</td>
<td>Number of nuclei per unit area</td>
<td>$\text{cm}^{-2}$</td>
</tr>
<tr>
<td>$N_o$</td>
<td>Maximum number of nuclei (or active sites)</td>
<td>$\text{cm}^{-2}$</td>
</tr>
<tr>
<td>$N_0$</td>
<td>Collection efficiency</td>
<td></td>
</tr>
<tr>
<td>$N_D$</td>
<td>Concentration of donors</td>
<td>$\text{mol} \cdot \text{cm}^{-3}$</td>
</tr>
<tr>
<td>$N_e$</td>
<td>Effective collection efficiency</td>
<td></td>
</tr>
<tr>
<td>$p_j$</td>
<td>Electrochemical reaction order on specie $j$</td>
<td></td>
</tr>
<tr>
<td>$Q$</td>
<td>Charge</td>
<td>$\text{C} \cdot \text{cm}^{-2}$</td>
</tr>
<tr>
<td>$Q_a$</td>
<td>Anodic charge due to active dissolution</td>
<td>$\text{C} \cdot \text{cm}^{-2}$</td>
</tr>
<tr>
<td>$Q_s$</td>
<td>Charge due to oxide dissolution</td>
<td>$\text{C} \cdot \text{cm}^{-2}$</td>
</tr>
<tr>
<td>$Q_f$</td>
<td>Charge in the film</td>
<td>$\text{C} \cdot \text{cm}^{-2}$</td>
</tr>
<tr>
<td>$Q_t$</td>
<td>Total charge</td>
<td>$\text{C} \cdot \text{cm}^{-2}$</td>
</tr>
<tr>
<td>$r$</td>
<td>Heterogeneous reaction rate</td>
<td>$\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas law constant ($8.31$)</td>
<td>$\text{J} \cdot \text{K}^{-1}$</td>
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<tr>
<td>$R_1$</td>
<td>Radius of a disc electrode</td>
<td>$\text{cm}$</td>
</tr>
<tr>
<td>$R_2$</td>
<td>Internal radius of a ring electrode</td>
<td>$\text{cm}$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------------------------------------------</td>
<td>------</td>
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<tr>
<td>$R_3$</td>
<td>External radius of a ring electrode</td>
<td>cm</td>
</tr>
<tr>
<td>$S$</td>
<td>Surface area</td>
<td>cm$^{-2}$</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>°K</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>s</td>
</tr>
<tr>
<td>$U$</td>
<td>Empirical constant in equation (68)</td>
<td>V</td>
</tr>
<tr>
<td>$U_c$</td>
<td>Energy of the conduction band</td>
<td>eV</td>
</tr>
<tr>
<td>$U_F$</td>
<td>Energy of the Fermi level</td>
<td>eV</td>
</tr>
<tr>
<td>$U_g$</td>
<td>Band gap energy</td>
<td>eV</td>
</tr>
<tr>
<td>$U_v$</td>
<td>Energy of the valence band</td>
<td>eV</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Constant defined in equation (32)</td>
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</tr>
<tr>
<td>$\alpha$</td>
<td>Transfer coefficient for one-electron</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Butler-Volmer equation</td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>Constant defined in equation (33)</td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>Transfer coefficient for multi-electron</td>
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<tr>
<td></td>
<td>Butler-Volmer equation</td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Surface tension</td>
<td></td>
</tr>
<tr>
<td>$\delta$</td>
<td>Thickness of the diffusion layer</td>
<td>cm</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Activation overvoltage</td>
<td>V</td>
</tr>
<tr>
<td>$\eta_c$</td>
<td>Concentration overvoltage</td>
<td>V</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
<td>cm</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Frequency of incident light</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Kinematic viscosity</td>
<td>cm$^2$.s$^{-1}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>gr.cm$^{-3}$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Induction time</td>
<td>s</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Photon flux</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular velocity</td>
<td>rad.s$^{-1}$</td>
</tr>
</tbody>
</table>
$\omega$ Angular frequency \[ \text{rad.s}^{-1} \]

**Superscript**

b Bulk

s Surface

$*$ Photoresponse

$0$ Equilibrium

**Subscript**

a Anodic, active dissolution

d Disc, diffusion controlled

F Flade

f Film

fb Flat band

i Initial process (leading to passivation breakdown)

inh Inhibition

inj Injection (of sulfide solution)

j Any specie

l Limiting

m Maximum

o Initial

p Pitting

pas Passivation

r Ring

rds rate determining step
s Oxide dissolution

T Total

+ Anodic, oxidation

- Cathodic, reduction

∞ Steady state, or after long time
APPENDIX 2

LIST OF EQUIPMENT

Amel Corporation Model 551 Potentiostat/Galvanostat
Amel Corporation Model 566 Function Generator
Apple //e Computer
Cyborg Model 91A A/D - D/A Converter.
ETEC Autoprobe, Electron Microprobe Analyzer
Hewlett-Packard Model 7044A X-Y Recorder
Jarrell Ash Model 82-410 Monochromator
Keithley Instruments Model 130 Digital Multimeter
Millipore Corporation Water Purification System
Oriel Corporation Model 6141 Xenon Lamp Assembly
Pine Instruments Model ASR2 Analytical Rotator and Speed Control
Pine Instruments Model RDE3 Double Potentiostat/Galvanostat
Princeton Applied Research Model 5204 Lock-In Amplifier
Princeton Applied Research Model 125A Mechanical Chopper
Princeton Applied Research Model 173 Potentiostat/Galvanostat
Princeton Applied Research Model 175 Universal Programmer
Princeton Applied Research Model 379 Digital Coulometer
Soltec Model B-181 X-T Strip Chart Recorder
Tektronix Model 7603 Oscilloscope
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