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PITTING CORROSION OF INCONEL 600 IN HIGH TEMPERATURE CHLORIDE
SOLUTION UNDER CONTROLLED HYDRODYNAMIC CONDITIONS

The Ohio State University

PH.D. 1983

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PITTING CORROSION OF INCONEL 600 IN
HIGH TEMPERATURE CHLORIDE SOLUTION UNDER
CONTROLLED HYDRODYNAMIC CONDITIONS

A DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE DOCTOR OF PHILOSOPHY IN THE
GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY.

BY

MOHAMAD KARAMEZHAAD RANJBAR, B.SC., M.SC.

* * * * *

THE OHIO STATE UNIVERSITY

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Advisor

Department of Metallurgical
Engineering

DEDICATION .

To the founder of Islamic Republic of Iran

Imam Khomaini

and

to Mr. Akbar Hashemi Rafsanjani for his en-

couragement for research and higher education.

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INTRODUCTION

At least three fundamental steps: (i) transport of the reactant to the metal surface, (ii) electron exchange resulting in metal loss, and (iii) transport of the corrosion products from the surface into the bulk solution are involved in the corrosion of metals and alloys in aqueous solution. These three steps occur in series and as a result each of these steps can control the rate of the overall process.

Many industrial systems involve the flow of corrosive fluids through pipes, channels, etc., at high velocities. Although mass transfer effects are well recognized as being of importance in determining the kinetics of corrosion processes, a significant body of data exists only for quiescent systems. Even now, a large part of corrosion research is carried out in quiescent systems, which do not effectively simulate the flow conditions in industrial environments.

The important question which arises, is whether we can use the available data safely for assessing the behavior of materials in industrial environments, or should we go to the trouble of carrying out all corrosion research and testing in a hydrodynamic regime which simulates that found in the

industrial systems, especially those which involve hostile environments at elevated temperatures and pressures.

Only a few papers (1-3) have been published which deal with the effect of hydrodynamics on pitting corrosion, and none of these deal with localized attack at high temperatures and pressures. Fluid flow, through shear and mass transfer effects, may have a profound effect on the rate of corrosion, either by effecting the rate of transport of chemical species to or from the surface or by shear stripping protective films from the alloy solution interface. Accordingly, an accurate simulation of corrosion phenomena that occur in the plant environment can be made in the laboratory only if the hydrodynamic effects are taken into account. The purpose of this work is to develop a suitable technique for accomplishing this task.

A variety of controlled hydrodynamic techniques, including rotating discs and cylinders, and flow-through ducts (tube, annuli, etc.), have been developed for use at ambient pressure and temperature, but few of these techniques have been employed at elevated temperatures and pressures. In the present study, an apparatus was designed to carry out corrosion and electrochemical experiments under well-defined hydrodynamic conditions at temperatures as high as 275°C. The apparatus employs an annular flow channel

which is capable of yielding Reynolds numbers over the range of 10^2 to 10^5 . An annular duct geometry was chosen for this work because this system has been subjected to both extensive theoretical and experimental analysis and mass transfer - correlations are available for this geometry at ambient temperature over a wide range of Reynolds numbers covering both the laminar and turbulent flow regimes.

This study has involved calibration of the mass transfer characteristics of an annular flow channel at temperatures over the range 25°C to 250°C , and these data have then been used to ascertain the effect of fluid flow on the pitting corrosion of Inconel 600 in 0.1M NaCl solution at elevated temperatures. The pitting characteristics of the alloy have been determined using both potentiostatic and potentiodynamic anodic polarization techniques.

Inconel 600 is a nickel-base austenitic alloy. It has good oxidation resistance and strength at elevated temperatures, and is also resistant to general corrosion in chloride and alkaline environments. For these reasons it is commonly used as tubing material in PWR steam generators. However, in response to reports of in-service failures of steam generator tubing more extensive corrosion testing of this alloy is necessary.

This dissertation is divided into four main sections. The literature survey provides the necessary background information concerning pitting corrosion and calibration of the mass transfer characteristics of the flow system. The section entitled "Experimental Procedure" describes the experimental facilities, the experimental procedure, and the metallurgical properties of the material used in the course of this investigation. Chapter III presents the experimental results and contains a discussion of the findings. The conclusions of this study are summarized in the final section.

Chapter I

LITERATURE SURVEY

I-1 Pitting Corrosion

Pitting is one of the most damaging forms of corrosion, because failure can occur with extreme suddenness at only a small percent of weight loss, and also because it is difficult to detect. Frequently, there exists an extended period for pit initiation which may range from months to years; however, after pits have initiated they tend to penetrate the material at an increasing rate.

As early as 1925, it was known that the environments within pits are acidic(4,5,6) and, as stated by Evans (7), this acidification is due to the hydrolysis of metal cations. It is also well known that most pitting failures are caused by chloride and chlorine-containing anions, and that pitting corrosion occurs on metals which are in the passive state. During the last 30 years extensive experimental work has been carried out to characterize this form of attack for a wide variety of materials and environments. Furthermore, numerous theories for pitting corrosion have been developed (8,9,10).

I-1-1 Passivity

Passivity is the property responsible for the corrosion resistance of many metals. According to one definition," a

metal or alloy is passive if it substantially resists corrosion in an environment where thermodynamically there is a large free energy decrease associated with its passage from the metallic state to appropriate corrosion products" (11).

There are two schools of thought regarding the nature of the passive film. The first point of view is that the passive film is always a diffusion barrier layer of reaction product which separates the metal from its environment and, as a result, reduces the corrosion rate. The second holds that when a clean metal surface is exposed to oxygen, an adsorbed layer of oxygen atoms is formed and a stable two-dimensional structure containing negative oxygen ions and positive metal ions is produced. Such a layer displaces adsorbed H_2O molecules and reduces the rate of corrosion.

The first point of view is usually referred to as the "oxide film theory" and the second one as the "adsorption theory" of passivity. Frankenthal (12) showed that less than a monolayer of oxygen can impart full passivity behavior to 304 Cr stainless steel in 1N H_2SO_4 . This implies that passivity occurs via the adsorption mechanism and not by formation of a diffusion barrier. Uhlig (13) showed that the passive film consisting of chemisorbed oxygen is favored by those metals with unfilled or uncoupled d electrons (the transition metals) with which adsorbed oxygen can interact.

On the other hand, in the case of the nontransition metals, the adsorbed oxygen film has either a short life or does not form at all, and the formation of a stoichiometric compound which acts as a diffusion barrier is favored.

Aronowitz and Hackerman (14), as well as Tomashov and Chernova(15), believe that the two theories supplement one another. They state that the film consists of an adsorbed monolayer of oxygen through which cations migrate to form an amorphous oxide layer over the adsorbed monolayer. They concluded that the retardation of the anodic process is enhanced by the combined adsorption layer-oxide film structure of the passive film.

To describe the formation of passive films on metals, three alternative processes have been suggested (16); (i) direct film formation, (ii) dissolution-precipitation, and (iii) anodic deposition. The direct film formation mechanism consists of direct reaction of metal with solution to form an oxygen adsorption film, a compact oxide film, or a protective solid salt film on the metal surface. The dissolution-precipitation process consists of anodic metal dissolution and precipitation of dissolved metal ions which can lead to a passivating oxide or insoluble salt film. The anodic deposition process is a consecutive reaction to the anodic dissolution process to produce an anodic deposit oxide or salt film.

As early as 1911, Flade (17) noted that the open circuit potential of a passivated metal decreases to an arrest potential before decaying to the active state. Later Bonhoeffer(18) suggested that this arrest potential should be equal to the passivation potential observed in the anodic polarization curve. According to Vetter (19) the Flade potential may be regarded as the potential of the oxide covered metal electrode. Uhlig (20) who suggested a layer of chemisorbed atomic and molecular oxygen on the surface, described the Flade potential as an oxygen adsorption potential.

Sato (21) classified passive films that form on metals into five types shown in Figure 1 :

Type 1 : The adsorption film consists of a monoatomic or multimolecular layer of oxygen or other species.

Type 2 : The barrier film consists of a three-dimensional oxide polymer layer sustaining a potential of 10^6 - 10^7 V/cm.

Type 3 : The barrier film forms on a less protective layer.

Type 4 : The barrier film is covered with a hydrated deposit layer.

Type 5 : The barrier film is covered with a porous layer of the same composition.

Figure 1. Five types of passive films(21).

The composition of passivating barrier films often changes with potential and solution composition. Enrichment of some of the alloying elements in the passivating film has been noted in many cases(22-23), and there is general agreement that probably all passivating films formed in aqueous solution contain a quantity of water. However it is not clear whether or not the passivating film is crystalline or amorphous(24,25).

Based on the present state of knowledge, the passivating film is a poor electronic conductor ranging from semiconductor to insulator. The mechanical properties of the passivating film are not well known, especially when the film thickness is of the order of 1 nm. The stresses in thick (40-300 nm) anodic oxide films formed on tantalum, niobium, aluminum, and tungsten were measured and found to be tensile (26). The stress in the film on zirconium is compressive in borate solution, but becomes tensile in the presence of fluoride ions; However, after breakdown it again becomes compressive in nature (27).

Goswami and Staehle(28), studied the steady-state growth of the passivating film on Fe-10Ni, Fe-10Cr, and Fe-10Ni-10Cr alloys in borate buffer solution. Their data fit the inverse logarithmic rate law. Bulman and Tseung(29), studied the passivation of Type 316 austenitic stainless steel and reported that their kinetic data follow a direct logarithmic

law. Since the logarithmic law and inverse-logarithmic law are almost mathematically equivalent when the change in thickness is small, many cases are known where the experimental data may fit both laws equally well (28-30). Oliver (31), by measuring the anodic polarization curves for a series of Fe-18 Cr alloys, concluded that the combined film formed in sulfuric acid solution is about 20Å thick.

Several models have been proposed over the past four decades to explain the growth kinetics of passive films. Mott and Cabrera (32) extended the model proposed by Mott (33) and obtained the following rate law for film growth

$$\frac{dL}{dt} = N\Omega\nu \exp \left[\left(-W^0 - \mu L + \frac{q\alpha\epsilon}{2} \right) / kT \right] \quad (1)$$

where N is the number of mobile ions per unit surface area, Ω is the molecular volume per cation, ν is the vibrational frequency, W is the activation energy for the rate-controlling step, q is the charge that the cation carries, α is the jump distance, and kT is the thermal energy. The assumptions which lead to the above rate law for film growth are as follows:

1. The transfer of metal cations across the oxide film to the film/solution interface is responsible for the film growth;

2. The high electric field strength, ϵ , which is assumed to exist within the oxide, assists the penetration of cations through the film.
3. The field strength is constant through out the film;
4. The total potential drop across the film is constant;
5. The emission of metal cations from metal into film at the metal/film interface is the rate controlling step.

Among many other theoretical models which are not much different from each other, the kinetic treatment based on the "place exchange" mechanism received some attention. Sato and Cohen (34) who studied the passivation of iron in pH 8.4 borate buffer solution derived a kinetic equation for the place exchange mechanism, and used this equation to explain their findings. Their equation is:

$$i = k' \exp(mV_{app} - Q_T / n) \quad (2)$$

where i is the external current, V_{app} , the applied potential, Q_T , the accumulated charge in the oxide film and k' , m' and n are parameters.

The "place-exchange" mechanism model assumes that: (i) a layer of oxygen is adsorbed onto the surface which then exchange places with underlying metal atoms; (ii) A second layer of oxygen is then adsorbed and the two M-O pairs

rotate simultaneously; (iii) This process is repeated and results in oxide film thickening. This mechanism does not provide an explanation for the growth of a film whose thickness is greater than one or two monolayers.

Recently Chao, Lin, and Macdonald (35) reviewed the existing models and concluded that "none of the existing models are completely satisfactory from a physical view point, nor are they in complete agreement with the experimental data". They introduce an alternative model, namely point defect model, and demonstrated that it is in substantial agreement with data that are currently available. This model is based on the movement of point defects in an electrostatic field. It considers the transport of both anions (oxygen ions) and cations (metal ions), or their respective vacancies. They concluded that the migration of oxygen anions or oxide ion vacancies (V_O) is essential for passive film growth, but cation diffusion results only in dissolution and not in the growth of the primary passive film. They derived the equation for the film growth which is expressed as

$$\exp(2KL) - 2KL - 1 = 2KA(B-1)t \quad (3)$$

where K is equal to $F\varepsilon/RT$, L is film thickness, E is the electric field strength, and A and B are functions of

external potential. They showed that this expression reduces to a logarithmic expression for thick films and yields a current transient which varies inversely with time. For very thin films, a current transient which varies inversely with the square root of time is indicated.

Due to the importance of the point defect model for the interpretation of the experimental data and for the understanding of the mechanism of passivity, film growth, and passivity breakdown, its basic feature according to Macdonald et al is given here. This model is based on the following assumptions: (i) Whenever the external potential, V_{ext} , is more noble than the Flade potential, a continuous passive film will form on the surface of a metal. For the present purpose, the film is assumed to be an oxide of composition $\text{MO}_{x/2}$. However, the model developed below is perfectly general and can be applied to other (oxide and nonoxide) films as well. (ii) It is assumed that the passive film contains a high concentration of point defects. High temperature studies indicate that the major point defects that exist in an oxide film are $V_M^{x'}$, $V_O^{\bullet\bullet}$, e' , and $h^{\bullet*}$. The

* The Kroger-Vink notation is adopted here for designating point defect species. According to the notation, X_Y means that a species X occupies a Y lattice site (e.g. V_M^y means a vacancy occupies a metal site in the oxide, i.e., a metal vacancy); e and h are electrons and holes. The superscript gives the number and the sign of the charge. Thus, $^{\bullet\bullet}$ means two positive charges. $^{x'}$ means x negative charges (e.g. $V_M^{x'}$ means a metal vacancy which carries x negative charge).

same species are expected to be present in a passive film.(iii) It is well known that passive films are characterized by high electrical fields (10^6 V/cm), and we assume that the field strength is of the same order as that required for dielectric breakdown. Accordingly, the passive film behave as an "incipient semiconductor", because it exists on the verge of dielectric breakdown. Consequently, the field strength is a function of the chemical and electrical characteristics of the film and therefore is independent of thickness even for potentiostatic conditions. (iv) Since passive films are regarded to be "incipient semiconductors," it is assumed that electrons (e') and electron holes (h') in the film matrix are in their equilibrium states, and that the electrochemical reactions involving electrons (or electron holes) are rate controlling at either the metal/film (m/f) or the film/solution (f/s) interfaces. On the other hand ,the rate controlling step for those processes which involve metal vacancies ($V_M^{x'}$) and oxide vacancies ($V_O^\bullet$),(i.e.,film growth) is assumed to be the transport of the vacancies across the film. The assumption implies that metal and oxide vacancies are in their equilibrium states at the m/f and the f/s interfaces."

I-2-1 Chemical Breakdown of Passivity

J. Kruger (36) defined chemical breakdown as those processes brought about by chemical alteration of the film

or the environment that produce changes in the passive film so that it can no longer effectively prevent damaging anodic currents from flowing.

It is a generally accepted fact that the following events should occur in leading to pit initiation:

- 1) A critical potential, called the pitting potential, must be exceeded.
- 2) Damaging species are required to initiate and propagate breakdown.
- 3) Pit initiation occurs at highly localized sites.
- 4) There is an induction time separating the time when conditions conducive to breakdown occur and the time when pit initiation begins.

Any reasonable model must satisfy the above requirements and answer questions concerning the effect of composition, and electronic structure, of the film on the kinetics of its growth.

Seven pit nucleation models have been proposed. These theories are the result of modification of earlier theories and are as follows:

- 1) Adsorbed Ion Displacement Models.
- 2) Ion Migration or Penetration Models.
- 3) Chemico-Mechanical Models.
- 4) Localized Acidification Models.
- 5) Depassivation-Repassivation Models.

6) Point Defect Models.

7) Combination of Above Models.

I-2-2 Adsorbed Ion Displacement Models

Two theories have been suggested in the adsorbed ion displacement category. The first theory considers the passive film to be an adsorbed film of oxygen. Breakdown occurs when a more strongly adsorbing damaging anion displaces the adsorbed oxygen which forms the passive film. Once the damaging ion is adsorbed at the surface, breakdown occurs. This theory was suggested by Kolotyrkin (37) and Uhlig (38,39). Rozenfeld and Maksimchuck (40), by using radioactive Cl^- , have provided direct evidence that the above reactions occur.

Theories suggested by Hoar and Jacob (41) fall under the above heading, but are different from the first group. In this second model, 3 or 4 halides jointly adsorb on the surface of the passive film around a lattice cation. Once this happens, the halide ions will remove the cation from the three dimensional passive film lattice and make the film thinner at this site.

When this happens, the stronger anodic field at the thinned site will rapidly pull another cation through. This cation will meet with more halide ions and then form a complex which will dissolve into the solution and finally cause breakdown of the film at that site. Once this process starts it proceeds at an ever increasing rate

I-2-3 Ion Migration or Penetration Models

Theories in the ion migration or penetration category are composed of many models that all require the penetration of damaging anions through the passive film. Pits will initiate when the anions reach the metal/film interface. The models differ widely in the mode of penetration, but all consider the passive film to be three dimensional in structure.

Evans (42) was the first to suggest the original version of this model, which was later revised by Richardson and Wood (43,44) to account for the observed incubation time for pit initiation. The processes which involve ion migration in a lattice can occur in a variety of ways. Hoar, et al (45), and Pryor and co-workers (46,47) suggested that this migration occurs through a site in the film which is contaminated by the damaging anion.

I-2-4 Chemico-Mechanical Models

The theoretical models which can be grouped under this heading involve those which give rise to chemically-induced mechanical disruption of the passive film. According to Hoar (48), the adsorption of a damaging anion on the surface of the passive film lowers the interfacial surface tension at the film/solution interface. The adsorbed anions repel one another, thereby inducing local stresses which result in slip and ultimately in the

formation of cracks. These cracks act as the nuclei for pits. Sato (49) suggested that when the film pressure, p , exceeds some critical value, breakdown will occur. This film pressure which results from both electrostriction and interfacial effect is expressed as

$$P = P_0 + \frac{\delta(\delta - 1)\epsilon^2}{8\pi} - \gamma/L \quad (4)$$

where p_0 is the atmospheric pressure, δ is the film dielectric constant, ϵ is the electric field strength, γ is the surface tension, and L is the film thickness. Based on this assumption, he derived the relationship between the breakdown potential, E_p , and the concentration of anions in solution as follows:

$$\frac{dE_p}{d \ln a_{MA}} = \frac{8 \pi k T \Gamma_{A^-}}{\delta(\delta+1)\epsilon} \quad (5)$$

where a_{MA} is the activity of the salt MA , Γ_{A^-} is the adsorption density of A^- , k is Boltzman's constant, and T is the temperature.

I-2-5 Localized Acidification

According to this model, pitting starts as a result of localized acidification that takes place at the

metal-solution interface, which hinders the reformation of the passive film (50). This mechanism was modified by Galvele et al (51-56), who emphasized that pit nucleation occurs at microchemical and/or microstructural heterogeneities (e.g. inclusions) which exist at the film/solution interface. The existence of this heterogeneity is a necessary condition for maintaining the dissolution process.

Vetter and Strehblow (57), on the grounds that no significant changes could be expected at the initial steps of pitting, questioned the mechanisms of pitting based on local changes in the composition of the solution. Galvele (58) used a simplified model for a pit and repeated the calculations made by Vetter and Strehblow and found that, although the local chloride ion concentration changes were not significant in the initial stages of pitting, the pH changes were very important, even for the earliest stages of pit growth. Figure 2 presents concentration diagrams for ions inside pits based on his calculations. In this figure, x is the pit depth, in cm, and i is the current density in the pit, in A/cm^2 . He explained that: "There is a potential below which no localized acidification can be maintained at the metal/solution interface". This potential is given by the corrosion potential of the metal in the acidified solution, E_c^* . When measuring the pitting potential, a positive

Figure 2. Concentration of Fe^{2+} as a function of the depth, x , and the current density, i , in a unidirectional pit(58)

polarization, η , is added to the corrosion potential to maintain a net anodic current density inside the pit, and secure the minimum $X.i$ value. From transport considerations (59) it was concluded that a further contribution has to be accounted for, due to effect of inhibitors in the solution, E_{inh} . Finally, since the current density inside the pit is high, there is a contribution due to the electrical potential, ϕ , that must be added. In this way, the measured pitting potential is the total of the above mentioned factors.

$$E_p = E_c^* + \eta + E_{inh} + \phi \quad (6)$$

I-2-6 Depassivation-Repassivation Models

Sato (60) has extended the concept of chemical-mechanical breakdown and suggested that high fields could lead to mechanical rupture of thin films. He proposed that whether a pit nucleates or passivates depends not only on the breakdown phenomenon but also on those processes that lead to film reformation.

Videm (61) has proposed that it is the interplay between breakdown and repassivation that determines whether a passive film will suffer permanent breakdown that leads to pitting. He proposed that the critical pitting potential is determined by the relative rates of breakdown and repassivation. This proposal is based on his experiments

that showed a narrow potential region where repair and breakdown were competitive. Below this region, repair predominated and above it, breakdown was the major process.

Kruger (62) argued that because potential can effect the repassivation kinetics (63) (Figure 3), and because as Videm suggest, initiation of localized attack depends on a dynamic balance between breakdown and repair, kinetic factors in determining E_p must be considered.

It is known that pit nucleation is related to the presence of defects in the oxide film. These defects may preexist in the oxide film, or may be, as this theory suggests, be continuously produced by a dynamic process of film rupture and repassivation.

I-2-7 Point Defect Models

Lin, Chao, and Macdonald (64) have extended their point defect theory for explaining the kinetics of growth of passive films, which was reviewed previously, to account for chemical breakdown. They have pointed out that "one consequence of the diffusion of metal cations from the metal/film to the film/Solution interface is that metal vacancies are created at the metal/film interface. These metal 'holes' will tend to submerge into the bulk of the metal and hence to 'disappear'. However, when the cation diffusion rate (the metal hole production rate) is higher than the rate of 'metal hole' submergence into the bulk, the

Figure 3. Effect of potential repassivation rate as shown by changes in film thickness, x , for Ti alloy in 1N NaNO_3 (solid line) and in 1N NaCl (dotted line) at -222 and +706 mv (SHE) at 25°C(63).

metal holes will start piling up and hence will form a void at the metal/film interface (this is the process of pit incubation). When the void grows to a certain critical size, the passive film suffers local collapse which then marks the end of the pit incubation period. Subsequently, the collapsed site dissolves much faster than any other place on the surface thereby leading to pit growth."

This model provides quantitative explanations for the dependence of breakdown potential and incubation time on halide concentration. The breakdown potential for the specific case of chloride attack is given as

$$V_o = \frac{4.606RT}{\alpha F} \log \frac{J_m}{J^* u^{-x/2}} - \frac{2.303RT}{\alpha F} \log a_{Cl^-} \quad (7)$$

where α is the dependence of the film/solution interfacial potential on the applied voltage, and J^* , J_m and U are constants which depend only on the properties of the film. The incubation time, t , is expressed mathematically as :

$$t = \xi \left[\exp \left(\frac{\alpha F \Delta V}{2RT} \right) - 1 \right]^{-1} + \tau \quad (8)$$

where

$$\xi = \ell / J^* u^{-x/2} (a_{Cl^-})^{x/2} \exp \left(\frac{\alpha F V_o}{2RT} \right) \quad (9)$$

and ξ is the critical amount of metal hole accumulation to cause breakdown. ΔV is the breakdown overpotential ($\Delta V = E - E_p$) where E_p is the stationary breakdown potential. However, it does not take into account the surface "structure".

I-3-1 Pit Growth and Morphology

Engell and Stolica (65) probably were the first to study the kinetics of pit growth under potentiostatic conditions. They found that the current for a growing pit is related to time according to equation (10),

$$i = Kt^b \quad (10)$$

where K is a constant which depends upon the concentration of Cl^- ions, t is time, and b has a value of 2 or 3, depending upon the nucleation distribution function. When the number of pits (N) is constant with time, b is equal to 2, but if the pit number is proportional to t , then $b = 3$.

Smialowska and Czachor (66), in their study of the pitting of 16 Cr-Fe alloy in solutions containing different $\text{Cl}^-/\text{SO}_4^{2-}$ ratios, found values higher than 3 for the exponent b . Smialowska and Mankowski (67) considered two different geometries and proposed the following relationships:

$$\text{for cap shaped pits } i = \frac{h^2 R (3-h/r)}{t} \quad (11)$$

$$\text{and for cylindrical pits } i = \frac{r^2 h}{t} \quad (12)$$

where r is the radius, and h is the height of the cap or cylinder. The h and r values are time dependent; therefore i is not simply related to the inverse of time. The model does not provide a ready explanation for why, in different cases, pits develop faster in width than in depth, or vice versa.

Vetter and Strehblow(57) proposed that the edges of pits are sharp (Figure 4a).Galvele(56), suggested that this description cannot be taken as a general property of pitting,since covered pits have been reported in many cases.Yahlom, Ives,and Kruger(68)have shown that the film covering the opening of the pits was the original passive film. Figure 4b presents the modified model which, according to Galvele(56), would give a better description of the pitting process in many cases.

Although in recent years much attention has been given to the morphology of pits, it is still not clear what conditions must be fulfilled to realize the formation of pits of a particular shape. It is known that the shape of the pit depends upon the environment within the pits.This environment is related to the composition of the external solution,and to the properties of the given metal.Many types of pits have been observed,including hemispherical, flat-walled, formless, uncovered,and covered.

Figure 4. (a) Pit borders according to Vetter and Strehblow; (b) Modified model based on the existence of oxide covered pits (56).

Recently Hue(69) studied the effect of flow velocity on the morphology of localized attack on Type 304 stainless steel at temperatures up to 275° C, and reported that the shape of the pits formed depends upon the flow velocity of the solution. He observed that at temperatures up to 175° C, all the pits were aligned in the flow direction. Furthermore, the depth of the pits were found to decrease with increasing flow velocity

I-4-1 The Effect of Hydrodynamics on Pitting Corrosion

Although only a few papers dealing with the effect of hydrodynamics on pitting corrosion have been published, the importance of mass transfer in pitting corrosion can be deduced from the literature.

Postlethwaite et al (1) studied the effect of fluid flow on the pitting corrosion of zirconium and zircaloy-2 in alkaline chloride solutions by using a tubular flow system. They showed that the breakdown potential for these material is independent of flow velocity. Figures (5) and (6) show the effect of flow on the anodic current following passivity breakdown for zircaloy-2 in NaOH+H₃BO₃, pH 10.5 with 100 ppm NaCl at 25°C and 160°C, respectively. The rate of attack following breakdown at high potentials, as reflected by the total current density, is decreased by an increase in flow velocity. However, the pits increased in number but

Figure 5. Effect of flow on the electrolysis curves for Zircaloy-2 in NaOH + H_3BO_3 , pH 10.5, 100 ppm NaCl at 25°C(1).

Figure 6. Effect of flow on the anodic current following passivity breakdown at elevated temperature (160°C). Zircaloy-2 in NaOH + B(OH)₃, pH 10.5, 100 ppm NaCl. (a) Reynolds number 91,000, velocity 3.77 ft/s; (b) Reynolds number 10,000, velocity 0.45 ft/s(1).

decreased in depth with an increase in the flow rate. Another effect of flow was the removal of the solid corrosion products from the site of attack, especially at elevated temperatures where little corrosion product remained on the surface outside the corrosion pits.

In another study (70), it has been found that the rate of pitting attack on nickel in $\text{H}_2\text{SO}_4 + \text{NaCl}$ solutions was reduced with increasing flow velocity. In this case, the corrosion products are soluble. These workers concluded that the study of the effect of flow velocity should be extended to other metals which have been previously studied under conditions of natural convection.

The effect of fluid flow on the induction time for pit initiation has been studied by Schwabe (71). He studied the breakdown of iron in alkaline-chloride solutions, and showed that when the Cl^-/OH^- ratio is low, the induction time is flow-dependent.

Beck (2), by using an artificial pit in the side of a flow channel, studied the influence of hydrodynamic factors on the pitting rate of a variety of metals in aqueous environments. A similar technique was also used by Muller (72) and Frankenthal et al. (73); in this case the artificial pits consist of a corroding metal surface at the base of a hole in an insulating medium. Beck reported that for iron, titanium, and aluminum in chloride, bromide, and

iodide-containing solutions under potentiostatic control, two modes of pitting are observed. At high current densities, the rate of pit growth is limited by ohmic resistance in solution, whereas at lower current densities, the process is limited by mass transfer. Beck found that the mass transfer limited current density increased with flow rate, but was not always well-defined because solid corrosion products in the pit disturbed the solution flow pattern. In case of iron, transport of FeCl_2 away from the corroding surface limited the corrosion rate. In this case the pitting current density in the plateau region between 1.6 and 3.6 volts was a function of flow rate (Figures 7,8,9).

Recently deCastro and Wilde (3) studied the effect of peripheral velocity on the pitting and passivation of iron in chloride-containing media. They used cylindrical iron specimens which were machined from bar stock and annealed at 1100°C in hydrogen. The surfaces of the specimens were polished by abrasion down to a 600 grit silicon carbide finish. The interface between the metal and Teflon gasket was painted with an alkyd resin to avoid complications from crevice corrosion. Polarization curves, with and without rotational velocity, were determined by using a 25 mV "step-by-step" procedure with 3 minutes intervals between each step. Figure (10) shows typical anodic polarization

Figure 7. Calibration data for mass transport in artificial pit in flow channel(2).

Figure 8. Pitting current density for titanium in 1M KBr at a potential of 5V(SCE) as a function of Reynolds number for two pit depths(2).

Figure 9. Correlation of limiting current density with diffusion layer thickness for artificial pit with iron in 4M NaCl(2).

curves, with and without rotation, obtained for iron in 1M LiCl. From this figure the influence of rotation on the shape of the curve is obvious. The influence of rotation speed on the anodic dissolution kinetics at pH 8 was investigated at rotational velocities of 50, 100, 200, 400, 800, 1600, and 3200 rpm. At all rotational speeds, the polarization curve was the same as that shown in Figure 10. As figure 11 shows, flow velocity does not effect the pitting potential.

1-5 The effect of other factors on pitting corrosion

The effect of alloy composition on the passivity of steels and on their susceptibility to localized attack has been the object of many investigations. It appears that the passivity of the film increases as the concentrations of nitrogen, nickel, and especially chromium and molybdenum increase.

Mac Bee and Kruger (74) examined the films formed on a series of Fe-Cr alloys by electron diffraction. They concluded that the films tend to become amorphous as the Cr content increases. Other studies (75) showed that the relative Cr content of the film increases sharply when the Cr content in the alloy exceeds 12 percent.

More work is needed to elucidate the effect of molybdenum content of the alloy on the composition and

Figure 10. Anodic polarization curve for iron in lithium chloride solution, showing the influence of electrode rotation(3).

Figure 11. The influence of rotational speed on the pitting potential of iron in 1M lithium chloride(3).

properties of the film. Molybdenum reduces the susceptibility of stainless steels towards pitting and crevice corrosion.

Hoar (76) suggested that molybdenum may form an acidic oxide between the metal and the more basic iron oxide, or that it may lead to a glassy structure which is more stable. Other studies(77,78), have shown that there is no enrichment of the passivating film in molybdenum.

Smialowska (79), in a concise survey of factors influencing the rate of pitting of iron and steel, concluded that the alloying elements Cr, Mo, V, and Si increase the resistance of steels to pitting in chloride media. She pointed out that this beneficial effect is most probably due to improvement of the protective properties of the passive film.

In the same paper, she reviewed recent studies concerning the influence of heat treatment and cold work on pitting (80-85), and came to the conclusion that plastic deformation which does not mechanically damage the passivating oxide film, does not affect pitting. However heat treatments which increase the homogeneity of the material should increase the resistance to pitting.

Increasing the concentration of the aggressive anion in the bulk solution reduces the pitting potential. In general, a relation of the type

$$E_p = A - B \log C_x \quad (13)$$

is found, where A and B are constants, and C_x is the aggressive anion concentration. In most of the published work on pitting of metals, chloride ion has been used as the aggressive anion. However, it is well known that many other anions can act as aggressive species.

Anions such as SO_4^{2-} , OH^- , ClO_3^- , CO_3^{2-} and CrO_4^{2-} shift E_p to more positive values. Prazak, Tousek, and Spainily (86) measured pitting potential as function of SO_4^{2-} and Cl^- ion concentration and found the following relationship between E_p and concentration of aggressive (C_x^-) and nonaggressive (C_A^{2-}) anions:

$$E_p = Kt \log \frac{(C_A^{2-})^n}{(C_x^-)^p} \quad (14)$$

No systematic studies of the effect of temperature on the pitting potential have been reported. Most of the existing data suggest that the breakdown potential decreases with increasing temperature. Pourbaix and his co-workers (87), Fochhammer and Engell (88), and Leckie and Uhlig (89) reported that for stainless steels in near neutral sodium chloride solutions in the temperature ranges of 25 to 80 °C, 25 to 100 °C, and 0 °C to 25 °C, respectively, the breakdown potential decreases with an increase in temperature. Engell

et al (88) studied the effect of temperature on the pitting potential of 18Cr-Fe, 17Cr-10Ni-Fe, and 18Cr-10Ni-0.3Mo-Fe stainless steels in 3% NaCl solution at temperatures in the range of 25 to 90°C (Figure 12). These data clearly show that for the various alloys studied, the relationships between E_p and temperature are different. However, Postlethwaite et al (3) reported that for pure iron in 0.1N NaOH+0.1M NaCl, the breakdown potential increases with increasing temperature, following an initial decrease between 25 and 125°C (Figure 12).

It has been found that for several systems pH does not have much effect on the pitting potential in neutral and acidic solutions (90-92). However, there is no general agreement about the effect of pH on pitting corrosion in alkaline solutions. For iron in chloride solutions, Strehblow and Titze (90), reported that there were no changes in the pitting potential for pH values from 8 up to 13. On the other hand Heusler and Fisher(91), reported that no pitting could be found for a pH higher than 10.4. Alvarez and Galvele(92), working with pure iron in NaCl solution found that the pitting potential was constant for pH values from 7 to 10, but increased with the pH for pH values higher than 10.

Figure 12. Relationship between breakdown potential and temperature for different steels in 3% NaCl at 22°C (88).

Figure 13 Effect of temperature on passivation breakdown potentials of pure iron in 0.1N NaOH + 0.1N NaCl(3).

I-6 Electrochemical Methods for the Measurement of Pitting Potentials

When a metal specimen is immersed in a corrosive medium, both reduction and oxidation processes occur on its surface. Typically the specimen oxidizes (corrodes) and the medium (solvent) or some component (e.g. dissolved oxygen) is reduced. The specimen must function as both an anode and a cathode, and both anodic and cathodic currents occur simultaneously on the specimen surface at the same interfacial potential difference. Since the rates of individual processes depend upon the potential drop across the metal/solution interface, it is advantageous to control the electrochemical potential of the specimen when studying corrosion processes.

Experimentally, one measures polarization characteristics by plotting the current response as a function of applied potential. Since the measured current can vary over several orders of magnitude, usually the log current function is plotted vs. potential on a semi-log chart.

An anodic polarization curve, such as that shown schematically in Figure (14), can yield important information on the electrochemical characteristics of a metal in any given environment. The information yielded includes the following:

Figure 14. Schematic polarization curve for a passivable metal.

- 1) The ability of the material to spontaneously passivate in the particular medium;
- 2) The potential over which the specimen remains passive;
- 3) The corrosion rate in the passive region; and
- 4) The breakdown potential for pitting corrosion.

There are several different controlled-potential methods for determining the breakdown potential:

- 1) Potentiostatic (constant potential) techniques
- 2) Potentiokinetic techniques
- 3) quasi-stationary methods.

Using these techniques polarization plots, beginning at E_{corr} and extending to some point beyond the knee (E_{np}), are produced and then by reversing the potential scan to the corrosion potential, another characteristic potential can be distinguished; E_{pp} the repassivation potential.

Smialowska and Czachor (93) compared these electrochemical methods and concluded that E_{np} values depend upon the experimental procedure. They pointed out that "only determination of the Cd(current density) vs time at various constant potentials by using a new sample for each curve can give an exact value of E_{np} ."

It is known that the pitting potential as determined potentiodynamically is a function of the voltage scan rate.

Leckie(94)(Figure 15), and Brenner (95) are among those who found that high voltage scan rates gave too noble pitting potentials. Leckie concluded that in the case of stainless steels, a voltage scan rate equal to or less than 10 mv/h will give pitting potentials very close to the correct ones. Broli and Holton (96) used the three potentiokinetic methods, potentiostatic (constant potential), potentiokinetics, and quasi-stationary techniques, to determine the pitting potential (E_{np}) for unalloyed aluminum in a deaerated solution of 3% NaCl at 0° and 30° C. Their results from the potentiodynamic examinations show that the dependence of E_{np} on voltage scan rate is approximately the same for both temperatures

(Figure 16). Szauer and Jakobs (97), investigated the pitting corrosion of selected steels in 0.005N, 0.05N, and 0.1N, KCl solutions. They emphasized that the most reliable values for E_{np} can be obtained only if the potential scan rate is very low, or by using a stationary potentiostatic method. Increase in the applied potential scan rate from 20 to 200 mv/h caused the pitting potential to shift an average of 30-40 mv to a more noble value. Further increasing the potential scan rate up to 1000 mv/h resulted in an E_{np} shift of up to 100 mv. He concluded that the observed phenomenon (Figure 17) was probably due to the finite induction time (Figure 17) for breakdown of the passive film.

Figure 15. Pitting potential vs the voltage scan rate for stainless steel in 0.1M NaCl solution at room temperature(94).

Figure 16. Pitting potential vs the voltage scan rate for unalloyed Al in 3% NaCl solution at 0 and 30°C (96).

Figure 17 Pitting potential vs potential scan rate (mv/h) for carbon steel, copper bearing steel, and two different low alloy steels in buffered(pH =8.4) 0.5N KCl solution at room temperature(97).

I-6 Limiting Current Techniques in Electrochemical Mass Transfer Studies

The dependence of the limiting current density for charge transfer processes on fluid motion was first recognized in the beginning of this century by Nernst (98) and Brunner (99). Tobias et al (100) developed a calibration technique based on this concept and demonstrated its effectiveness in obtaining transport rate correlations. Over the past thirty years the limiting current techniques have gained wide application as a tool for obtaining mass transport correlations from hydrodynamic studies (101), fluid velocity measurements (102), and in many other related areas (103-107).

The limiting current is defined as the maximum current that can be generated by a given electrochemical reaction, at a given reactant concentration, under well-established hydrodynamic conditions, in the steady state. The technique is based on driving an electrochemical reaction to its maximum possible rate where it is limited by the rate at which reactants or products can be transported to or from the surface, respectively. This limiting current is indicated by a current plateau on a current-potential plot (108,109) (Figure 18).

Figure 18. Typical current/potential curve for a diffusion controlled reaction.

The reaction may be cathodic or anodic; it may be a deposition reaction, or a redox reaction. In order to illustrate the essential features of the technique, the cathodic deposition reaction

is considered here. By applying a cathodic potential, positive ions are consumed by the charge transfer reaction and result in the deposition of the metal M onto the cathode. As a result, a region depleted of reacting species near the electrode is established. This region is termed the diffusion boundary layer. The balance of the reactant must be supplied to the cathode by transport across this concentration gradient.

Movement of ions between the bulk of the solution and the electrode-solution interface can occur in three ways: (i) diffusion down the concentration gradient; (ii) ionic migration under the influence of an electric field; and (iii) transport by convection due to the bulk velocity. If excess supporting electrolyte, that is one which does not participate in the charge transfer reaction directly, is added to the solution the migration of the reacting ion will be negligible. Consequently, diffusion is the principal mechanism for transport of ions near the electrode surface, and the flux (N_1) of reacting species is given by Fick's first law

$$N_i = -D_i \left(\frac{dc_i}{dy} \right)_{y=0} \quad (16)$$

where y is the coordinate perpendicular to the electrode surface, and c_i is the concentration of the electroactive species i . The relationship of current to the flux is expressed by:

$$i = nFN_i \quad (17)$$

where F is Faraday's constant. Therefore,

$$N = \frac{i}{nF} = -D \left(\frac{dc}{dy} \right)_{y=0} \quad (18)$$

The subscript i was dropped because electrode reactions involving only one species are considered. Equation (18) shows that by increasing the current, the concentration gradient at the cathode surface becomes steeper.

It is more convenient to define an equivalent Nernst diffusion layer of thickness δ with a linear concentration gradient, so we have:

$$i = -nFD \left(\frac{dc}{dy} \right) = -nFD \frac{C_b - C_0}{\delta} \quad (19)$$

where C_b represents bulk reactant concentration and C_0 is reactant concentration at the electrode surface.

Since the concentration at the electrode cannot be less than zero, there is a limit which the current cannot exceed. This mass transport limiting current is determined by setting $C_0 = 0$ in equation (19)

$$i = -nFD \left(\frac{dc}{dy} \right) = -nFD \frac{C_b}{\delta} \quad (20)$$

When the limiting current condition is approached, the overpotential increase rapidly for every increment of the current; hence, a plateau is reached which ends when the change in electrode potential allows a subsequent reaction to proceed. In case of anodic reactions in aqueous solution this reaction is usually the oxidation of water to evolve oxygen.

The limiting current provides a convenient technique for calculating the mass transport coefficient, K_L , which is defined by:

$$N_i = K_L (C_b - C_o) = \frac{i}{nFA} \quad (21)$$

At the limiting current $C_o = 0$, so that

$$K_L = \frac{i_L}{nFAC_b} \quad (22)$$

The overpotential of the working electrode is measured most conveniently with respect to a reference electrode immersed in the bulk solution. The overpotential is the deviation, upon current passage, of the electrode potential from the value measured at equilibrium, that is, at zero net current.

The total overpotential in limiting-current measurements consists of three components:

$$\eta = \eta_c + \eta_s + \Delta\phi_\Omega \quad (23)$$

where η_c and η_s are concentration and surface (activation) polarization, respectively, and $\Delta\phi_\Omega$ is the total ohmic drop. The concentration overpotential is usually identified with the "Nernst Potential" of the working electrode with respect to the reference electrode. This potential is the component directly responsible for the steep increase in the potential observed as the current approaches the limiting current.

Concentration polarization is expressed as follows (110):

$$\eta_c = (RT/nF) \ln (C_{R, \text{ electrode}}/C_{R, \text{ bulk}}) \quad (24)$$

where C_R is the concentration of reacting species. As the above equation shows concentration polarization becomes very large as the concentration of the reacting ion at the electrode approaches zero.

The surface overpotential η_s and the ohmic contribution also increase with increasing current. The ohmic contribution to the overpotential can be minimized by suitable placement of the reference electrode, but the surface overpotential cannot be reduced similarly. As a result, in the measurement of limiting currents, the surface overpotential and its increase with current density, should be low enough to permit observation of a long, clearly defined limiting current plateau.

Experimental measurement of limiting currents for the determination of maximum reaction rates and of mass transport coefficients are in principle similar to other

non-electrochemical, methods. Their unique and important advantages stem from the fact that driving forces, i.e. applied potential, can be easily controlled, and the current, which corresponds to the rate, can be readily and precisely monitored.

Currents are measured with conventional instrumentation to within a few microamperes, corresponding to fluxes in the range of 10^{-6} mg/sec which is much better than any other analytical instrumentation. Overall, the accuracy of the limiting current technique generally far exceeds that of other methods for transport rate measurements, including weight

loss, heat transport, and hydrodynamic pressure drop measurements. It is a relatively simple, fast, and inexpensive method. Fluxes and driving forces are directly measured in terms of electrical signals which are readily collected and analyzed. However, improper design of the experimental system can lead to extraneous effects and make it difficult to interpret the measurements correctly.

There are severe limitations placed on the choice of electrode reaction (111-118). According to Gabe (119) the following criteria must be met.

- i) The reaction is diffusion-controlled.
- ii) The reaction is stoichiometric and the number of electrons, n , involved discharge is known and constant.

iii) The current efficiency is 100%.

iv) A limiting current density can be clearly read from a potential-current density polarization graph.

In practical applications, excess supporting electrolyte consisting of an inert electrolyte which does not participate in the electrode reaction is added. Applying analogies between momentum, heat and mass transport, electrochemical measurements provide insight into the fundamental aspects of transport, particularly in turbulent flow, and are convenient for obtaining transport rate correlations(120,121).

Transport phenomena in the kinetics of electrode processes have been considered on a more rigorous mathematical basis during the last twenty years as a consequence of the work of Levich on the rotating disk electrode (122-124). This development is based on the solution of the mass transport differential equation taking into account concepts from hydrodynamic boundary-layer theory (125).

I-7 Mass Transfer Correlations in Annular Electrodes

Studies of mass transfer have been carried out in many types of cells (126-130). The choice of system and its geometry depend a great deal on the particular application envisaged.

Theories of mass transfer in various cell geometries

under a range of flow patterns have been reviewed by Newman (131). Lin et al (132) studied mass transfer from a flowing electrolyte to the core of an annulus, where the electrode of interest formed part of inner cylinder while outer cylinder formed the counter electrode.

I-7-1 Laminar Flow Regime

The solution developed by Levich for the heat transfer coefficient in laminar flow can be expressed in mass-transfer terms and applied to the case of annuli by modification of the velocity profile terms. Lin et al (132) worked with a number of different electrochemical reactions and reported that their mass-transfer measurements were in agreement with the Levich solution for laminar flow. They assumed that the Levich circular tube equation may be applied to the annular space merely by replacing the diameter by the equivalent diameter, d_e , of the annulus.

Friend and Metzner (133) criticized Lin et al's approach and argued that the additional variables, which the annulus geometry involves, require an extra dimensionless group which is a function of d_1/d_2 in order to fully characterize the mass transfer properties. They concluded that for interpretation of experiments designed to measure mass transfer, it is important to be clear about the different relationships which apply to various geometries and flow regimes.

Bazan and Arvia (134) studied electrochemical reactions involving mass transfer at the outer electrode of an annular cell, and presented the mass transfer correlation as

$$Sh = 0.647 Re^{1/2} Sc^{1/3} \quad (25)$$

Sh, Re, and Sc are the Sherwood, Reynolds, and Schmidt numbers, respectively and are defined as

$$\text{Reynolds number: } Re = \frac{U_m d_e \rho}{\mu} \quad (26)$$

$$\text{Schmidt number: } Sc = \frac{\mu}{\rho D} \quad (27)$$

$$\text{Sherwood number: } Sh = \frac{K_L d_e}{D} \quad (28)$$

where ρ is the density and μ is viscosity of the solution.

They assumed that the flow in the electrodes was fully developed laminar, because the hydrodynamic boundary layers formed on the inner and outer walls of the tube become very thick and yield parabolic velocity distributions.

Ross and Wragg (135) determined rates of mass transfer by measuring the limiting electrolysis current for the cathodic deposition of copper from solutions of cupric sulphate containing excess sulphuric acid as a function of velocity. They derived mass transfer correlations for annuli based on the Levich solution for laminar flow past a flat plate by using a suitable modification of the velocity profile terms. They derived the following formula for calculating the velocity distribution in an annulus:

$$U_x = 2U_m \left\{ \frac{1 - \left(\frac{r}{r_2}\right)^2 + \left(\frac{1+a}{\ln(\frac{1}{a})}\right) \ln \frac{r}{r_1}}{\left(\frac{1-a^4}{1-a^2}\right) - \left(\frac{1-a^2}{\ln(\frac{1}{a})}\right)} \right\}, \quad (29)$$

where $a = \frac{r_1}{r_2}$ = annulus radius ratio, and U_m is the mean flow velocity. For the inner wall they showed that

$$\beta = \left(\frac{\partial u}{\partial r} \right)_{r=r_1} = \frac{8U_m \phi(a)}{d_e}, \quad (30)$$

$$\text{where } \phi(a) = \frac{1-a}{a} \left\{ \frac{0.5 - \frac{a^2}{(1-a^2)} \ln \left(\frac{1}{a}\right)}{\left(\frac{1+a^2}{1-a^2}\right) \ln \left(\frac{1}{a}\right) - 1} \right\}, \quad (31)$$

and d_e is the annulus diameter equivalent ($= d_2 - d_1$).

Their derived mass-transfer correlation from the Levich solution is:

$$Sh = \frac{K_L d_e}{D} = 1/614 (\phi(a))^{\frac{1}{3}} \left(Re.Sc. \frac{d_e}{L} \right)^{\frac{1}{3}}, \quad (32)$$

For fully-developed laminar flow, the experimental results of Ross and Wragg were fitted to the following correlations for different annulus diameter ratios,

$$\text{for } \frac{d_1}{d_2} = \frac{1}{2}, \quad Sh = 1.76 \left(Re.Sc. \frac{d_e}{L} \right)^{\frac{1}{3}} \quad (33)$$

$$\frac{d_1}{d_2} = \frac{1}{4}, \quad Sh = 1.8 \left(Re.Sc. \frac{d_e}{L} \right)^{\frac{1}{3}} \quad (34)$$

and for $\frac{d_1}{d_2} = \frac{1}{8}$, $Sh = 2.02 \left(Re.Sc. \frac{d_e}{L} \right)^{\frac{1}{3}}$ (35)

where L is the electrode length.

I-7-2 Turbulent Flow Regime

By Application of analogies between momentum, heat, and mass-transfer, to fully developed turbulent flow in annuli many mass-transport correlations have been proposed (136). Meyerink and Friedlander (137) studied the dissolution of benzoic acid in water and obtained the following correlation

$$Sh = 0.07 Re^{0.94} \quad (36)$$

Ross and Wragg (135) calculated the correlation in the manner suggested by Knudsen (138) and Rothfus (139). Their experimental results are well-represented by the equation:

$$St = 0.2995 Re^{-0.42} Sc^{-\frac{2}{3}} \left(\frac{d_e}{L} \right)^{\frac{1}{3}} \quad (37)$$

where St is Stanton number and is defined as

$$\text{Stanton number : } St = \frac{K_L}{U_m} \quad (38)$$

They derived this mass-transfer correlation by assuming an approximately linear velocity distribution in the region close to the wall, and by using Blasius' formula for the friction factor with account taken of the annular geometry. They solved the basic differential equation for diffusion and convection to yield the mass transfer coefficient:

$$K_L = 0.807 D \left(\frac{\beta}{DL} \right)^{\frac{1}{3}} \quad (39)$$

where β' is the velocity gradient at the wall in turbulent flow. The velocity near the wall expressed in terms of the friction factor, f , is given as

$$U_x = \frac{f}{v} U_m^2 y, \quad (40)$$

$$\text{where } \beta' = \frac{f U_m^2}{2v} \quad (41)$$

Their experimental data have been correlated for an annulus diameter ratio of 0.5 as:

$$St = 0.276 Re^{-0.42} Sc^{-\frac{2}{3}} \left(\frac{de}{L}\right)^{\frac{1}{3}} \quad (42)$$

The brief account given above of the hydrodynamic and mass transfer characteristics of the annular flow system provides the basis for calculating linear flow velocities, as described later in this report. It is important to recognize that the correlations discussed above have been confirmed only for near ambient conditions. Accordingly, it is assumed that the influence of temperature is restricted to changes in density and viscosity, and that the basic equations remain valid over the 25-250°C range of interest in this study.

Chapter II

EXPERIMENTAL PROCEDURE

In this chapter the apparatus, material, and the procedure used in the present study will be described.

II-1 Test Loop

A high pressure/high temperature recirculating system (Figure 19) was designed for this investigation (69). Its various components include a 20 liter stainless steel storage tank, a 2 liters/hr capacity pulsating diaphragm pump, an accumulator, heat exchanger, autoclave, and a back pressure regulator. The accumulator is installed between the pump and the autoclave to dampen the pressure fluctuations. In this circuit, the solution exiting the test cell passes through the heat exchanger to recover heat from the returning hot solution. The solution, after being cooled to room temperature, returns to the storage tank via a back pressure regulator.

II-2 Test Cell

The test cell is composed of an autoclave, magnetic drive, thermocouple, working electrode, counter electrode, reference electrode, and an annular flow channel (Figure 20). Five holes were machined in the top of the two liter pressure vessel to accommodate the solution inlet and outlet, magnetic drive, thermocouple, and counter electrode.

Figure 19. Schematic of recirculating test loop(69).

Figure 20. Dimensions and assembly of pressure vessel.

Two holes were machined in the bottom to take the working and reference electrodes. A Type 316 stainless steel impeller was fixed to the central shaft of the magnetic drive. A 1/2 HP Blue Chip 2 adjustable motor was used to rotate the impeller at a controllable speed. The rotation speed of the impeller was monitored by a tachometer.

The annular flow channel, which was used to direct the solution flow over the specimen, was fabricated from 2 1/2" and 1 1/2" Type 316 stainless steel and 1 1/2" Teflon rod. A hole was machined at the bottom of the channel to guide the reference electrode Luggin probe to a point just opposite the specimen.. Three Type 316 stainless steel plates were welded to the top of the flow channel. Those legs were attached to the top of the autoclave by stainless steel screws (Figure 21).

II-2-1 Working Electrode

The working electrode was fabricated from 3/4" schedule 40 cold drawn seamless Inconel 600 tube. Samples were machined into 1/2" long and 1" OD from this as-received tube material. A camber with a slope of 30° was machined at both ends of the sample (Figure 22). The sample holder was so designed in order to yield a well-defined hydrodynamic condition, and was axially located inside the flow channel by Swagelok fittings (Figure 23). Electrical connection to

Figure 21. Dimensions and assembly of flow channel.

Figure 22. The dimensions of the samples.

Figure 23. Dimensions and assembly of working electrode.

specimen was made through an insulated Inconel wire which was also covered with heat shrinkable PTFE tubing for additional protection. The wire was welded to a V shaped stainless steel rod which was mechanically connected to the sample.

II-2-2 Counter Electrode

The 1 1/2" stainless steel tube of the flow channel acts as the counter electrode(see Figure 21). It is isolated by a PTFE tube from the autoclave body. A 1/16" hole was machined in the counter electrode opposite the specimen to accomodate the tip of the reference electrode. Insulated Inconel wire was connected to the bottom of the electrode by a screw.

II-2-3 Reference Electrode

The reference electrode used in this study(Figure 24) was an external pressure balanced Ag/AgCl/0.1m KCl type (140).The electroactive silver rod was plated with silver chloride in a 0.1m HCl solution at a current density of 5 mA/cm² for 18 hours. The stability of the reference electrode was checked against a saturated calomel electrode. The potentials measured vs. the Ag/AgCl electrode were converted to potentials vs. SHE_T (Standard Hydrogen Electrode at the experimental temperature) using the data plotted in Figure (25).

Figure 24. The newly designed Ag/AgCl/0.1M KCl reference electrode(140).

Figure 25. Plots for conversion of potential vs Ag/AgCl electrode to potential vs SHE_T (Standard Hydrogen Electrode at the Experimental Temperature)(141)

II-2-4 Impeller

Different types of impellers were designed and tested at room temperature and outside of the test cell to observe directly their performances in creating a well-defined flow. Figure (26) shows the view of different parts of the pressure vessel including the impeller which was chosen for this study. Suitable flow was obtained by using baffles inside the flow channel to prevent spiralling of the fluid.

II-3 Material

In order to understand the corrosion behavior of a metal or alloy, it is necessary to begin with a knowledge of the metallurgical properties of the material.

The nickel-chromium-iron alloy Inconel 600, which is commonly used as tubing material in PWR steam generators, contains approximately 75% nickel, 15% Cr, and 9% Fe (Figure 27). It is not only because of the corrosion resistant and strengthening characteristic of nickel itself that a good many of the most corrosion-resistant alloys are nickel-based, or contain considerable amounts of nickel, but more importantly it is because nickel is metallurgically compatible over a considerable composition range with a number of other metals such as copper, chromium,

Figure 26. View of pressure vessel flow channel, impeller, and working and reference electrodes.

Figure 27. Composition of Fe-Cr-Ni alloy used in this study.

molybdenum, iron, and tungsten, which have their own unique corrosion-resisting properties. These alloys have the austenitic face-centered cubic structure. The reason that nickel has high tolerance for alloying without phase instability is largely due to its favorable atomic size, its nearly filled third electron shell, and its FCC lattice structure. Chromium is added to nickel to improve its resistance to strongly oxidizing environments.

Inconel 600 is susceptible to pitting attack in hot chloride-containing solutions. In this study, 1/2" ring specimens were cut from an as-received Inconel 600 seamless pipe (3/4" sch. 40). The chemical composition and the mechanical properties of the alloy are given in Table (1) and its microstructure in Figure (28). This figure shows that carbide precipitates are both on the grain boundaries and inside the grains. It is clear that the alloy is sensitized and therefore should show a tendency toward intergranular attack. Some twins are also seen in the microstructure.

II-4 Test Procedure for Mass Transfer Calibration

Platinized Inconel 600 specimens were used to calibrate the mass transfer characteristics of the flow system. The specimens were plated with nickel at 50°C for 6 hours using

Figure 28. Microstructure of as-received Inconel 600 seamless tube, etched by Nital.

Table 1

Chemical Composition and Mechanical Properties (25°C) of Inconel 600^{*}

Elements	C	Mn	Fe	S	Si	Ar	Ni	Cr
Wt%	0.02	0.23	9.75	0.004	0.13	0.36	74.60	14.90
Tensile strength				90.8 ksi				
Yield strength				38.6 ksi				
% Elongation				55				

^{*} Producer's Data

a solution of the following composition:

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	400 g/L
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	50 g/L
B(OH)_3	40 g/L

at an applied current density of 80 mA/cm^2 .

For platinum plating, a chloro-platinic acid solution was used. The composition of this solution was as follows:

$(\text{NH}_4)_2 \text{HPO}_4$	20 g/L
$\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$	100 g/L
$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	4 g/L

Plating was carried out at 75°C at current density of 10 mA/cm^2 for 4 hours (141).

After platinum plating, platinum black was finally deposited onto the surface. The platinum black was deposited from a 1% chloroplatinic acid solution containing 80 mg/100 cm^3 of lead acetate. A cathodic current of 30 mA/cm^2 was passed for 3 minutes, then the polarity of electrode was reversed for 5 seconds. This process was repeated until a uniform black surface was obtained.

Anodic polarization curves for the platinized electrode in hydrogenated systems were measured in the temperature range from 25°C to 250°C . Rates of mass transfer were determined by measuring the limiting currents. A 0.1 NaOH electrolyte solution was used for this calibration work.

This solution was continuously purged with "pure" hydrogen for 4 hours before starting the experiment, and hydrogen sparging was continued during the test. As is discussed in chapter III, this will establish a concentration of 7.1×10^{-4} mole/l of hydrogen at room temperature. However due to the expansion of the solution, this value is reduced with increasing temperature. Since some parts of the sample holder were fabricated from PTFE measurements were started at 25°C and then the temperature of the solution was raised in the desired increments (50°C) to 250°C. Experiments in the reverse direction may be subject to some error because of the shrinkage of PTFE, which may loosen the sample and hence introduce crevices at the junctions between the specimen and the PTFE former.

Two different methods were used to measure the limiting current:

1. Polarization curves were obtained using a scan rate of 7200 mV/hr for each individual rotation rate, and
2. A constant potential in the limiting current plateau region was applied at all rotation rates at each specific temperature studied.

After the limiting current was aquired at the highest

rotation rate, the rotation rate was reduced to lower values and the new limiting currents were recorded. To make sure that the results of this method are correct, the rotation rate was then increased to the original value. If the limiting current was the same as previously determined the results were considered to be acceptable. However, if the limiting current was different, the tests were stopped and repeated using a different potential.

II-5 Test Procedure for Pitting Study

The polarization behavior and pit morphology studies were carried out in 0.1M NaCl+0.001M $B(OH)_3$ + 0.001M LiOH solutions which were prepared using demineralized distilled water and reagent grade NaCl, LiOH, and $B(OH)_3$. The solutions were deaerated in the reservoir using purified nitrogen. The specimens were polished successively with 240, 320, 400, and 600 grit SiC paper, rinsed in distilled water, and immediately placed in the test cell.

The electronics used for both the hydrodynamic calibration and pitting studies were as follows:

1. A Princeton Applied Research Model 173 Potentiostat/Galvanostat with a Model 376 current to voltage converter.
2. An Ervin Halstrup model 165 Motorpotentiometer .
3. An Esterline Angus X-T Recorder.

Figure 29 shows a schematic diagram of the experimental set up and Figure 30 presents the view of the assembly used to study the effect of fluid flow on the pitting corrosion of Inconel 600.

In order to develop a passive film of reproducible thickness at each testing temperature, the specimens were cathodically polarized at a potential of -1000 mV vs Ag/AgCl, $0.1M$ KCl, for 5 minutes in order to reduce any preexisting film, and then the potential was immediately changed to a specific potential in the passive region. Samples were kept at this potential for 10 minutes and then anodically polarized at a voltage scan rate of 300 mV/hr (0.083 mV/sec) in the active-to-noble direction until breakdown occurred. At $200^{\circ}C$ the passivity range was very short and difficult to locate, so samples were anodically polarized from E_{Corr} . After the breakdown was achieved, polarization was continued at a constant potential of 100 mV above breakdown for one hour. The autoclave was then cooled using a fan, and the samples were removed and washed with distilled water.

The specimens were prepared for SEM examination by exposure for 1 hour to a solution containing 20 wt% NaOH and 3 wt% $KMnO_4$ at its boiling temperature, followed by rinsing

Figure 29. Schematic diagram of the experimental set up used to study the effect of fluid flow on the pitting corrosion of Inconel 600 in 0.1M NaCl solution at high temperatures and pressures.

Figure 30. View of assembly used to study the effect of fluid flow on pitting corrosion at high temperature and pressure.

with distilled water. This procedure is recommended for removing corrosion products without dissolution of the alloy for Inconel 600 after immersion in high temperature water(143,144).

III. RESULTS AND DISCUSSION

III-1 Calibration of Mass Transfer Characteristics

In order to study the effect of fluid flow on the pitting corrosion of Inconel 600, an annular channel geometry was used. Fluid flow through the annulus was affected by the impeller which is fixed to the central shaft of the magnetic driver. The rotation speed of the impeller was controlled externally by an adjustable speed motor and monitored by a tachometer.

To determine the relationship between the rotation speed of the impeller and the average linear velocity in the annulus, a calibration of the flow system was performed using a technique based on limiting current mass transfer measurements of the oxidation of dissolved hydrogen in 0.1M NaOH.

Anodic polarization curves for the oxidation of hydrogen on platinized Inconel 600, obtained in a 0.1M NaOH solution at 250°C using a scan rate of 2 mV/sec, with the rotating speed as the experimental variable are shown in Figure (31). The values of the limiting current density, i_L , as a function of rotation rate for the oxidation of hydrogen at various temperatures are presented in Table 2. The limiting current density increases with increasing speed of rotation of the impeller, as well as with increasing temperature of the solution.

Figure 31. Anodic polarization curves for the oxidation of hydrogen in 0.1 NaOH solution at 250°C.

Table 2
Anodic Limiting Current Densities, I_L (mA/cm²) for the
Oxidation of Hydrogen in 0.1N NaOH Solution
as a Function of Rotation Speed and Temperature.

Rotation Speed (rpm)	Temperature (°C)					
	25	50	100	150	200	250
200	0.41	0.70	1.60	2.40	3.40	5.00
400	0.83	1.68	3.46	5.90	8.90	11.6
600	1.14	2.12	4.40	7.67	11.1	15.3
800	1.34	2.34	4.98	9.00	13.0	17.8
1000	1.44	2.53	5.52	9.83	14.2	18.9
1200	1.52	2.69	5.97	10.6	15.1	19.9
1500	1.60	2.88	6.54	11.3	16.0	21.0

The observed limiting currents are the result of complete mass transfer control of the following reaction

As previously described, the mass transfer limiting current for a reaction can be expressed as

$$i_L = \frac{nFDC_b}{\delta} \quad (20)$$

where n is the number of electrons involved in the reaction, F is Faraday's constant, D is the diffusivity of the diffusion limited species, C_b is the bulk concentration, and δ is the effective diffusion layer thickness.

Solubility data for slightly soluble gases is usually reported in form of Henry's law. The Henry's law coefficient, $B_{T,P}^O$ (mole/1000 g water), for solubility of hydrogen in water is given(145) as

$$-\log B_{T,P}^O = -\frac{1321}{T} + 10.703 - 0.010468T \quad (44)$$

For room temperature, $T=298^\circ\text{K}$, and at atmospheric pressure;

$$B = 7.1 \times 10^{-4} \text{ mole/1000 g}$$

so,

$$C_b = 7.1 \times 10^{-7} \text{ mole/cm}^3$$

Since the concentration of NaOH is small(0.1M), and because there is no chemical interaction between hydrogen and NaOH,

it is assumed that the solubility of hydrogen in 0.1M NaOH solution is the same as that in pure water. Note that since the experimental system operates in the single (liquid) phase mode, the concentration of hydrogen in the high temperature zones is determined by the solubility of the gas in the reservoir at ambient temperature. However, as the temperature increases, C_b is reduced because of the expansion of the solution. Its value at each temperature, C_{bT} , is calculated according to

$$C_{bT} = C_b \times \rho_T / \rho_R \text{ (mole/cm}^3\text{)} \quad (45)$$

where ρ_T is the solution density at the temperature of interest, and ρ_R is the solution density at the ambient temperature. Values for the density and dynamic viscosity (μ) for 0.1M NaOH solution at elevated temperatures were not found in literature. However, at room temperature, the differences between the density and viscosity of water, and the reported values for these properties for 0.1M NaOH (146), are less than 2%. Furthermore, the effect of these small differences will be much less for the kinematic viscosity ($\nu = \mu/\rho$). Another important point is that the equation for U_m (equation 55) is not very sensitive to uncertainties in ν . This does not mean that U_m is not sensitive to changes in the kinematic viscosity of the fluid over the experimental range in temperature, but simply that for a given value for

i_L , which is measured experimentally, using a value of v which is slightly different from the actual one will not introduce any significant error in the calculated value for U_m . For the above reasons, the density and dynamic viscosity data for pure water (Figure 32, 33, Table 3) were used for calibrating the mass transfer properties of the system.

Different values have been reported for the diffusion coefficient for hydrogen in water. Vivian et al (148) compared various experimental results and concluded that a value of $4.8 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 25°C is more accurate than any of the other reported values. They calculated the percentage of error and found that it is less than 4%. The diffusion coefficient of hydrogen in 0.1M NaOH could not be found in literature. Accordingly, it is assumed that because of the low concentration of NaOH, the diffusion coefficient of hydrogen in this alkali solution is equal to that in water. The diffusion coefficients at higher temperatures were calculated by using Einstein's equation;

$$\frac{D_1 \mu_1}{T_1} = \frac{D_2 \mu_2}{T_2} = \text{const.} \quad (46)$$

where D_1 and μ_1 are the known values for the diffusion coefficient and dynamic viscosity, respectively, at temperature T_1 , and D_2 and μ_2 are the corresponding values

Figure 32. Plot of density of water vs temperature(147).

Figure 33. Plots of dynamic and kinematic viscosity of water vs temperature (148)

at some other temperature T_2 . Because the dynamic viscosity at temperature T_2 is known (Table 3) the diffusion coefficient is readily computed.

Since diffusion coefficients at various temperature are dependent on the ratio μ_2/μ_1 , the error incurred by using viscosity data for water instead of the solution is negligible. Calculated values of C_{bT} and D at various temperatures are presented in Table 4.

Mass transfer coefficients, K_L , were calculated from the measured limiting current density, I_L , using the following equation:

$$K_L = \frac{I_L}{nFC_b} \quad (22)$$

taking $F = 96500$ coulombs, and $n=2$ for the oxidation of hydrogen. The calculated values of the mass transfer coefficients for this system are presented in Table 5. These data show, K_L , increases both with increasing speed of rotation and temperature.

As discussed in Chapter I, dimensionless groups are useful tools to relate the experimental variables of a diffusion convection controlled electrochemical process. The dimensionless groups of interest for this case are:

$$\text{Reynolds number: } Re = \frac{U_m d_e \rho}{\mu} \quad (26)$$

Table 3
Selected Data Used For Mass Transfer Calculation for
Oxidation of Hydrogen at Different Temperatures

Parameter	Temperature °C					
	25	50	100	150	200	250
g/cm.sec	8.92×10^{-3}	5.54×10^{-3}	2.90×10^{-3}	1.85×10^{-3}	1.40×10^{-3}	1.13×10^{-3}
(g/cm ³)	0.9971	0.9881	0.9584	0.9190	0.8644	0.7987

Table 4
Selected Values of Parameters Used For Mass Transfer Calculations
for Oxidation of Hydrogen at Various Temperatures

Parameter	Temperature °C					
	25	50	100	150	200	250
D (cm ² /sec)	4.80×10^{-5}	8.47×10^{-5}	1.9×10^{-4}	3.30×10^{-4}	4.85×10^{-4}	6.64×10^{-4}
(cm ² /sec)	8.98×10^{-3}	5.61×10^{-3}	3.03×10^{-3}	2.01×10^{-3}	1.62×10^{-3}	1.41×10^{-3}
C_b (mole/cm ³)	7.1×10^{-7}	7.02×10^{-7}	6.8×10^{-7}	6.52×10^{-7}	6.14×10^{-7}	5.67×10^{-7}
Sc	187.1	66.2	15.9	6.09	3.34	2.12
$\bar{D}$						

Table 5
Mass Transfer Coefficients, K_L (cm/s), as Determined
from the Oxidation of Hydrogen in 0.1M NaOH Solution as a Function
of Rotation Speed and Temperature

Rotation Speed (rpm)	Temperature (°C)					
	25	50	100	150	200	250
200	2.99×10^{-3}	5.17×10^{-3}	1.22×10^{-2}	1.91×10^{-2}	2.87×10^{-2}	4.57×10^{-2}
400	6.06×10^{-3}	1.24×10^{-2}	2.63×10^{-2}	4.69×10^{-2}	7.51×10^{-2}	1.06×10^{-2}
600	8.32×10^{-3}	1.57×10^{-2}	3.35×10^{-2}	6.09×10^{-2}	9.37×10^{-2}	1.40×10^{-1}
800	9.78×10^{-3}	1.73×10^{-2}	3.79×10^{-2}	7.15×10^{-2}	1.10×10^{-2}	1.63×10^{-1}
1000	1.05×10^{-2}	1.87×10^{-2}	4.20×10^{-2}	7.81×10^{-2}	1.20×10^{-1}	1.73×10^{-1}
1200	1.11×10^{-2}	1.99×10^{-2}	4.55×10^{-2}	8.42×10^{-2}	1.27×10^{-1}	1.82×10^{-1}
1500	1.17×10^{-2}	2.13×10^{-2}	4.98×10^{-2}	8.97×10^{-2}	1.35×10^{-1}	1.92×10^{-1}

$$\text{Schmidt number: } SC = \frac{\mu}{\rho D} = \frac{\nu}{D} \quad (27)$$

$$\text{Sherwood number: } Sh = \frac{K_L d_e}{D} \quad (28)$$

$$\text{Stanton number: } St = \frac{K_L}{U_m} \quad (38)$$

where ρ is the density and μ is the dynamic viscosity of the solution.

The Reynolds number relates the driving forces acting on the liquid and viscous forces which tend to slow down the stream. Its value is a criterion for determining whether or not the flow is laminar or turbulent. Only after the condition of flow is known, can U_m be calculated. Both the Sherwood and Stanton numbers are linearly related to the mass transfer coefficient, K_L , and hence describe the maximum rate at which species may be transported from the bulk of the solution to the metal surface.

III-2 Laminar Flow

In order to calculate the laminar flow velocity, Levich's solution, which was developed for mass transfer in laminar flow past a flat plate, can be used by suitable modification of the velocity profile terms.

Mass transfer in uni-directional, fully-developed laminar flow can be described by the continuity equation for a Newtonian fluid

$$U_x \frac{\partial C}{\partial x} = D \left(\frac{\partial^2 C}{\partial y^2} \right) \quad (47)$$

where x and y are the parallel and perpendicular coordinates, respectively, to the direction of the flow, and U_x is the point liquid velocity in the x direction. In the region near the wall, the variation of U_x with y is approximately linear. Accordingly, the velocity gradient in the region close to the interface becomes

$$\beta = dU_x / dy = U_x / y \quad (48)$$

assuming that the velocity at the wall is zero. Therefore, equation(47) can be written as;

$$\beta \left(\frac{\partial C}{\partial x} \right) = D \left(\frac{\partial^2 C}{\partial y^2} \right) \quad (49)$$

Mizushina (149), Solved the above equation by using a similarity transformation and obtained the concentration gradient at a position on the electrode surface as

$$\left. \frac{\partial C}{\partial y} \right|_{y=0} = (1/9D)^{1/3} \frac{C_b}{0.893} \frac{\beta^{1/2}}{\left[\int_0^x \beta^{1/2} dx \right]^{1/3}} \quad (50)$$

Since the variation of β over the small length of the electrode is negligible, the integration of the above

equation, from 0 to L give the value of the mass transfer coefficient.

$$K_L L/D = \frac{1}{C_b} \int_0^L \left. \frac{\partial C}{\partial y} \right|_{y=0} dx$$

and hence

$$K_L = 0.807 D \left(\frac{\beta}{DL} \right)^{\frac{1}{3}} \quad (29)$$

The Levich solution for the velocity distribution in an annulus is given by equation (26)

$$U_x = 2 U_m \left\{ \frac{1 - \frac{r^2}{r_2^2} + \frac{1+a}{\ln(1/a)} \ln \frac{r}{r_1}}{\frac{1-a^4}{1-a^2} - \frac{1-a^2}{\ln(1/a)}} \right\}, \quad (29)$$

where $a = r_1/r_2$ = annulus radius ratio. For the inner wall the velocity gradient can be derived from the above equation as follows

$$\beta = \left(\frac{\partial U_x}{\partial r} \right)_{r=r_1} = \frac{8 U_m \phi(a)}{d_e} \quad (30)$$

where

$$\phi(a) = \frac{1-a}{a} \left\{ \frac{0.5 - \frac{a^2}{(1-a^2)} \ln(1/a)}{\frac{1-a^2}{(1-a^2)}} \right\}, \quad (31)$$

and

$$d_e = \frac{4 \times \text{cross sectional area}}{\text{wetted perimeter}} = d_2 - d_1$$

III-3 Turbulent Flow

When there are both convection and diffusion in the system, the basic differential equation may be written as:

$$U_x \left(\frac{\partial \bar{C}}{\partial x} \right) = \left(\frac{\partial}{\partial x} \right) D \left(\frac{\partial \bar{C}}{\partial x} \right) + \left(\frac{\partial}{\partial y} \right) D \left(\frac{\partial \bar{C}}{\partial y} \right) - \left(\frac{\partial \overline{U_f C_f}}{\partial x} \right) - \left(\frac{\partial \overline{V_f C_f}}{\partial y} \right) \quad (51)$$

where subscript f indicates fluctuating velocity and concentration components, and the superscript bar designates time-averaged values. The above equation was simplified by Linton and Sherwood (150) and by Van Shaw, Reiss and Henratty (151). They assumed that diffusion in the flow direction is negligible, and that for fully developed flow V_f , and U_f are equal zero. Accordingly, three of the terms on the right side of the above equation can be neglected to yield

$$\bar{U}_x \left(\frac{\partial \bar{C}}{\partial x} \right) = D \left(\frac{\partial^2 \bar{C}}{\partial y^2} \right), \quad (52)$$

which is similar in form to equation (47).

By assuming an approximately linear velocity distribution in the region close to the wall Ross and Wragg (135) calculated the mean mass-transfer coefficient which was presented as equation (39) in Chapter I.

An average liquid velocity, U_m , can be calculated by modifying equation (41)

$$\beta' = \frac{f U_m^2}{2\nu} \quad (41)$$

where β' is the velocity gradient at the wall of electrode, f is the friction factor, and ν is the kinematic viscosity. The velocity gradient may be computed from the mass transfer coefficient using equation (39)

$$K_L = 0.807 D (\beta' / DL)^{1/3} \quad (39)$$

where D is the diffusion coefficient and L is the electrode length. By combining equations (39) and (41) one can obtain:

$$f = 3.805 \frac{L K_L^3 \nu}{D^2 U_m^2} = 3.805 \frac{L d_e^2 K_L^3}{D^2 \nu Re^2} \quad (53)$$

To calculate Re (or U_m) and f using equation (53), it is necessary to use another expression relating f and Re (or f and U_m). For turbulent flow, the friction factor depends on both the Reynolds number and surface conditions characterized by the relative roughness, ϵ/d_e (ϵ is absolute roughness, "height of roughness"). In this case the equation given by Moody (152) is useful:

$$\frac{1}{\sqrt{f}} = -4 \log \frac{\epsilon/d_e}{3.7} + \frac{1.255}{Re \sqrt{f}} \quad (54)$$

by combination of this equation with equation (53) we obtain

$$U_m = -7.803 \nu \sqrt{\frac{L K_L^3}{D^2}} \log \left(\frac{\epsilon/d_e}{3.7} + \frac{0.643}{d_e \sqrt{\frac{L K_L^3}{D^2}}} \right) \quad (55)$$

The reported value(153), for the absolute roughness for drawn tubing is 0.0015mm. Since the flow channel and working electrode surfaces used in this investigation were smoother than drawn tubing and using this value for instead of zero has an effect of less than 2%, the effect of relative roughness is ignored. Table 6, 7, and 8 show the calculated values for Re , δ , and U_m . Flow velocity increases both with increasing temperature and rotation rate within the range of 7 to 158 cm/sec. Figures (34) and (35) illustrate the effect of temperature and rotation rate on the limiting current and on the average linear solution flow velocity.

Figure (36) shows the variation of limiting current density for the oxidation of dissolved hydrogen in sodium hydroxide solution as a function of Reynolds number, Figure (37) presents the variation of mass transfer coefficient with linear average flow velocity. There is no change of slope for all tests conducted above 50°C, implying the presence of only one flow regime, namely that of turbulent flow. However, a change in slope occurs for the tests conducted at 25 and 50°C, indicating that a transition takes place from the laminar to turbulent flow regimes. The Reynolds number for transition is between 2000 and 3000. Due to limited number of tests involving laminar flow, the exact value for the Reynolds number at the transition cannot

Table 6
Velocity Gradients at the Wall, β (s^{-1}), as Determined
from the Oxidation of Hydrogen in 0.1M NaOH Solution
as a Function of Rotation Speed and Temperature

Speed Rotation (rpm)	Temperature ($^{\circ}C$)					
	25	50	100	150	200	250
200	28.1	46.5	121	154	256	523
400	233	643.4	1224	2282	4358	6526
600	603	1293	2517	5014	8454	14973
700	981	1739	3650	8100	13581	23578
1000	1217	2197	4971	10554	17700	28225
1200	1431	2641	6287	13234	21283	32946
1500	1669	3241	8267	16032	25320	38717

Table 7
Reynolds Numbers, Re , as Determined from
the Oxidation of Hydrogen in 0.1M NaOH Solution
as a Function of Rotation Speed and Temperature

Rotation Speed (rpm)	Temperature ($^{\circ}\text{C}$)					
	25	50	100	150	200	250
200	2.44×10^2	1.036×10^2	2.66×10^3	3.900×10^3	5.78×10^3	9.77×10^3
400	2.03×10^3	4.95×10^3	1.03×10^3	1.86×10^4	3.03×10^4	4.12×10^4
600	3.62×10^3	7.42×10^3	1.55×10^4	2.90×10^4	4.41×10^4	6.57×10^4
800	4.81×10^3	8.81×10^3	1.92×10^4	3.81×10^4	5.76×10^4	8.48×10^4
1000	5.45×10^3	1.01×10^3	2.29×10^4	4.42×10^4	6.68×10^4	9.37×10^4
1200	5.99×10^3	1.12×10^4	2.62×10^4	5.02×10^4	7.40×10^4	1.02×10^5
1500	6.55×10^3	1.26×10^4	3.06×10^4	5.60×10^4	8.16×10^4	1.12×10^5

Table 8
Average Liquid Velocities, U_m (cm/s), as Determined
from the Oxidation of Hydrogen in 0.1M NaOH Solution
as a Function of Rotation Speed and Temperature

Rotation Speed (rpm)	Temperature (°C)					
	25	50	100	150	200	250
200	2.2	5.81	8.1	7.84	9.4	13.8
400	18.2	27.7	31.1	37.3	48.1	58.1
600	32.5	41.6	47.1	58.4	71.4	92.7
800	43.2	49.4	58.2	76.6	93.2	119.5
1000	49.0	56.6	69.4	88.9	108.2	132.1
1200	53.8	62.9	79.3	101.0	120.0	144.1
1500	58.9	70.8	92.6	112.5	132.2	157.6

Figure 34. Variation of limiting current density vs rotation rate for the oxidation of hydrogen in 0.1M NaOH solution at various temperatures.

Figure 35. Variation of average liquid velocity vs temperature for the oxidation of hydrogen in 0.1M NaOH solution.

Figure 36. Plot of I_L vs log Re for the oxidation of hydrogen in 0.1M NaOH solution.

Figure 37. Plot of $\log K_L$ vs $\log U_m$ for the oxidation of hydrogen in 0.1M NaOH solution.

be determined. A Reynolds number of 3700 was obtained by Ross and Wragg (135) for an annular flow channel at ambient temperature.

Table(9) presents values for the friction factor calculated using equation (53). This table shows that the calculated friction factor decreases with increasing temperature and flow velocity. These values are in good agreement with the Moody chart(154) for pipe friction with smooth walls.

The Sherwood number involves the mass transfer kinetic constant and it can be taken as a ratio between the characteristic length and the thickness of the effective diffusion layer. As its definition implies, the effect of temperature on the Sherwood number is very small because of

the compensating changes in K_L and D ($Sh = \frac{K_L d_e}{D}$),

but it should be a strong function of flow velocity. Table (10), shows the calculated values of Sherwood number as a function of flow velocity and temperature. The results are in good agreement with the above argument. The effect of temperature is not very obvious and the table shows scattered data, but the increase of Sherwood number with flow velocity is very clear.

Table 9
Friction Factors, f , as Determined from the Oxidation
of Hydrogen in 0.1M NaOH Solution as a Function
of Rotation Speed and Temperature

Rotation Speed (rpm)	Temperature (°C)					
	25	50	100	150	200	250
200	.0656	.0247	0.0113	.0101	.0090	.0078
400	.0077	.0094	.0077	.0066	.0059	.0055
600	.0103	.0084	.0069	.0059	.0054	.0049
800	.0095	.0080	.0065	.0056	.0051	.0047
1000	.0091	.0077	.0063	.0054	.0049	.0046
1200	.0089	.0075	.0061	.0052	.0048	.0045
1500	.0087	.0073	.0058	.0051	.0047	.0044

Table 10

Sherwood Numbers, Sh , as Determined from the
Oxidation of Hydrogen in 0.1M NaOH Solution
as a Function of Rotation Speed and Temperature

Rotation Speed (rpm)	Temperature ($^{\circ}\text{C}$)					
	25	50	100	150	200	250
200	62.3	61.0	64.1	57.8	59.2	68.8
400	126	146	138	142	155	160
600	173	185	176	185	193	211
800	204	204	200	217	226	245
1000	219	221	221	237	247	260
1200	231	235	239	255	263	274
1500	243	251	262	272	279	289

According to the equation $Sh.\delta = de$ (combination of equations 20, 22, and 28) values for δ were calculated and are summarized in Table 11. Figure (38) shows the variation of δ with I_L at 250°C. Beck (2) presented the same type of correlation for his calibration of flow past a flat plate which contained an artificial pit. However, his data were highly scattered, as shown in Figure (9). According to him "the scatter may be attributed to several factors: disturbance of flow in the pit by bubble, salt deposits and uneven shape developed on the corroding surface, as well as non-uniform salt film thickness and change in electrolyte composition and properties in the pit." Because none of these problems existed in the present study, a much better correlation was expected, as observed.

The Schmidt number is a function only of the solution properties. Accordingly, it does not change with the velocity of flow of the fluid as is evident from the data summarized in Table 4. However, this dimensionless group decreases rapidly with increasing temperature due to the combined effects of temperature on ν and D .

The calculated values for Stanton number (St) which is a velocity-dependent mass transfer coefficient, are presented in Table 12. This dimensionless group increases with increasing temperature, but decreases with increasing

Table 11
Diffusion Layer Thickness, (cm), as Determined
from the Oxidation of Hydrogen in 0.1M NaOH Solution
as a Function of Rotation Speed and Temperature

Rotation Speed (rpm)	Temperature (°C)					
	25	50	100	150	200	250
200	1.61×10^{-2}	1.64×10^{-2}	1.56×10^{-2}	1.73×10^{-2}	1.69×10^{-2}	1.45×10^{-2}
400	7.92×10^{-3}	6.83×10^{-3}	7.21×10^{-3}	7.04×10^{-3}	6.45×10^{-3}	6.26×10^{-3}
600	5.77×10^{-3}	5.41×10^{-3}	5.67×10^{-3}	5.42×10^{-3}	5.18×10^{-3}	4.75×10^{-3}
800	4.91×10^{-3}	4.90×10^{-3}	5.01×10^{-3}	4.62×10^{-3}	4.42×10^{-3}	4.08×10^{-3}
1000	4.57×10^{-3}	4.53×10^{-3}	4.52×10^{-3}	4.23×10^{-3}	4.05×10^{-3}	3.85×10^{-3}
1200	4.32×10^{-3}	4.26×10^{-3}	4.18×10^{-3}	3.92×10^{-3}	3.80×10^{-3}	3.65×10^{-3}
1500	4.10×10^{-3}	3.98×10^{-3}	3.82×10^{-3}	3.68×10^{-3}	3.59×10^{-3}	3.46×10^{-3}

Table 12

Stanton Number, St , for the Oxidation of Hydrogen
in 0.1N NaOH Solution as a Function of
Rotation Speed and Temperature

Rotation Speed (rpm)	Temperature ($^{\circ}\text{C}$)					
	25	50	100	150	200	250
200	1.36×10^{-4}	8.89×10^{-4}	1.51×10^{-3}	2.43×10^{-3}	3.06×10^{-3}	3.32×10^{-3}
400	3.33×10^{-4}	4.47×10^{-4}	8.47×10^{-4}	1.26×10^{-3}	1.53×10^{-3}	1.82×10^{-3}
600	2.56×10^{-4}	3.76×10^{-4}	7.12×10^{-4}	1.04×10^{-3}	1.31×10^{-3}	1.51×10^{-3}
800	2.26×10^{-4}	3.50×10^{-4}	6.52×10^{-4}	9.33×10^{-4}	1.18×10^{-3}	1.36×10^{-3}
1000	2.14×10^{-4}	3.30×10^{-4}	6.06×10^{-4}	8.78×10^{-4}	1.11×10^{-3}	1.31×10^{-3}
1200	2.06×10^{-4}	3.16×10^{-4}	5.73×10^{-4}	8.34×10^{-4}	1.06×10^{-3}	1.26×10^{-3}
1500	1.98×10^{-4}	3.01×10^{-4}	5.38×10^{-4}	7.98×10^{-4}	1.02×10^{-3}	1.22×10^{-3}

Figure 38. Correlation of limiting current density with diffusion layer thickness for the oxidation of hydrogen in 0.1M NaOH solution.

According to the equation $Sh.\delta = de$ (combination of equations 20, 22, and 28) values for δ were calculated and are summarized in Table 11. Figure (38) shows the variation of δ with I_L at 250°C. Beck (2) presented the same type of correlation for his calibration of flow past a flat plate which contained an artificial pit. However, his data were highly scattered, as shown in Figure (9). According to him "the scatter may be attributed to several factors: disturbance of flow in the pit by bubble, salt deposits and uneven shape developed on the corroding surface, as well as non-uniform salt film thickness and change in electrolyte composition and properties in the pit." Because none of these problems existed in the present study, a much better correlation was expected, as observed.

The Schmidt number is a function only of the solution properties. Accordingly, it does not change with the velocity of flow of the fluid as is evident from the data summarized in Table 4. However, this dimensionless group decreases rapidly with increasing temperature due to the combined effects of temperature on ν and D .

The calculated values for Stanton number (St) which is a velocity-dependent mass transfer coefficient, are presented in Table 12. This dimensionless group increases with increasing temperature, but decreases with increasing

rotation rate. This latter trend is due to the fact that as the rotation rate increases, the increases in U_m more than compensates for the increase in K_L . On the other hand, as the temperature increases, the increase in K_L more than outweighs the increase in U_m . This is reasonable because U_m is a strong function of rotation rate whereas K_L is a strong function of temperature.

The mass transfer characteristics of the annular flow channel employed in this study may be correlated using the following equations expressed in terms of the dimensionless groups:

$$Sh = A Re^B \quad (56)$$

$$St = C Re^D \quad (57)$$

The empirical parameters A, B, C, and D were obtained by regression analysis of the experimental data.

Figure (39) presents log-log plots of Sherwood vs Reynolds numbers. Straight lines with slopes of 0.58 have been drawn through the data points. This number corresponds to the value of B in equation (56). Log-log plots of Stanton number vs Reynolds numbers (Figure 40) also yields a set of straight lines. Each line corresponds to a particular temperature. Tables (13) and (14) list the values obtained for A, B, C, and D from the regression analysis for the oxidation of hydrogen over a range of temperature from 25°C to 250°C.

Figure 39. Plot of $\log Sh$ vs $\log Re$ for the oxidation of hydrogen in 0.1M NaOH solution.

Figure 40. Plot of $\log St$ vs $\log Re$ for the oxidation of hydrogen in 0.1M NaOH solution.

Table 13

Parameters A and B Obtained From the Correlation Equation $Sh = A R_e^B$
for the Oxidation of Hydrogen in 0.1M NaOH Solution
at Temperatures over the Range 25°C-250°C.

Parameter	Temperature (°C)					
	25	50	100	150	200	250
A	1.582	1.200	0.679	0.470	0.371	0.308
B	0.573	0.575	0.576	0.581	0.585	0.588

Table 14

Parameters C and D Obtained From the Correlation Equation $St = CRe^D$
for The Oxidation of Hydrogen in 0.1M NaOH Solution
at Temperatures over the Range 25°C-250°C.

	Temperature (°C)					
	25	50	100	150	200	250
C	0.009	1.810	0.042	0.072	0.111	0.145
D	-0.427	-0.426	-0.423	-0.419	-0.415	-0.412

The values for exponents B and D remain fairly constant over the temperature range employed indicating that for the turbulent flow regime the experimental data may be successfully correlated using equations (56) and (57).

III-4 Effect of Fluid flow on the Pitting Corrosion of Inconel 600

(i) Potentiodynamic Studies

The polarization behavior and pit morphology of Inconel 600 in 0.1M NaCl+ 0.001M B(OH)₃, + 0.001M LiOH solution were studied as a function of temperature and flow velocity. Before using this solution, different concentrations of NaCl(0.01, 0.05, 0.1, and 0.5M), were used to choose an optimum value. Too low a concentration of NaCl caused severe crevice corrosion and too high a concentration reduced the difference between E_{np} and E_{corr} .

In order to evaluate the effect of voltage scan rate on E_{np} , and hence to choose a suitable scan rate for the potentiodynamic tests, a series of experiments were conducted using different scan rates. In these tests, and in the other potentiodynamic experiments at 25°C, the specimens were cathodically polarized at a potential of -1000 mV vs. Ag/AgCl, 0.1KCl (25°C) for 5 minutes and then

the potential was immediately changed to -250 mV which is in the passive region. The specimen was kept at this passive potential for 10 minutes to develop a passive film of reproducible thickness.

The effect of voltage scan rate is illustrated in Figure (41)(Table 15). This figure reveals that the effect of scan rate becomes negligible at low scan rates. By extrapolation of this curve to zero scan rate, it is possible to evaluate the stationary (i.e. potentiostatic) value for E_{np} . By using a scan rate of 300mV/hr values for E_{np} which are only about 15 mV higher than the potentiostatic values were obtained. Given the probable error of ± 10 mV in the value of E_{np} , due to the poorly-defined breakdown point, the uncertainty incurred in evaluating E_{np} at a scan rate of 300mV/hr is considered to be negligible.

Anodic polarization curves at a voltage scan rate of 300 mV/hr and at temperature of 25°C for 5 different flow velocities are presented in Figures(42-46). Figure (47) presents the superimposed curves for 0 and 54 cm/sec flow velocities. As these curves show, fluid flow velocity does not have any effect on the breakdown potential, and only after the breakdown a slight decrease in current is observed. Corrosion potential is around 120mV and the

Figure 41. The effect of voltage scan rate on the breakdown potential of Inconel 600 in 0.1M NaCl +0.001M B(OH)₃+0.001M LiOH solution at 250°C.

Table 15
Dependence of the Breakdown Potential On the
Voltage Scan Rate (mV/hr) for Inconel 600
In 0.1M NaCl Solution at 250°C.

	Scan Rate mV/hr							
	15	100	200	300	500	1000	2000	3000
E_{np} (mv) vs. SHE_T	-95	-92	-90	-88	-83	-78	-46	-18

Figure 42. Anodic polarization curve for Inconel 600 in 0.1M NaCl + 0.001M $\text{B}(\text{OH})_3$ + 0.001M LiOH solution, at 25°C for zero flow velocity.

Figure 43. Anodic polarization curve for Inconel 600 in 0.1M NaCl + 0.001M $\text{B}(\text{OH})_3$ + 0.001M LiOH solution, at 25°C for and 18.2 cm/sec flow velocity.

Figure 44. Anodic polarization curve for Inconel 600 in 0.1M NaCl + 0.001M $\text{B}(\text{OH})_3$ + 0.001M LiOH solution, at 25°C for 43 cm/sec flow velocity.

Figure 45. Anodic polarization curve for Inconel 600 in 0.1M NaCl + 0.001M $\text{B}(\text{OH})_3$ + 0.001M LiOH solution, at 25°C for 54 cm/sec flow velocity.

Figure 46. Anodic polarization curve for Inconel 600 in 0.1M NaCl + 0.001M $\text{B}(\text{OH})_3$ + 0.001M LiOH solution, at 25°C for 59 cm/sec flow velocity.

Figure 47. Anodic polarization curves for Inconel 600 in 0.1M NaCl +0.001M $B(OH)_3$ +0.001M LiOH solution, at 25°C for zero and 54 cm/sec flow velocities.

breakdown potential is about 500mV. The observed range of passivity is about 300mV. Anodic polarization curves for 100°C, and 200°C are presented in Figures (48-59). none of these curves show any effect of the flow velocity on the breakdown potential. At 100°C, the range of passivity is about 200 mV, and breakdown occurs at a potential of about 175 mV. The range of passivity at 200°C is less than 100 mV and the breakdown potential is about 70 mV.

Since this study is more interested in the corrosion behavior of the alloy at high temperatures, anodic polarization curves for 8 different flow velocities were produced (Figures 60-68). In these tests, when current densities reached a value of 0.1 mA/cm², the potential scan was reversed to obtain the repassivation potential, E_{pp} . In all of these tests no detectable effect of flow velocity on the breakdown potential, E_{np} , was observed. As Figure 68 shows, the effect of flow velocity on the repassivating potential is small. E_{pp} for the highest flow velocity is about 10 mV higher than that for stagnant solution. The range of passivity is about 180 mV which is greater than that of 200°C.

The effect of rotation rate on the breakdown potential of Inconel 600 in 0.1M NaCl solution at Various temperatures

Figure 48. Anodic polarization curve for Inconel 600 in 0.1M NaCl +0.001M B(OH)₃+0.001M LiOH solution, at 100°C for zero flow velocity.

Figure 49. Anodic polarization curve for Inconel 600 in 0.1M NaCl +0.001M $\text{B}(\text{OH})_3$ +0.001M LiOH solution, at 200°C for and 31 cm/sec flow velocity.

Figure 50. Anodic polarization curve for Inconel 600 in 0.1M NaCl +0.001M $\text{B}(\text{OH})_3$ +0.001M LiOH solution, at 100°C for 58³ cm/sec flow velocity.

Figure 51. Anodic polarization curve for Inconel 600 in 0.1M NaCl + 0.001M $\text{B}(\text{OH})_3$ + 0.001M LiOH solution, at 100°C for 79³ cm/sec flow velocity.

Figure 52. Anodic polarization curve for Inconel 600 in 0.1M NaCl +0.001M B(OH)₃+0.001M LiOH solution, at 100°C for 93³cm/sec flow velocities.

Figure 53. Anodic polarization curves for Inconel 600 in 0.1M NaCl +0.001M $\text{B}(\text{OH})_3$ +0.001M LiOH solution, at 100°C for zero and 93 cm/sec flow velocities.

Figure 54. Anodic polarization curve for Inconel 600 in 0.1M NaCl +0.001M $\text{B}(\text{OH})_3$ +0.001M LiOH solution, at 200°C for zero flow velocity.

Figure 55. Anodic polarization curve for Inconel 600 in 0.1M NaCl +0.001M B(OH)_3 +0.001M LiOH solution, at 200°C for 48³cm/sec flow velocity.

Figure 56. Anodic polarization curve for Inconel 600 in 0.1M NaCl + 0.001M $\text{B}(\text{OH})_3$ + 0.001M LiOH solution, at 200°C for and 93 cm/sec flow velocity.

Figure 57. Anodic polarization curve for Inconel 600 in 0.1M NaCl +0.001M $\text{B}(\text{OH})_3$ +0.001M LiOH solution, at 200°C for 120 cm/sec flow velocity.

Figure 58. Anodic polarization curve for Inconel 600 in 0.1M NaCl + 0.001M $\text{B}(\text{OH})_3$ + 0.001M LiOH solution, at 200°C for 132 cm/sec flow velocity.

Figure 59. Anodic polarization curves for Inconel 600 in 0.1M NaCl + 0.001M $\text{B}(\text{OH})_3$ + 0.001M LiOH solution, at 200°C for zero and 132 cm/sec flow velocities.

Figure 60. Anodic polarization curve for Inconel 600 in 0.1M NaCl +0.001M B(OH)_3 +0.001M LiOH solution, at 250°C for zero flow velocity.

Figure 61. Anodic polarization curve for Inconel 600 in 0.1M NaCl + 0.001M $\text{B}(\text{OH})_3$ + 0.001M LiOH solution, at 250°C for 13.8 cm/sec flow velocity.

Figure 62. Anodic polarization curve for Inconel 600 in 0.1M NaCl + 0.001M $\text{B}(\text{OH})_3$ + 0.001M LiOH solution, at 250°C for 58.1 cm/sec flow velocity.

Figure 63. Anodic polarization curve for Inconel 600 in 0.1M NaCl +0.001M $\text{B}(\text{OH})_3$ +0.001M LiOH solution, at 250°C for 93 cm/sec flow velocity.

Figure 64. Anodic polarization curve for Inconel 600 in 0.1M NaCl +0.001M $\text{B}(\text{OH})_3$ +0.001M LiOH solution, at 250°C for 120 flow velocity.

Figure 65. Anodic polarization curve for Inconel 600 in 0.1M NaCl +0.001M $\text{B}(\text{OH})_3$ +0.001M LiOH solution, at 250°C for 132 cm/sec flow velocity.

Figure 66. Anodic polarization curve for Inconel 600 in 0.1M NaCl +0.001M $\text{B}(\text{OH})_3$ +0.001M LiOH solution, at 250°C for 144 cm/sec flow velocity.

Figure 67. Anodic polarization curve for Inconel 600 in 0.1M NaCl +0.001M B(OH)_3 +0.001M LiOH solution, at 250°C for 158 cm/sec flow velocity.

Figure 68. Anodic polarization curves for Inconel 600 in 0.1M NaCl +0.001M $\text{B}(\text{OH})_3$ +0.001M LiOH solution, at 250°C for zero and 158 cm/sec flow velocities.

is illustrated in Figure (69). Table (16) presents the dependence of the breakdown potential at various temperature, and Table (17) shows the dependence of passivating potential, E_{pp} , at 250°C (Figure 70) on the flow velocities for Inconel- 600 in 0.1M NaCl solution.

Figure 71 presents the effect of temperature on the breakdown potential of Inconel 600 in 0.1M NaCl solution. The breakdown potential sharply reduces for temperatures up to 200°C, However it reduces smoothly by further increases of temperature.

(ii) Potentiostatic(stationary) Studies

Stationary potentiostatic tests were carried out at different potentials around E_{np} obtained by potentiodynamic tests. The duration time was 18 hours. The E_{np} obtained by this method was equal to the value obtained by extrapolation of E_{np} -scan rate curve. For potentials 20-30 mV lower than E_{np} (potentiodynamic), some crevice attack was observed but no pit nucleation occurred on the surface. Lowering the potential more than the above values, eliminated the crevice corrosion and the specimens were almost unchanged after 18 hours. Figure (72) presents the change of current vs time at potentials around E_{np} .

Figure 69. Plot of breakdown potential vs flow velocity for Inconel 600 in 0.1M NaCl +0.001M $B(OH)_3$ +0.001M LiOH solution at 25, 100, 200, and 250°C.

Table 16
Dependence of the Breakdown Potential On the
Rotation Rate and temperature
For Inconel 600 In 0.1M NaCl Solution.

Temperature (° C)	Rotation Rate							
	0	200	400	600	800	1000	1200	1500
250	-.086	-.088	-.094	-.078	-.090	-.086	-.096	-.088
200	-.070		-.069		-.069		-.075	-.071
100	.175		.180		.171		.176	.172
25	.501		.495		.503		.502	.498

Table 17

Dependence of the Passivating Potential On the
Rotation Rate at 250°C For Inconel 600
In 0.1M NaCl Solution.

	Rotation Rate							
	0	200	400	600	800	1000	1200	1500
E_{pp}	-0.252	-0.250	-0.243	-0.240	-0.240	-0.244	-0.240	-0.238
$V, \text{ vs } SHE_T$

Figure 70. The dependence of passivating potential, E_{pp} , for Inconel 600 in 0.1M NaCl + 0.001M $B(OH)_3$ + 0.001M LiOH at 250 °C on the flow velocity.

Figure 71. Plot of breakdown potential vs temperature for Inconel 600 in 0.1M NaCl + 0.001M B(OH)₃ + 0.001M LiOH solution.

Figure 72. Plots of current vs time for potentiostatic(stationary) tests for Inconel 600 at 250°C in $0.1\text{M NaCl} + 0.001\text{M B(OH)}_3 + 0.001\text{M LiOH}$ solution at various potentials.

In order to study the effect of flow velocity on the incubation time at 250°C , samples were cathodically polarized at a potential of -1000 mV , vs Ag/AgCl , 0.1M KCl , for 5 minutes and then the potential was immediately changed to -250 mV . The specimen were kept at this potential for 10 minutes. These processes of dissolution and thickening of the film was done at quiescent solution. Flow velocity was increased gradually to a certain value and then potential was immediately changed to a potential close to the breakdown potential and time to breakdown was recorded. The experimental results are presented in Table(18). As this table shows, data is not reproducibel. High sensitivity of the incubation time to potential is the main reason for the above observation. This will become evident from the stationary potentiostatic results, Figure (72). Change of potential of only 10 mV can have a large influence on the incubation time. The experimental data for the breakdown potential shows that the breakdown potential for each sample can be about 10 mV different from other one at the same testing condition. As a result the incubation time of each sample will be different from the other one at the same potential. Another important point about these tests is that the incubation time for samples hold at above breakdown potential was less than a minute and as a result difficult

Table 18

Dependence of the Incubation Time, minute, On the
Rotation Rate at 250°C For Inconel 600
In 0.1M NaCl Solution.

	Rotation Rate				
	0	400	800	1200	1500
Potential V vs SHE _T					
.080	<1	3	<1	<1	5
.085	4	1	5	<1	<1
0.095	2	>120	<1	>120	10
0.105	>120	30	>120	90	>120
0.115	>120	>120	>120	>120	>120

to measure accurately and use them as a base for comparison. However there was no evidence that flow velocity has a considerable effect on the incubation time.

III-5 Thermodynamic Analysis of Results.

In order to determine whether or not the observed behavior of the alloy is consistent with the known thermodynamic properties of the component metals at various temperatures in a 0.1M NaCl + 0.001M LiOH + 0.001M B(OH)₃ solution, it is necessary to know the pH of the solution at each temperature. The values of pH for this specific solution were not available in the literature, however pH values for 0.01M B(OH)₃ + 0.001M LiOH are available (155) (Table 19). Reported pH values for the more concentrated B(OH)₃ solution at temperatures over the range of 25 to 250°C fluctuate around 8. It is reasonable to assume that by reducing the acid concentration, the pH of the solution increases, however since B(OH)₃ is a very weak acid the increase may be very small. (This becomes more clearer when the change of pH with reducing B(OH)₃ be considered as reported in Table(19)). The pH values of 0.01M and 0.001M B(OH)₃ are 5.46 and 5.57, respectively, which shows an increase of only 2%. From the above argument it is clear that pH values for all the reported temperatures for the presented solution are somewhere between 8 and 9.

Table 19
Calculated pH Values for Various $\text{B(OH)}_3/\text{LiOH}/\text{H}_2\text{O}$ Systems
as a Function of Temperature and Composition(153).

M^{O}_{B}	M^{O}_{Li}	Temperature($^{\circ}\text{K}$)					
		298	373	473	498	523	548
0.1	--	5.11	4.96	4.99	5.03	5.08	5.15
0.01	--	5.60	5.45	5.41	5.42	5.46	5.49
0.001	--	6.10	5.88	5.60	5.57	5.57	5.60
0.01	0.0001	7.22	6.92	6.83	6.85	6.90	6.99
0.01	0.001	8.27	7.96	7.86	7.88	7.93	8.02
0.01	0.01	10.62	9.59	9.06	9.04	9.06	9.14
--	0.01	12.00	10.29	9.34	9.27	9.26	9.32
--	0.1	13.02	11.33	10.42	10.37	10.38	10.46

Once pH and breakdown potential for each temperature are known, it is possible to use potential-pH or Pourbaix (156), diagrams for interpretation of the data. Fortunately, these diagrams are available for 25, 200, and 250°C (157,158). Breakdown potential at each temperature is located on the appropriate diagram for each component metal (Figures 73-79). The fact that all of these locations are just above the dissolution line of chromium oxide according to reaction

supports the idea that at the breakdown potential Cr_2O_3 dissolves into the solution. For iron breakdown potentials are located on the domain of Fe_2O_3 stability, so iron oxide dissolution does not occur at the breakdown potentials. For nickel at 25 and 200°C, the E_{np} is located in the domain of Ni_3O_4 stability, hence the dissolution of Ni is not expected at these temperatures. At 250°C, E_{np} is inside the domain of HNiO_2^- , However it is well above the equilibrium line of $\text{Ni}/\text{HNiO}_2^-$ and so, it is unlikely that the dissolution of Ni is responsible for the breakdown. The protection potential, E_{pp} , at 250°C is also shown on the E-pH diagrams. Its location on the iron and nickel diagram is in the same domain as E_{np} . However, for chromium, its location is just below the dissolution line of Cr_2O_3 . From the above

Figure 73. Potential-pH diagram for Ni in high-salinity brine at 25°C (155). E_{Ni} for Inconel 600 in 0.1M NaCl + 0.001M B(OH)_3 + 0.001M LiOH solution (pH 8.5) at 25°C is shown as an open rectangle.

Figure 74. Potential-pH diagram for Cr in high-salinity brine at 25°C (155). E_{ref} for Inconel 600 in 0.1M NaCl + 0.001M B(OH)_3 + 0.001M LiOH solution (pH= 8.5) at 25°C is shown as an open rectangle.

Figure 75. Potential-pH diagram for Fe in high-salinity brine at 25°C(155). E_{red} for Inconel 600 in 0.1M NaCl + 0.001M $\text{B}(\text{OH})_3$ + 0.001M LiOH solution (pH= 8.5) at 25°C is shown as an open rectangle.

Figure 76. Potential-pH diagram for Ni in high-salinity brine at 250°C(155). E_{cp} and E_{pr} values for Inconel 600 in 0.1M NaCl + 0.001M $B(OH)_3$ + 0.001M LiOH solution (pH=8.5), at 250°C are shown as a closed and open rectangle, respectively.

Figure 77. Potential-pH diagram for Cr in high-salinity brine at 250°C (155). E_p and E_{dp} values for Inconel 600 in 0.1M NaCl + 0.001M B(OH)₃ + 0.001M LiOH solution (pH=8.5), at 250°C are shown as a closed and open rectangle, respectively.

Figure 78. Potential-pH diagram for Fe in high-salinity brine at 250°C (155). E_{np} and E_{p} values for Inconel 600 in $0.1\text{M NaCl} + 0.001\text{M B(OH)}_3 + 0.001\text{M LiOH}$ solution ($\text{pH}=8.5$), at 250°C are shown as a closed and open rectangle, respectively.

Figure 79. Potential-pH diagram for Cr in low-salinity brine at 200°C(156). E₀ for Inconel 600 in 0.1M NaCl + 0.001M B(OH)₃ + 0.001M LiOH solution (pH= 8.5) at 200°C is shown as an open rectangle.

discussion, it can be concluded that chromium oxide dissolution is most likely to be the dominant process to occur at pitting potential for the present alloy in this solution.

111-6 Theories of Pitting and the Effect of Flow velocity on the Breakdown Potential

As was discussed in chapter I, it would appear that the flow conditions examined so far, have little effect on the pitting potential. Any valid model of pitting should account for this experimental observation. Most of these models can explain with some degree of uncertainty, why fluid flow velocity does not effect pitting potential. In the case of acidification model, it may be argued that fluid flow cannot remove the acidified solutions from inside of all the flaws of the passive film simply because these flaws are very small. Models based on adsorption can use the same argument for the adsorption of ions by the film flaws.

Those models which suggest that passivity is a result of dissolution and subsequent precipitation, are not able to explain how this precipitation is not effected by fluid flow. Models based on the chemico-mechanical breakdown can be modified by considering the effect of shear stresses introduced by the flow velocity on the film internal stresses and surface tension.

Point defect model actually predict quantitatively that fluid flow velocity does not effect breakdown potential. According to this model E_{np} is expressed as equation (7).

$$E_{np} = \frac{4.606RT}{xF\alpha} \log \frac{J_m}{J^\circ u^{-x/2}} - \frac{2.303RT}{\alpha F} \log a_{Cl^-} \quad (7)$$

in which all terms are independent of flow velocity. In order to demonstrate that E_{np} according to this model is not a function of velocity, each term will be examined separately. J_m which is the rate of submergence of the metal holes into the bulk metal is independant of flow velocity, because there is no way that fluid flow can effect the rate of submergence of the vacancies beneath the film.

$$J^\circ = xKD_{vM}x' N_v/\Omega^{1+x/2} \exp (-\Delta G_s^\circ/RT) \quad (59)$$

where x is the charge on a cation, K is equal to $F\epsilon/RT$, ϵ is the electric field strength in the film, $D_{vM}x'$ is the diffusivity of the cation vacancy, N_v is Avogadro's number, Ω is the molecular volume per cation and ΔG_s° is the change in Gibbs energy for the schottky-pair reaction. None of these terms are flow dependent, hence J° is independent of flow velocity. u is defined as:

$$u = N_v/\Omega \exp \frac{\Delta G_{A-1}^\circ - F\beta pH - F\phi_{f/s}^\circ}{RT} \quad (60)$$

where ΔG_{A-1}° is the standard Gibbs energy change of

reaction;

which can be expressed as:

$$\Delta G_{A-1}^{\circ} = \eta_{Cl_{\ddot{O}}}^{\circ} - \eta_{Cl^{-}}^{\circ} - \eta_{V_{\ddot{O}}}^{\circ} \quad (62)$$

and is independent of flow velocity. β is pH dependence of the potential drop at the film/solution interface, ϕ , which is expressed as:

$$\left(\frac{dL}{dpH} \right)_{V_{ext}, t, \phi_{f/s}} = - \beta / \epsilon \quad (63)$$

Since the left side of the above equation is independent of flow velocity, the right side cannot be flow dependent, so β is not flow dependent and as a result u is not a function of flow velocity. α is the potential dependent of the potential drop at the film/solution interface and is expressed as:

$$dL/dV_{ext, t, pH, \phi_{f/s}}^{\circ} = \frac{1 - \alpha}{\epsilon} \quad (64)$$

which indicates that is independent of flow velocity.

III-7 Effect of Fluid Flow on the Morphology of Pits

After the samples were anodically polarized and breakdown potential were reached, they were kept at potentials 100 mv higher than their breakdown potential for one hour. Then, the

test cell was cooled down by an electric fan, and the specimens were taken out. At this stage all the pits were covered with a thick brown layer of corrosion products. It leads to the conclusion that erosion corrosion could not be the mode of corrosion attack.

At room temperature for high velocities the number of pits was much higher but they were very small. In this case the surface of the specimens were covered with a uniformly spaced layer of thick yellow to green corrosion products. In regions which were not covered no significant pitting corrosion was observed. After washing the specimen, a severe localized attack was observed. Even though the individual pits could not be seen by the naked eye, the corroded regions had the appearance of many scratches along the fluid flow direction. SEM study of the specimen showed that hundreds of very small pits are presented along those lines and many of these pits have joined each other and lined up in the direction of fluid flow (Figures 80,81).

In the absence of fluid flow at all the temperatures a uniform pitting attack was observed all over the surface of the specimen. However the morphologies of pits at various flow velocities were a characteristic of each temperature. At 100°C flow velocity does not effect the number or the sizes of pits. However the tips of the pits are sharper and

Figure 80. The surface morpholog of Inconel 600 after exposure to 0.1 M NaCl +0.001M B(OH)₃+0.001M LiOH at 25°C and zero flow velocity.

Figure 81. Effect of flow velocity on surface morphology of Inconel 600 after exposure to 0.1 M NaCl + 0.001M $B(OH)_3$ + 0.001M LiOH at 25°C, flow velocity: 59 cm/sec.

many of them align themselves in the direction of flow (Figures 82,83). At 200°C flow velocities higher than 50 cm/sec produce pits which were connected together in the flow direction, but also they align themselves in many branches vertical to the direction of flow (Figures 84-87).

At 0 RPM and 250°C there were a large number of pits which were uniformly distributed all over the surface. By increasing the flow velocity the number of pits reduces, however they become wider. At 1500 RPM only 5 relatively big pits were observed. SEM examination showed that under the influences of fluid flow pits join each other and line up in the direction of flow. In some cases the tips of the pits were like the tip of an arrow in the direction of flow. Figures (88-94) show the effect of flow velocity on the morphology of pits. Intergranular attack was also observed inside the pits developed under the influences of flow velocity (Figure 95).

It is important to note that when you have a closed pit and the corrosion product does not dissolve into the solution and is so strongly bonded to the surface of the specimen that the applied flow velocity cannot wash it away, you should not expect to observe any significant effect of flow velocity over the repassivation potential " E_{pp} " (Table 17) (Figure 70).

Figure 82. Effect of flow velocity on surface morpholog of Inconel 600 after exposure to 0.1 M NaCl +0.001M $B(OH)_3$ +0.001M LiOH at 100°C, and zero flow velocity.

Figure 83. Effect of flow velocity on the surface morpholog of Inconel 600 after exposure to 0.1 M NaCl +0.001M $B(OH)_3$ +0.001M LiOH at 100°C, flow velocity: 93 cm/sec.

Figure 84. Effect of flow velocity on surface morpholog of Inconel 600 after exposure to 0.1 M NaCl +0.001M $B(OH)_3$ +0.001M LiOH at 200°C, and zero flow velocity.

Figure 85. Effect of flow velocity on surface morpholog of Inconel 600 after exposure to 0.1 M NaCl +0.001M B(OH)₃+0.001M LiOH at 200 °C, flow velocity: 49 cm/sec.

Figure 86. Effect of flow velocity on the surface morphology of Inconel 600 after exposure to 0.1 M +0.001M $B(OH)_3$ +0.001M LiOH NaCl at 200°C, flow velocity: 93 cm/sec.

Figure 87. Effect of flow velocity on the surface morpholog of Inconel 600 after exposure to 0.1 M NaCl +0.001M $B(OH)_3$ +0.001M LiOH at 200°C, flow velocity: 132 cm/sec.

Figure 88. The surface morphology of Inconel 600 after exposure to 0.1 M NaCl +0.001M $B(OH)_3$ +0.001M LiOH at 250°C and zero flow velocity.

Figure 89. Effect of flow velocity on surface morpholog of Inconel 600 after exposure to 0.1 M NaCl +0.001M $B(OH)_3$ +0.001M LiOH at 250°C, flow velocity: 58 cm/sec.

Figure 90. Effect of flow velocity on surface morpholog of Inconel 600 after exposure to 0.1 M NaCl +0.001M $B(OH)_3$ +0.001M LiOH at 250°C, flow velocity: 92 cm/sec.

Figure 91. Effect of flow velocity on surface morpholog of Inconel 600 after exposure to 0.1 M NaCl +0.001M $B(OH)_3$ +0.001M LiOH at 250°C, flow velocity 119 m/sec.

Figure 92. Effect of flow velocity on surface morpholog of Inconel 600 after exposure to 0.1 M NaCl +0.001M $B(OH)_3$ +0.001M LiOH at 250°C, flow velocity: 132 m/sec.

Figure 93. Effect of flow velocity on surface morpholog of Inconel 600 after exposure to 0.1 M NaCl at 250°C, flow velocity: 144 cm/sec.

Figure 94. Effect of flow velocity on the surface morphology of Inconel 600 after exposure to 0.1 M NaCl + 0.001M $B(OH)_3$ + 0.001M LiOH at 250°C, flow velocity: 158 cm/sec.

Figure 95. Effect of flow velocity on the surface morphology of Inconel 600 after exposure to 0.1 M NaCl +0.001M $B(OH)_3$ +0.001M LiOH at 250°C, flow velocity: 144 cm/sec.

SUMMARY AND CONCLUSIONS

1. A flow system for testing the effect of flow velocity on pitting corrosion was designed and fabricated. The mass transfer characteristics of the flow system have been calibrated by measuring the limiting currents of the oxidation of hydrogen in 0.1M NaOH at temperatures over the range of 25°C to 250°C, as a function of the flow inducing impeller and the temperature of the test solution. Flow velocities ranging from 2 to 158 cm/sec were obtained for the annular flow geometry. Laminar flow was observed only at very low stirring rates at room temperature.
2. The experimental data have been successfully correlated using the equations $Sh = A Re^{0.58}$ and $St = C Re^{-0.42}$. The exponents (0.58 and -0.42) remained fairly constant over the temperature range studied (25°C to 250°C) for the oxidation of hydrogen, while the values of A and C were relatively temperature dependent.
3. At room temperature for low flow velocities and at 200 rpm for temperatures up to 100°C laminar flow is observed while for higher temperatures and flow velocities, turbulent flow is the only regime existed.

4. The effect of scan rate on the breakdown potential of the Inconel 600 was examined. The breakdown potential as a function of scan rate was drawn. The curve was extrapolated to zero scan rate. E_{np} at 300 mV/hr was only 10 mV higher than that of E_{np} at zero scan rate.
5. Anodic polarization curves for 250°, 200, 100, and 25°C for various flow velocities were produced using 300 mV/hr as the voltage scan rate. To double check the result, stationary potentiostatic measurements were carried out below the measured breakdown potentials. These tests showed that the actual breakdown potentials are equal to the extrapolated values.
6. The flow velocity has at most a minor influence on the breakdown potential of Inconel 600 in 0.1M NaCl solution both at high and low temperatures.
7. To observe the effect of the flow velocity on the repassivation potential, the potential was scanned back after the current reached 0.1 mA/cm^2 . At the maximum flow velocity only 10-15 mV increase in the protection potential was observed. Because the pits were covered with corrosion product the flow velocity had only a minor effect on the protection potentials.
8. The morphology of localized attack under various flow velocities and temperatures were examined by SEM. For

quiescent solution at high and low temperatures uniformly distributed pits all over the surface of the specimens were observed. Pits at low temperature were much smaller than those at high temperature. By increasing the flow velocity at 250°C the number of pits was reduced but their size increased. Intergranular attack was observed inside the big pits. At 100°C the number and the size of pits were independent of flow velocity. At room temperature the number of pits increased with increased flow velocity but their size was reduced.

9. At all temperatures, some pits aligned themselves in the direction of fluid flow and some of them had tips similar to an arrow tip pointed in the flow direction.

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