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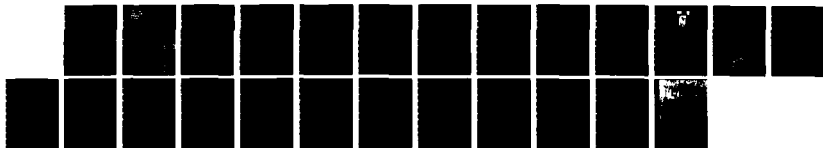
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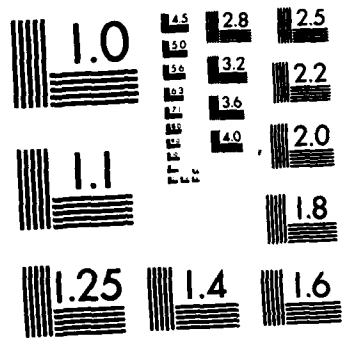
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DEPARTMENT OF MATERIALS SCIENCE  
METALLURGY PROGRAM

TECHNICAL REPORT

November 1983

OFFICE OF NAVAL RESEARCH

Contract No. N000-14-81-K-0025

AD-A134729

THE EFFECT OF GAS BUBBLES AND CAVITY DIMENSIONS ON THE LOCAL  
ELECTRODE POTENTIAL WITHIN PITS, CREVICES AND CRACKS

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4. TITLE (and Subtitle) <b>The Effect of Gas Bubbles and Cavity Dimensions on the Local Electrode Potential within Pits, Crevices and Cracks</b>		5. TYPE OF REPORT & PERIOD COVERED <b>Technical Report</b>
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) <b>H. W. Pickering</b>		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS <b>Metallurgy Program, 209 Steidle Building The Pennsylvania State University University Park, PA 16802</b>		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS <b>Metallurgy Branch Office of Naval Research Arlington, VA 22217</b>		12. REPORT DATE <b>November 7, 1983</b>
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)
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16. DISTRIBUTION STATEMENT (of this Report)  <b>Distribution of this document is unlimited</b>		
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20. ABSTRACT continued

concentration gradients are strong functions of the "sharpness" of the crack, the ohmic voltage increasing as the crack opening decreases, in agreement with earlier calculations of current distribution in slots by Wagner. By analogy, a similar result is expected for anodic polarization. The shift of the potential with increasing distance into a cavity is always in the direction of a decrease in anodic or cathodic polarization, is typically very large approaching the  $E_{LIM}$  value of the system, is largely independent of the cathodic or anodic polarization, is typically very large approaching the  $E_{LIM}$  value of the system, is largely independent of the cathodic or anodic polarization applied to the external surface and often places that base of the cavity in a potential regime of other reactions, e.g., anodic metal dissolution at the crack tip while the sample's outer surface is under effective cathodic protection.



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THE EFFECT OF GAS BUBBLES AND CAVITY DIMENSIONS ON THE LOCAL  
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BY

H. W. Pickering

Technical Report

to

Office of Naval Research

Contract NO. N000-14-81-K-0025

November 1983



## Introduction

Some years ago Pickering and Frankenthal (1) found that gas accumulated inside growing pits while the sample was anodically polarized in the passive region. This observation was aided by (i) the use of a low power microscope, (ii) the fact that in the acidic electrolyte the formation of solid corrosion products was suppressed, (iii) the formation of "open", hemispherically-shaped pits, and (iv) the use of a glass fiber to probe inside the pit. This observation had to be important since at the very least the kinetics of pit growth, and possibly the mechanism, would be affected by the presence of a major obstruction within the pit. Its importance was all the more accentuated when the local electrode potential at the base of the pit was found by direct measurement to shift, typically hundreds of mV, in the less noble direction, often putting the base of the pit in the normal active region of the polarization curve for the bulk electrolyte. Few of the earlier theories of pit growth and crevice attack included large potential gradients within the growing pit or crevice. In contrast, our studies have been largely motivated by the possibility that the value of the local electrode potential may be an important factor in causing pit and crevice growth.

What is needed is a systematic study of the relationship between potential gradients and accumulating gas in the cavities, and of their importance in the pit and crevice growth processes. In addition, mathematical modeling of these anodic processes should include the occurrence of the reaction on the side walls. When this was done in the modeling of cathodic polarization in crevices (2), it introduced the spacing between the crack walls (crack "opening") as an important parameter, in agreement with earlier calculations by Wagner (3) which showed that narrowness of the electrolyte path affected the current distribution in slots. By analogy, the same result is expected during anodic polarization, i.e., the ohmic voltage increases in the crack (to a limiting\* value) as the crack opening decreases. Thus, it seems likely in the case of sharp (closed) cracks, that during anodic polarization the local electrode potential at the crack tip will have a much less noble value and be in the active region while the sample's outer surface is in the passive region even without accumulation of gas in the crack.

It is the limited purpose of the present paper to focus on the effect of accumulating gas in the cavity and of the cavity dimensions on the value of the local electrode potential at the base of the cavity. Cathodic, rather than anodic polarization will be used for this part of the study since it provides a constant source of gas via the hydrogen evolution reaction (h.e.r.) and a control on the rate of gas accumulation in the cavity. In addition, mathematical modeling for cathodic polarization of creviced samples includes the occurrence of the h.e.r. on the crack walls (2). This feature in the model, in turn, leads to the above-mentioned important result that the potential gradient is a strong function of the crack opening. Another consequence of a cathodic polarization study is that the results will impact on the hydrogen cracking problem. Before proceeding

\*The existence of a limiting potential,  $E_{LIM}$ , has been proposed, and criteria which establish its value have been set forth (4). Some experimental evidence of its existence is also available in reference (2) and this paper.

to present a description of the conditions within cracks during cathodic polarization, the analogous situation of anodic polarization, will be reviewed in light of the early observation of in-place bubbles in pits and its significance for localized corrosion processes.

### Anodic Polarization

In anodic-polarization measurements of the local electrode potential existing inside growing, gas-containing pits, the least noble, measured potential in the pit was typically at negative potentials in the active dissolution region (1). This was so even when the sample's outer surface was anodically polarized well into the passive region, e.g.,  $> 1V$  (SHE). Hence, it was concluded that the simultaneously observed in-place gas bubbles which were identified as  $H_2$  were the cause of these large ( $\sim 10^3$  mV) changes in electrode potential within the iron cavity, and possibly also the cause of other earlier reported  $10^2$  to  $10^3$  mV changes within pits in austenitic stainless steel (5) and carbon steel (6) which were largely inexplicable at the time. For these large IR drops the resistivity of the electrolyte was probably too low to account for this magnitude of ohmic voltage for the existing thickness of the electrolyte path and pitting current, without imposing factors which reduce the solution cross section available for carrying the current. On the other hand, for narrow crevices and large currents the cross section of the electrolyte path may be small enough to produce  $10^3$  mV ohmic voltages within the crevice, as was suggested to explain other measured large ohmic voltages in titanium alloy (7) and stainless steel (8) although the calculations were not done.

Additional observations of accumulated gas within cavities also have been reported, including in the non ferrous alloys. In the case of Al, gas was observed to evolve from within the pits and found by analysis to be hydrogen (9). This observation of  $H_2$  gas was not for the usual conditions of hydrogen evolution during pitting at open circuit, for which  $E_{CORR} < 0.0$  V (SHE) and  $H_2$  is evolved on the outer surface as the cathodic reaction (10,11).<sup>2</sup> Rather, it was for anodic polarization to a potential ( $\sim 2$  V SHE) for which hydrogen evolution can not occur (at the outer surface), indicating that the local electrode potential in the pit was much less noble at a value below  $\sim 0.0$  V (SHE).

The measured potential in the cavity will not usually be the least noble potential existing in the cavity. This value, which may approach  $E_{LJM}$ , is expected to be in the most confined regions, e.g., between the bubble and cavity wall and, therefore, not measurable without disturbing the bubble. The least noble measured local electrode potentials of  $-0.2$  to  $0.2$  V (SHE) for Fe in different acidic solutions containing also  $Cl^-$  ion, which occur due to very effective constriction by in-place gas, are virtually independent of the extent of anodic polarization of the outer surface (1,4,12).

### Measurement Technique

The potential measurement technique which utilizes a micro Luggin capillary probe has been found to be reliable and accurate to at least  $\pm 50$  mV. This error limit was in part obtained from the following independent observations which confirm the reliability of the potential probe method.

(1) With the sample surface anodically polarized to potentials in the range  $0.7$  to  $1.2$  V (SHE), the gas forming within, and coming out of, growing pits in iron was analyzed as  $H_2$ . This places the local electrode potential in the pit at a value of  $< 0.0$  V, which is the most noble

equilibrium hydrogen potential possible at the base of the pits for any of the systems studied. The actual local electrode potential had to be more negative with its value dependent on the local h.e.r. current and pH. As mentioned above the most negative potentials within the pits would also be more negative than the measured values which were typically in the range, -0.2 to 0.2 V (1), in good agreement with the value of ~0.0 volts established by identification of the gas as hydrogen.

(2) In the same anodically polarized iron samples, ( $E_{\text{surface}} = 0.7$  to 1.2 V) and also in anodically polarized stainless steel samples ( $E_{\text{surface}} > 1.0$  V), the walls of the pits prior to salt film formation were observed to be crystallographically etched. Etched surfaces are typical of dissolution in the active region and, in particular, in the Tafel region. This would place the local electrode potential of the etched surface at less than approximately -0.2 V, which is also in good agreement with the measured values given above.

### Mathematical Modeling

From a theoretical point of view, if the current path in the cavity is obstructed by the presence of gas bubbles, calculations of the IR voltage which are based on the geometrical cross section of the cavity will under-estimate the actual IR voltage. Many such calculations of the potential and concentration variations in pits and crevices available in the literature (1,12-16) all show that for an electrolyte which is a good conductor the ohmic voltage between the base and opening of a growing pit (or crack) is  $\approx 10^2$  mV. Even in the case of dilute (poorly conducting) electrolytes, the ohmic voltage in the cavity (in the absence of constrictions) may be quite small since the ionic concentration and, hence, the conductivity of the electrolyte within a growing pit or crevice, increases above that of the bulk solution (1). Measured values of the ohmic voltage in pits as reported above, are often an order of magnitude larger. Thus, a discrepancy exists between calculation and experiment. The cause of this discrepancy is the absence of a parameter in the model which takes into account a narrowing, e.g., due to accumulating gas, of the electrolyte path in the cavity.

On the other hand, if gas does not accumulate but narrowness is intrinsic in the form of localized corrosion, as in the case of a sharp crack, an appropriate model needs only to include this narrowness. By analogy with cathodic-polarization modeling (2), this would appear to mean inclusion of side wall dissolution in existing models. The anticipated results of such a model for anodic polarization may well show that potential changes for sharp cracks or narrow crevices, would be comparable to those produced in wide crevices or pits containing in-place gas bubbles.

### Cathodic Polarization

#### Experimental

Following the above-mentioned anodic polarization behavior in cavities, large changes in electrode potential accompanied by accumulating gas were observed within crevice-like cavities during cathodic polarization (2,17). Figure 1 shows stable, in-place  $H_2$  bubbles that typically form within crevices during the normal occurrence at a rate  $i$  of the h.e.r. on the sample surface. Simultaneously, as the in-place bubbles formed, the measured potential gradients within the crevices were found to markedly increase. The solution potential expressed in terms of  $\phi_{x=0} = 0$ , where  $x=0$  is at the crevice mouth (Figure 6), is given in Figure 2 with and

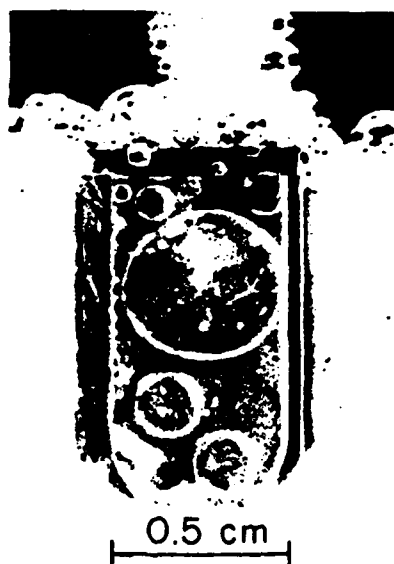


Figure 1. In-place hydrogen gas bubbles which formed during cathodic polarization at  $i_s = 9 \text{ A m}^{-2}$ , photographed through a transparent plastic which was used as one wall of the crevice. The other wall and outer surface were the iron sample. After Harris and Pickering (17).

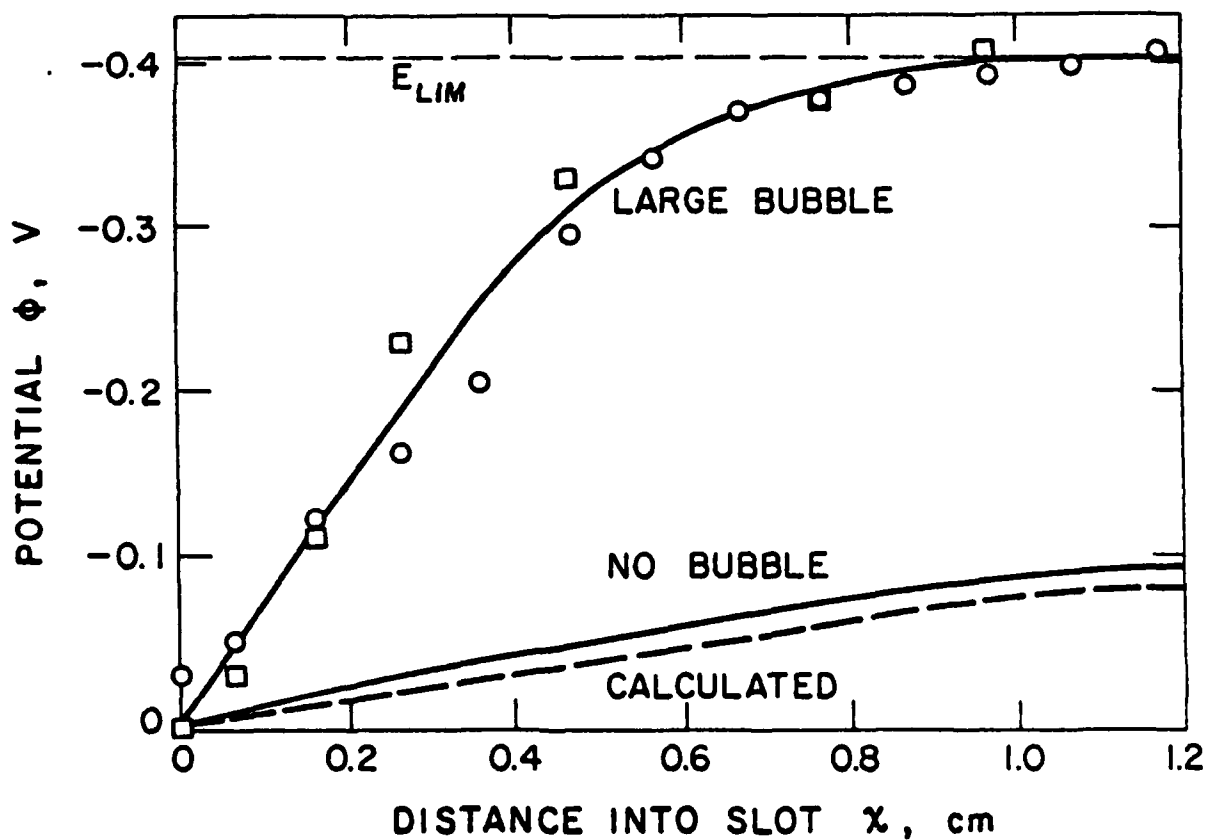


Figure 2. The measured potential profile as a function of distance  $x$  for crevices with and without bubbles during cathodic polarization at  $i_s = 52 \text{ A m}^{-2}$ . After Ateya and Pickering (2).

without in-place bubble formation. The upper curve corresponds to in-place bubbles of size comparable to the crevice cross section, as shown in Figure 1. For this situation the limiting potential,  $E_{LIM}$ , is reached near the bottom of the crevice ( $x > 0.9$  cm).

The slot in Figure 1 was relatively large in terms of real crevices and very large in terms of most cracks. However, in spite of the openness of the slot, the bubbles readily formed and filled the cross section. Similarly, bubble formation has been routinely observed within crevice-like slots in Cu, Ni and Fe samples (2). In the latter observations, made from the crevice opening, a transparent plastic was not used so that it was clear that the formation and stability of the in-place bubbles within the crevices were characteristic of metal crevices and not of the plastic surface used for visual observation (Figure 1). Large potential gradients were measured in all of these samples when the crevices contained in-place gas bubbles, as shown in Table I.

Table I. The measured solution potential,  $\phi_{x=L}$  and electrode potentials  $E_{x=0}$  and  $E_{x=L}$  where  $x \equiv 0$  at the crevice opening and  $x=L$  at its bottom (2).

<u>Metal</u>	<u>Solution</u>	$i_s, A m^{-2}$	$E_{x=0}, SHE, V$	$\phi_{x=L}, V$	$E_{x=L}, SHE, V$	Estimated $E_{LIM}, SHE, V$
Fe	0.5M Acetate, 0.5M Acetic Acid, (pH=5)	50	-0.9	-0.4	-0.5	$E_{mixed} = -0.4$
Ni	1M $HClO_4$	100	-0.7	-0.5	-0.2	$E_{mixed} = -0.1$
Cu	1M $HClO_4$	100	-0.7	-0.5	-0.2	$E_{equil} = 0.0$

Below, and in the region of contact of the bubbles with the iron (Figure 1), the iron underwent anodic dissolution during effective cathodic protection of the sample's outer surface, as revealed by the etched condition of the crevice wall (originally polished) in Figure 3. Other

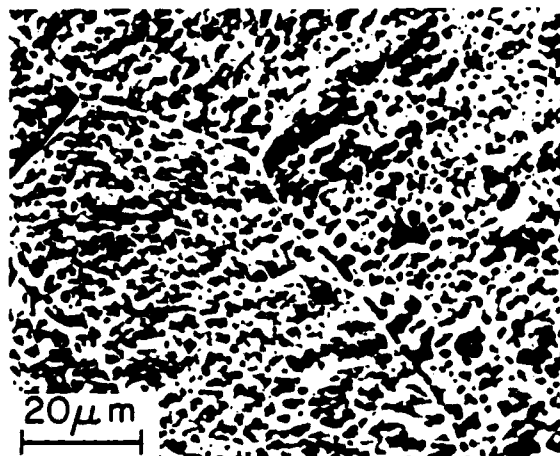


Figure 3. SEM micrograph illustrates etching of the crevice wall at the point of contact of the largest in-place bubble in Figure 1. After Harris and Pickering (17).

experiments were performed on the Fe, Ni and Cu samples to test for anodic dissolution within the crevices. In these experiments it was not possible to check for etching since the wall surfaces could not be polished prior to the experiment. Instead, solution was extracted from the crevice during the cathodic hydrogen evolution experiments, and analyzed for metal ions. The results of these analyses are shown in Table II. Estimated concentrations at the base of the crevices are also listed, and are much larger than the measured ("crevice") values in order to account for dilution of the crevice solution during extraction. In contrast to the dissolution of Fe and Ni in their crevices, the solution in the Cu crevice contained no copper ions within the accuracy of the measurement, in accord with the  $E_{LIM}$  condition as explained below.

Table II. The measured concentrations of  $Fe^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$  ions in samples of electrolyte extracted from within crevices and from bulk solution for the h.e.r. currents and solution compositions shown in Table I. (2).

Metal	Bulk [ $M^{2+}$ ] (ppm)	"Crevice" [ $M^{2+}$ ] (ppm)	Estimated [ $M^{2+}$ ] @ $x=L$ (ppm)
Fe	2	50	$\approx 5000$
Ni	0.2	15	$\approx 1000$
Cu	---	1	---

The change in solution potential,  $\phi$ , given in Figure 2, is related to the local electrode potential,  $E_x$ , in the cavity by (3)

$$E_x = E_{x=0} - \phi_x \quad (1)$$

Inserting the largest (measured) value of solution potential ( $\phi_{x=L} = -0.4V$ ) from Figure 2 and Table I, and the measured electrode potential at the outer surface ( $E_{x=0} = -0.9V$ ), Eq. 1 yields  $E_{x=L} = -0.5 V(SHE)$ . This is the most noble measured electrode potential in the crevice and is located below the large bubble in Figure 1. Since it is in the vicinity of the standard potential of Fe, anodic dissolution of iron is expected in the crevice and was observed (Table II). Hence, the situation in the crevices of iron containing in-place gas bubbles is as shown in Figure 4 where the  $\phi$  potential is sufficiently large to shift the local electrode potential (beneath and in the vicinity of the bubble) into the potential region of iron dissolution. A mirror-symmetry of Figure 4 is shown in Figure 5 for anodic polarization. Because current flows out of the cavity for anodic polarization, the electrode potential in the cavity is less, rather than more, noble than the value at the outer surface. The idea of an active pit base with an electrode potential which is  $10^2$  to  $10^3$  mV less noble than that at the outer passive surface goes back to the early discussions of Uhlig (4) and subsequently others (1,12,18,19).

The limiting potential,  $E_{LIM}$ , is the potential in the slot for which the iron dissolution and hydrogen evolution currents are equal ( $E_{mixed}$  in Table I). At the corresponding depth and below (for  $E_x < E_{LIM}$ ), current from the external polarization is essentially zero. However, it is finite to this depth so that, in principle,  $E_{LIM}$  can be reached for cathodic reactions, in contrast to those situations for anodic polarization where cavity growth, e.g., pit or crack, occurs by anodic metal dissolution at the pit base or crack tip. If  $E_{LIM}$  were to be reached for

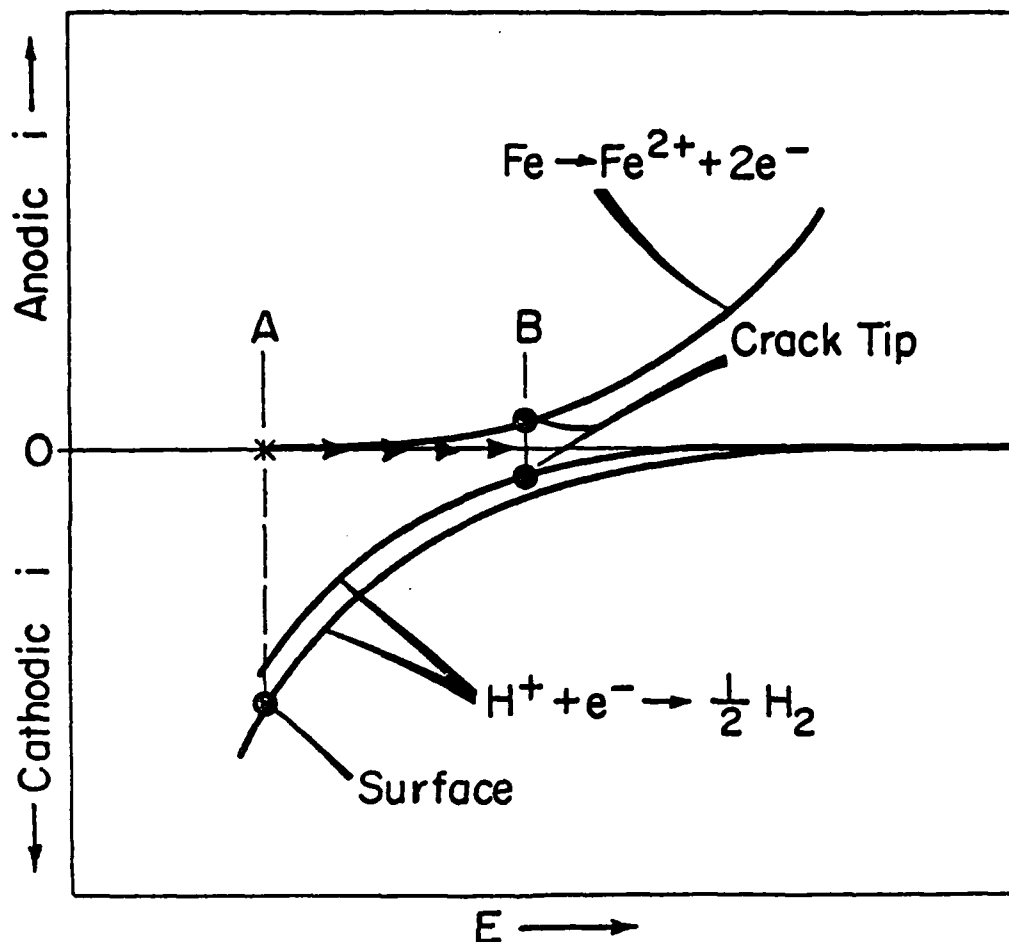


Figure 4. Schematic showing  $E_{x=L}$  (at the bottom of the crack) approaching  $E_B$  in the potential region of iron dissolution for cathodic polarization of the outer surface at  $E_A$  (2,4,12).  $E_{LIM} = E_B$ .

the latter ( $E_B$  in Figure 5), there would be zero net current flowing out of the cavity in which case the ohmic voltage would be zero and a potential less noble than  $E_A$  could not be supported in the cavity (4). On the other hand if  $E_{LIM}^A$  were to be reached during cathodic polarization, a finite  $i_{LIM}$  current could still flow into the cavity by virtue of the distribution of the h.e.r. on the side walls, and thereby maintain an ohmic voltage between the cavity opening and a depth into the cavity over which the h.e.r. occurs. Near, or at  $E_{LIM}$ , the situation is probably closest to what early workers referred to as the "occluded cell" in describing pitting although most emphasized ionic concentration gradients and did not include ohmic voltages as significant since measurement of their magnitude were largely unavailable.

The situation for Ni is qualitatively the same as shown in Figure 4 for iron. The situation for Cu is different in that the copper anodic dissolution curve does not overlap the h.e.r. cathodic polarization curve. It follows that  $E_{LIM}$  for the crevice in Cu is the equilibrium potential for the h.e.r.,  $E_{equil}$  (Table I), for the ionic concentrations existing in the crevice (4).

#### Mathematical Modeling

Mathematical modeling of the h.e.r. in crevices has been successful in the case of crevices free of gas (dashed curve in Figure 2). An important

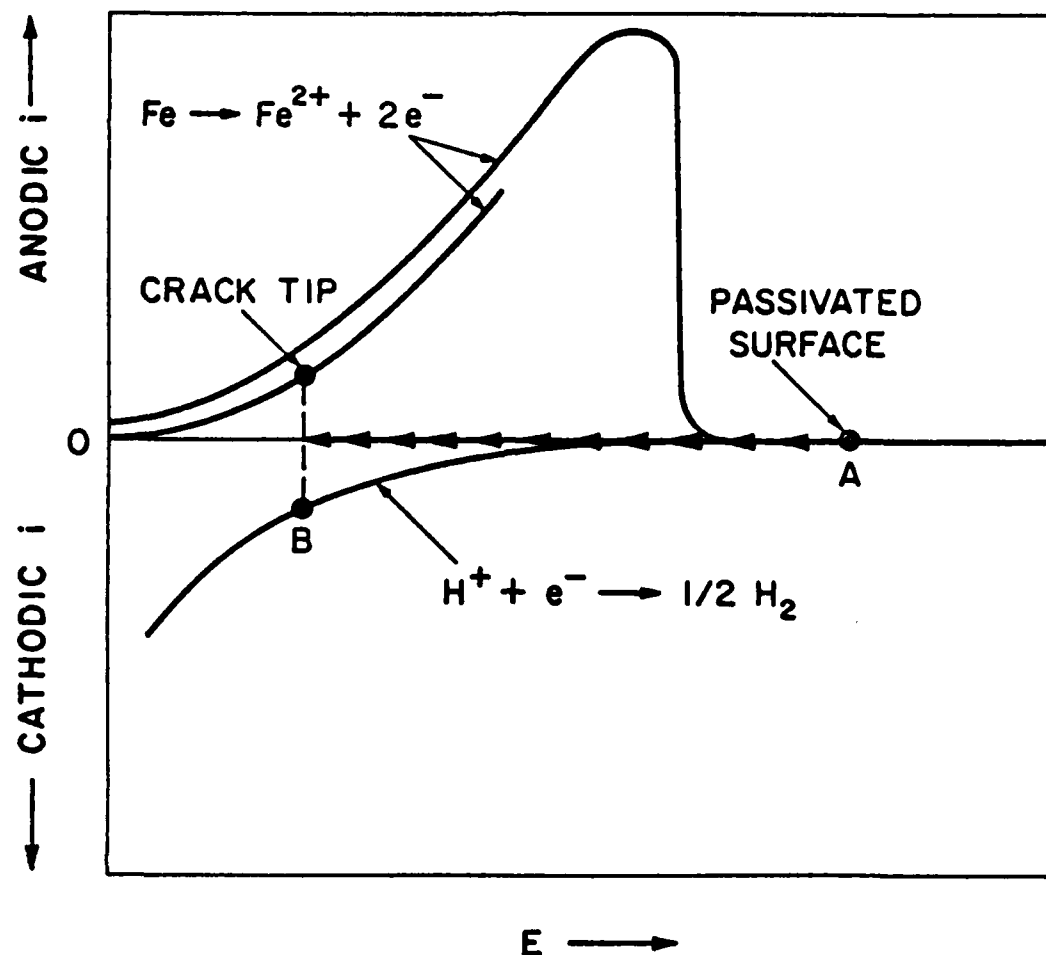


Figure 5. As in Figure 4 but for anodic polarization (1,3,5.12).  
 $E_{x=L}$  approaches  $E_B$  for  $E_{x=0} = E_A$  (4).  $E_{LIM} = E_B$ .

feature of these models is that they include the h.e.r. on the crevice walls and treat it as an unknown in the calculation (2). Let us consider the h.e.r. in a simple strong acid  $HY$  of monovalent ions and a crevice geometry shown in Figure 6. The cross section of the crevice is a rectangle of thickness  $a$  and width  $b$ , and its depth is  $L$  such that  $a \ll L$  and  $a \ll b$ , in which case the h.e.r. can be considered to occur only on the outer surface and on the crevice (or crack) walls. A more precise condition for validity of the equations is  $X \gg a$  where  $X$  is a characteristic distance defined below.

The fluxes,  $j$ , of the  $H^+$  and  $Y^-$  ions in the  $x$  direction within the crevice/crack are

$$j_{H^+} = -D_{H^+} \left( \frac{dc_{H^+}}{dx} + c_{H^+} \frac{F}{RT} \frac{d\phi}{dx} \right) = \frac{i}{F} \quad (2)$$

$$j_{Y^-} = -D_{Y^-} \left( \frac{dc_{Y^-}}{dx} - c_{Y^-} \frac{F}{RT} \frac{d\phi}{dx} \right) = 0 \quad (3)$$

where  $D$  and  $c$  are the diffusivity and concentration of the indicated species, respectively,  $\phi$  is the solution potential with respect to  $\phi = 0$  at  $x = 0$ , and  $i$  is the (unknown) current density distribution on the crack walls for the impressed h.e.r. current on the sample surface,  $i_s$ . The



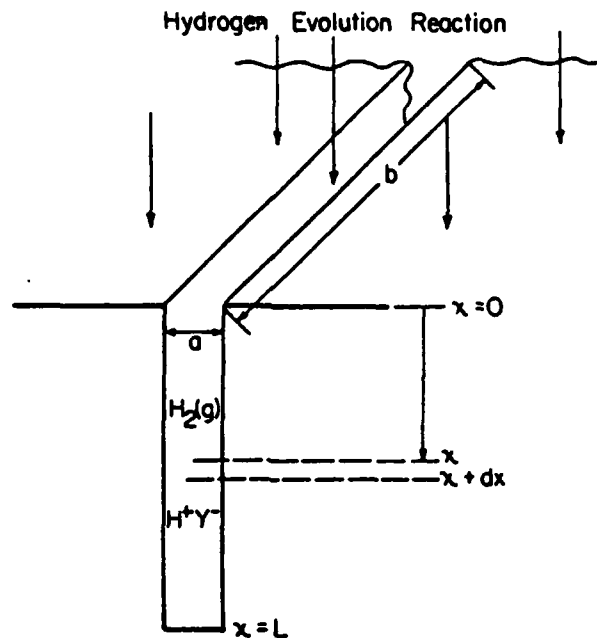


Figure 6. Model of crack.

electroneutrality equation is

$$c_{H^+} = c_{Y^-} = c \quad (4)$$

The boundary condition at  $x=0$  for a bulk acid concentration of  $c_0$  is

$$c_{H^+} = c_{Y^-} = c_0 \text{ and } \psi \equiv 0 \text{ at } x=0 \quad (5)$$

A boundary condition at  $x = L$  evolves from the calculation which can be found elsewhere (2). Equations (2) to (5) are then used to obtain  $\psi$ ,  $c_{H^+}$ ,  $c_{Y^-}$  and  $i$  as functions of  $x$ ,  $c_0$ ,  $a$  and  $i_s$ .

The characteristic length  $X$  is obtained as (2)

$$X = (D_{H^+} c_0 F a / i_s)^{1/2} \quad (6)$$

and the solutions for the unknowns are

$$\psi = \frac{RT}{F} \ln \frac{\cosh [(L-x)/X]}{\cosh [L/X]} \quad (7)$$

$$c_{H^+} = c_{Y^-} = c_0 \frac{\cosh [(L-x)/X]}{\cosh [L/X]} \quad (8)$$

$$i = i_s \frac{\cosh [(L-x)/X]}{\cosh [L/X]} \quad (9)$$

Equations (7) and (1) may be used to estimate the depth at which the electrode potential assumes a sufficiently noble value for anodic dissolution of the metal, within the constrain of  $E_{LIM}$ . Equations (8) and (9) may be used to estimate the depth at which depletion of  $H^+$  and decrease in the hydrogen evolution rate became significant, e.g., the depth corresponding to the equilibrium pH of the hydrolysis reaction. Equation (7) is the dashed curve in Figure 2 and compares well with the measured curve (lower solid curve) for experimental conditions which, although not exactly matching the model conditions, are for a bubble-free crevice.

One of the most important features of Equation (7) using also Equation (6) is that it includes the slot "openness",  $\alpha$ , in its solution. Thus, evaluation of Equation (7) shows that  $\phi$  becomes more negative as the crack dimension  $\alpha$  decreases, and from Equation (1)  $E_x$  becomes more noble. This strong effect of the crack openness on the local solution potential in Equation (7) is plotted in Figure 7. It shows that in the case of "sharp" cracks ( $\alpha \approx 50 \mu\text{m}$ ) very large (negative)  $\phi$  values are to be expected. This is quite a different situation than for most other models of mass transport for cathodic or anodic polarization, which do not show a strong relation between the ohmic voltage and the openness of the crack or crevice. Thus, the salient point is that this model successfully predicts large ( $10^2$  to  $10^3$  mV) ohmic voltages without incorporating constrictions such as gas bubbles in the cavity, but only for sharp, closed cracks, e.g.,  $\alpha \approx 50 \mu\text{m}$  for  $i_s = 100 \text{ A m}^{-2}$ . For more open cracks or crevices, the  $10^{-2}$  to  $10^{-3}$  mV measured ohmic voltages can only be accounted for by the presence of constrictions in the cavity. Similarly, Equations 8 and 9 show that the concentration and current-density gradients also become steeper as  $\alpha$  decreases, as shown in Figures 8 and 9, respectively.

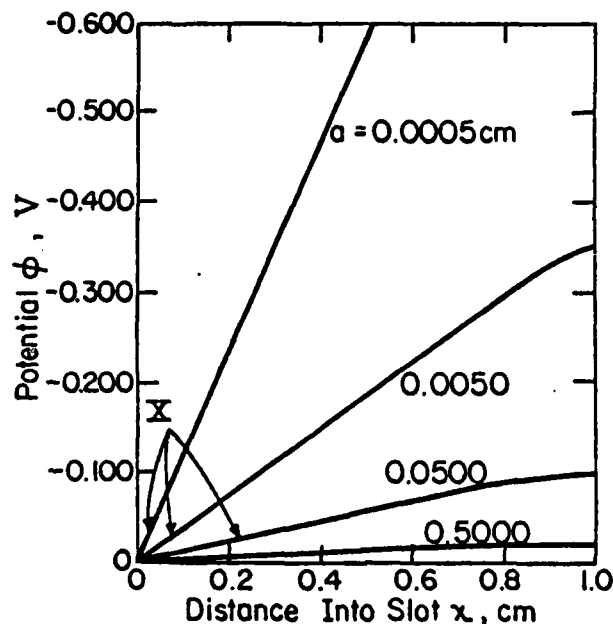


Figure 7. Effect of crack "openness",  $\alpha$ , on the solution-potential profile inside a crack of depth  $L = 1$  cm for  $i_s = 100 \text{ A m}^{-2}$  (2).

#### Conclusions

This paper reviews and elaborates on the relation between the local electrode potential in cavities and two parameters; accumulated gas in the cavity and the narrowness of the electrolyte path, e.g., the sharpness of a crack. It does this by considering experimental and theoretical results for both anodic and cathodic polarization. The discussion includes and elaborates on the limiting electrode potential within cavities.

The following observations are made:

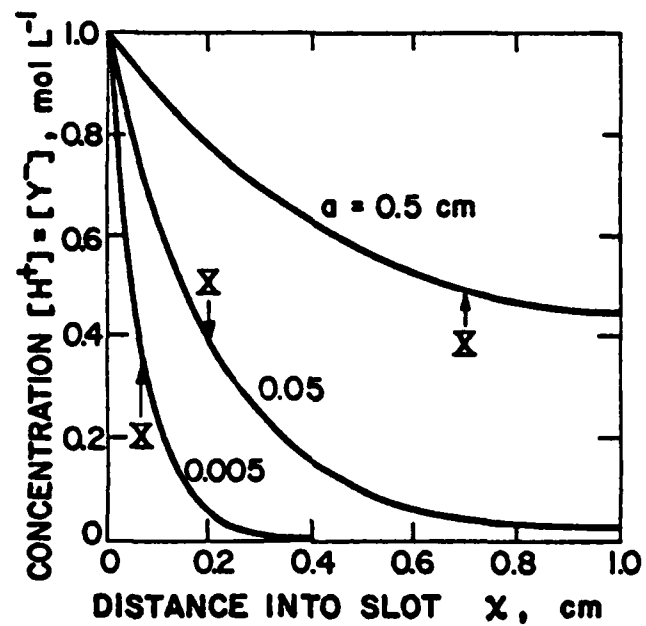


Figure 8. As in Figure 7 but illustrating the effect of  $\alpha$  on the concentration gradients of  $H^+$  and  $Y^-$  ions within the slot (2).

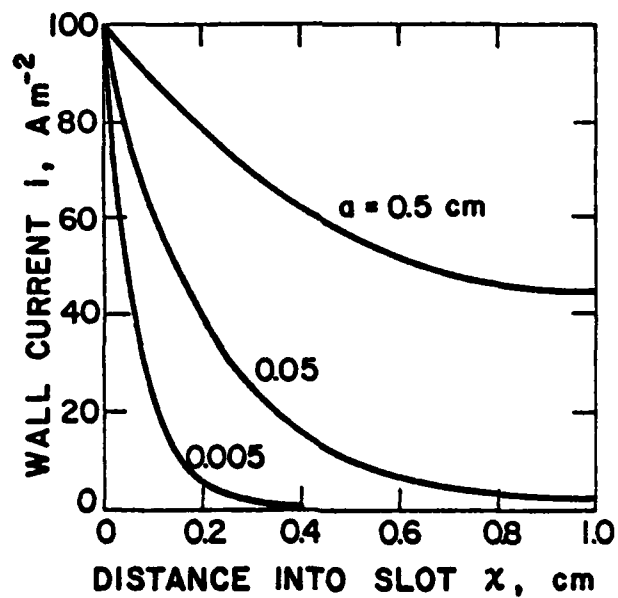


Figure 9. As in Figure 7 but illustrating the effect of  $\alpha$  on the current distribution of the h.e.r. on the slot walls (2).

- (1) Ohmic voltages of several hundred mV which have been measured in growing pits, wide crevices or open cracks can not be explained by simply considering the resistivity of the solution as was suggested in much of the early literature.
- (2) Two explanations of these large ohmic voltages exist. Both rely on making the cavity very narrow. In the case of "open" cavities (pits, crevices or cracks), gas or possibly solid corrosion product accumulation in the cavity is important. In the case of wharp cracks or crevices, narrowness is intrinsic in the form of corrosion (small  $a$  in Figure 6) and can be adequate, by itself, i.e.,<sup>3</sup> without involving constrictions, to produce large ( $10^2$  to  $10^3$  mV) ohmic voltages.
- (3) For sharp cracks or gas-filled pits or crevices the local electrode potential may approach or equal the limiting potential,  $E_{LIM}$ , and be largely independent of the applied (anodic or cathodic) polarization at the external surface of the sample.
- (4) Reactions in cavities are a function of the local electrode potential and solution composition and may be different than those at the external surface e.g., metal dissolution may occur at a crack tip during effective cathodic protection of its outer surface.

#### Acknowledgement

Financial support by the Office of Naval Research under Contract No. N00014-81-K-0025 and by CONICIT, Venezuela, (A.V.) is gratefully acknowledged.

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