



The Role of Oxygen on the Stability of Crevice Corrosion

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Crevice corrosion can initiate in a spontaneously active metal/electrolyte system even with some appreciable oxygen concentration in the crevice electrolyte, as indicated by the measured instantaneous milliamperic current and active $E_{x=L}$ potential values at the bottom of the crevice. However, for crevice corrosion to occur, the oxidant concentration has to be below a certain level, set by the metal/electrolyte system and the experimental conditions. Similarly, the oxidant concentration needs to be increased to some higher level to terminate an on-going crevice corrosion process. Reinitiation of crevice corrosion (on a passive crevice wall) is much more difficult than the original initiation. This is because the passive crevice wall provides a small ionic current which generates only a modest IR voltage that cannot shift the potential far enough on the crevice wall to reach the active region. Oxidant reduction at the anodic sites on the crevice wall resulted in a significant reduction in the ionic current, I , and hence in IR. This decrease in IR caused $E_{x=L}$ to increase to a value in the passive region which resulted in passivation of the entire crevice wall and termination of the crevice corrosion process. Conversely, removal of the oxidant caused I to increase and $E_{x=L}$ to shift negatively back to the active region resulting in reactivation of crevice corrosion.

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It is generally believed that oxygen depletion may be a prerequisite for the initiation and stabilization of crevice corrosion.¹⁻⁴ Within this context, Yao *et al.*⁵ found that by increasing the concentration of dissolved oxygen in the electrolyte within a crevice in titanium, the incubation time increased. In an earlier work, Ruskol and Klinov⁶ found that oxygen depletion increased with time, depth into the crevice, and decrease in the crevice gap dimension.

Crevice corrosion is characterized by a highly constricted geometry, which hinders the transport of the ionic species in and out of the crevice, and leads to the separation of the anodic and cathodic reactions and resulting large IR voltages, and to changes in the composition of the crevice electrolyte, *e.g.*, localized acidification and chloride ion accumulation. The theory of achieving a critical composition within the crevice electrolyte, *e.g.*, localized acidification, attributes the initiation and stabilization of crevice corrosion to the breakdown of the passive film on the crevice wall.^{2,3}

On the other hand, the IR theory stipulates that crevice corrosion is initiated and stabilized when the electrode potential, $E(x)$, at some distance into the crevice is in the active region of the polarization curve that exists on the crevice wall.⁷ An induction period is often required to achieve this condition, *i.e.*, the active peak is initially too small, or nonexistent as in spontaneously passive metal/electrolyte systems. During this (induction) time, the composition of the crevice electrolyte needs to change in the direction of destabilizing the passive film and forming, and increasing the size of, an active peak in the polarization curve of the crevice electrolyte. The induction period ends and crevice corrosion starts when the IR voltage associated with the ionic current flowing through the crevice electrolyte places the bottom of the crevice in the potential region of the growing active peak.⁷ Thus, when the active peak reaches the critical size for the given crevice aspect ratio, solution resistivity, and polarization conditions, crevice corrosion begins and is stabilized by the IR voltage. The latter maintains the active region of the polarization curve on the crevice wall as described elsewhere.⁷ Acidification and/or chloride ion accumulation in the crevice electrolyte initiates and enlarges an active peak for many spontaneously

passive systems. This IR theory⁷ has been adopted by others to describe the localized corrosion behavior of spontaneously passive systems.^{8,9}

In the case of spontaneously active metal/electrolyte systems, for conditions in which the aspect ratio, AR, of the crevice is greater than the critical aspect ratio, AR_c , crevice corrosion occurs immediately upon polarizing the outer surface of the sample into the passive region.¹⁰ Thus, no change in composition of the crevice electrolyte is needed for the start of crevice corrosion in these cases. This immediate onset of crevice corrosion when $AR > AR_c$ was experimentally demonstrated in several spontaneously active systems.¹¹⁻¹⁵

Since the induction time was zero in these experiments, acidification or chloride ion accumulation could not occur in the crevice electrolyte prior to the start of crevice corrosion. Furthermore, a specially designed cell/procedure was used that maintained either the pH or the entire crevice electrolyte at essentially the same pH or composition as the bulk electrolyte, allowed visual observation of the crevice wall, and permitted measurement of the $E(x)$ profile.¹¹⁻¹⁵ As a result, it was also determined that crevice corrosion continued indefinitely in the region of the crevice wall where the $E(x)$ potential was in the active region of the polarization curve existing on the crevice wall. From these proof-of-concept experiments, it was clear that crevice corrosion was solely caused by the IR voltage in these spontaneously active systems when $AR > AR_c$.

The objective of this paper is to provide an additional critical test of the IR mechanism of crevice corrosion in spontaneously active systems and to investigate the role of oxidants in the crevice corrosion process. We are presenting here the results of novel experiments in which various oxidants were suddenly added to the crevice electrolyte in order to quickly shift the $E(x)$ values within actively corroding crevices from the active to the passive regions, and to see if the crevice corrosion process was simultaneously terminated. The experiments were designed to simultaneously measure the potential at the bottom of the crevice, $E_{x=L}$, and the crevice corrosion (ionic) current, I , flowing out of the crevice, before and after an oxidant was added to the crevice electrolyte. The results of these measurements also have an important bearing on the questions of oxygen depletion and the separation of the anodic and cathodic partial reactions as a requirement for the onset of IR-induced crevice corrosion.

Experimental

The iron (99.95%) sample was placed into a Teflon mount so that only two of its surfaces (crevice wall: 5 × 10 mm, and external surface: 5 × 20 mm) were exposed to the electrolyte. These surfaces were polished with 0.5 μm alumina to a mirror-like finish and

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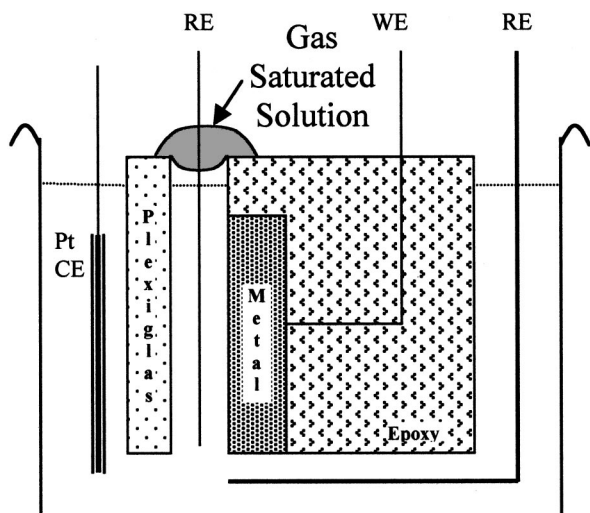


Figure 1. Experimental setup of the iron sample in a Teflon mount. The sample is in the upside-down orientation, enabling gas-saturated electrolyte to be added at the top opening of the crevice.

cleaned with acetone and methanol. Plexiglas plates allowing various opening dimensions, $a = 0.1$ to 0.6 mm, were placed over the one surface of the iron sample to form the crevice of 10 mm depth. The mounted sample was oriented upside down such that the entire crevice wall and only part of the mount were submerged in the solution, as shown in Fig. 1. In this arrangement the lower crevice opening is available to the electrolyte while the upper opening (which is not accessible to the electrolyte) enables insertion of a potential microprobe into the crevice, and addition of drops of gas-saturated electrolyte to the crevice electrolyte (Fig. 1). This upside-down orientation also promotes convective mixing of the bulk and crevice solutions, since the denser electrolyte containing the corrosion products can flow downward through the crevice opening under the influence of gravity and the lighter bulk solution can flow upward.¹²⁻¹⁴ The tip of the fine (<0.1 mm diam Luggin capillary) microprobe was located inside the crevice furthest from its opening, throughout the experiment, in order to continuously measure the electrode potential, $E_{x=L}$, at the $L = 10$ mm distance into the crevice. The external surface of the iron sample was polarized to 0.800 V_{SCE} in the passive region using a potentiostat controlled by the saturated calomel electrode (SCE) located at the outer surface of the sample (Fig. 1), in an aqueous solution of 0.5 M $Na_2SO_4 + 0.1$ mM $NaCl$ (pH 6) for the duration of the experiment. The $E(x)$ profile on the crevice wall was also intermittently measured by moving the potential probe from $x = 0$ to $x = L$. The polarization curves were measured using similarly prepared crevice-free samples. Other details of the experimental design are available elsewhere.¹⁵

To determine the effect of oxidant concentration in the crevice electrolyte on the crevice corrosion process, bulk electrolyte saturated with either N_2 , air, or O_2 was added to an actively corroding crevice at different times using a syringe at the top of the metal in Fig. 1. Drops of the gas-saturated electrolyte, added to the top opening of the crevice (Fig. 1), flowed into the crevice under the force of gravity, replacing the (deaerated) crevice electrolyte. Commercial grade 3% H_2O_2 was also similarly added to the crevice to determine its effect on the crevice corrosion process. Similar experiments were performed after crevice corrosion was terminated by the oxidant addition, in order to determine if crevice corrosion could be reinitiated.

Results and Discussion

Polarization curves, $E(x)$ profiles, and IR-induced crevice corrosion.—Figure 2 shows the polarization curve of Fe in a nearly

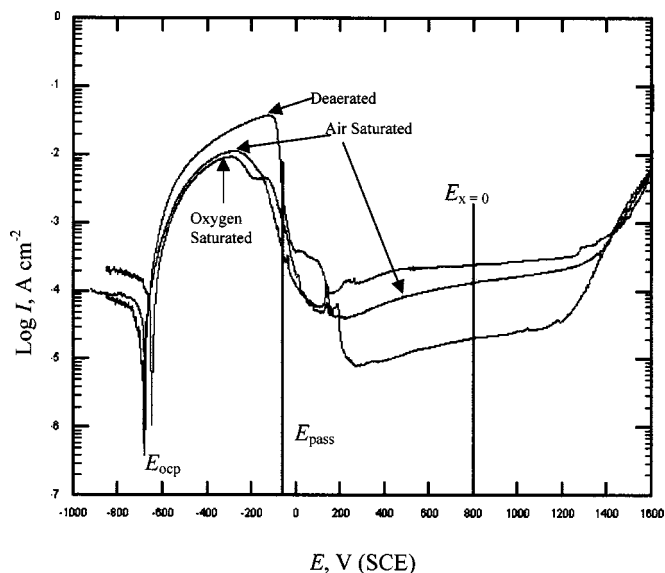


Figure 2. Polarization curves of iron in deoxygenated, air-saturated, and O_2 -saturated 0.5 M $Na_2SO_4 + 0.1$ mM $NaCl$ solution; scanned from 1.600 to -0.800 V_{SCE} at 1 mV s^{-1} .

neutral solution (pH 6) of deaerated 0.5 M $Na_2SO_4 + 0.1$ mM $NaCl$. It has a large active peak and a distinct active-to-passive transition centered at $E_{pass} \approx -0.05$ V_{SCE} accompanied by a decrease of over two orders of magnitude in the anodic current. The polarization curves for iron in air and O_2 -saturated solutions (pH 6) are similar to the deaerated solution and are also shown in Fig. 2. The polarization curve of iron in the hydrogen peroxide solution revealed less of its active peak as a result of a more positive open-circuit (corrosion) potential, but was otherwise similar to the others. The open circuit potentials (OCPs) were $E_{oc} = -0.69$, -0.68 , and -0.62 V_{SCE} for the deaerated, air-saturated, and O_2 -saturated solutions at pH 6; and -0.13 V_{SCE} for the hydrogen peroxide solution. An OCP ($E_{oc} = -0.74$ V_{SCE}) and polarization curve for a deaerated 0.5 M $Na_2SO_4 + 0.1$ mM $NaCl$ solution of pH 4.5 were also measured; the latter was similar to the other polarization curves in Fig. 2.

Figure 3 shows some *in situ* measured, $E(x)$ profiles on the walls

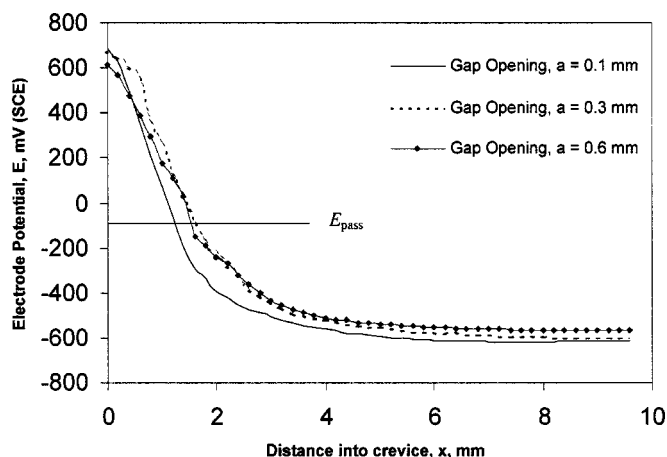


Figure 3. Measured electrode potential profiles inside crevices of different opening dimension for the upside-down orientation at approximately 50 min of crevice corrosion of iron in 0.5 M $Na_2SO_4 + 0.1$ mM $NaCl$ solution with $E_{x=0} = 0.800$ V_{SCE} .

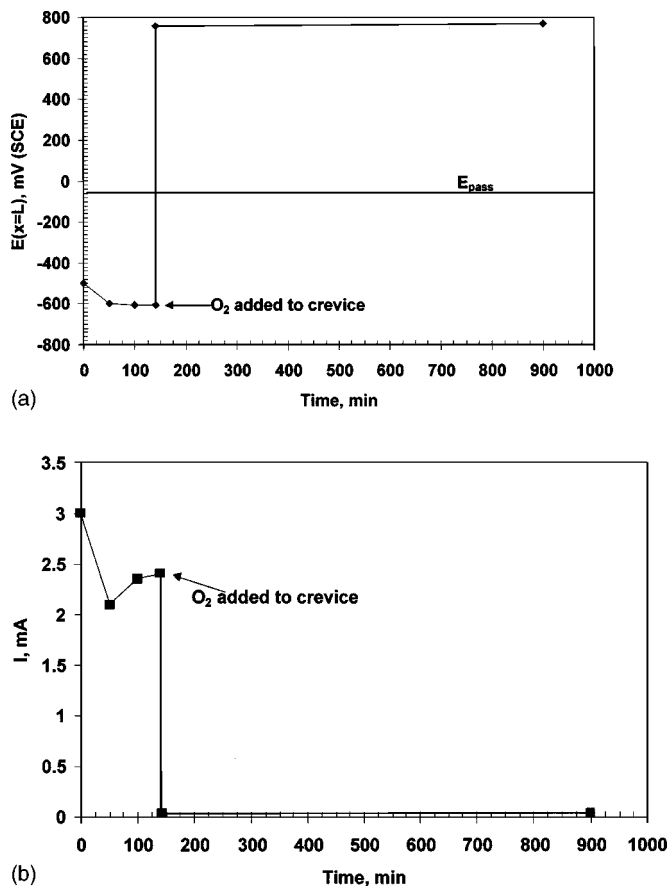


Figure 4. The initial stable crevice corrosion of iron in an air-saturated crevice electrolyte is indicated by (a, top) $E_{x=L} \approx -0.65$ V_{SCE} in the active region and (b, bottom) I in the milliamperic range. The sudden large changes in $E_{x=L}$ and I at 140 min when 20 mL of O₂-saturated electrolyte was added to the crevice electrolyte indicate the termination of crevice corrosion: (a) $E_{x=L}$ jumped to near $E_{x=0} = 0.800$ V_{SCE} in the passive region and (b) I dropped to the passive value.

of crevices with gap opening dimensions of $a = 0.1, 0.3,$ and 0.6 mm that were polarized at $E_{x=0} = 0.800$ V_{SCE} and were undergoing crevice corrosion in 0.5 M Na₂SO₄ + 0.1 mM NaCl. Note the remarkable (>1 V) shift in potential in the active direction over a distance of 2 mm at the crevice mouth. These $E(x)$ profiles confirm that the visually observed corrosive attack on the crevice wall and immediately measured milliamperic currents are due to the IR-induced form of crevice corrosion, *i.e.*, the corroding part of the crevice wall, had E values that were negative of the E_{pass} value (Fig. 2) and, hence, were in the active region of the polarization curve, as reported previously for this and other spontaneously active systems.¹¹⁻¹⁵ In these measured profiles, of which there were more than 25, there was also a perceptible change in the measured limiting potential, E_{lim} , deep inside the crevice to more positive values (from approximately $E_{\text{lim}} = -0.63$ to approximately $E_{\text{lim}} = -0.57$ V_{SCE}) as the opening dimension of the crevice decreased from $a = 0.6$ mm to $a = 0.1$ mm. This trend of E_{lim} can be seen in Fig. 3. These measured E_{lim} values are somewhat positive of the theoretical limiting values, which for base metal systems, is the OCP for the deaerated crevice electrolyte, *i.e.*, $E_{\text{OC}} = -0.69$ V_{SCE} from the deaerated polarization curve in Fig. 2.^{7,16} This positive shift of the measured E_{lim} values from the theoretical value has been reported as 20 to 200 mV for other spontaneously active systems.¹⁴ In the experiments to follow in which the $E_{x=L}$ value (where $L = 10$ mm) was measured continuously throughout the experiment,

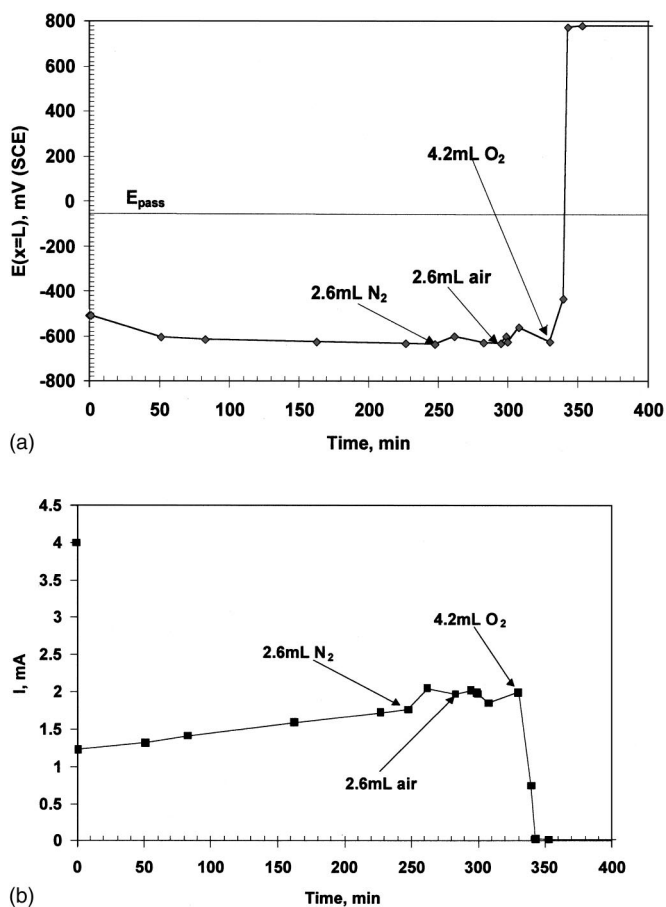


Figure 5. $E_{x=L}$ (a, top) and I (b, bottom) transients show immediate crevice corrosion of iron; no destabilization of crevice corrosion by air or N₂-saturated electrolyte, whereas O₂-saturated electrolyte (at 328 min) abruptly terminated crevice corrosion; (a) $E_{x=L}$ shifted from ~ -0.65 V to ~ -0.78 V_{SCE} in the passive region and (b) I dropped to the passive value.

it can be seen from Fig. 3 that the measured $E_{x=L}$ value is the E_{lim} value.

Upon applying the $E_{x=0} = 0.800$ V_{SCE} potential (at $t = 0$) to the outer surface of the iron crevice sample in the air-saturated electrolyte, crevice corrosion began immediately, as revealed by the immediately measured milliamperic level current and $E_{x=L} \approx -0.65$ V_{SCE} potential in the active peak region of the polarization curve (Fig. 2), Fig. 4-8. This instantaneous onset of crevice corrosion has been demonstrated before and is a strong confirmation that acidification and/or other solution concentration changes are not the critical factors in stabilizing the crevice corrosion process in this and other spontaneously active, metal/electrolyte systems.¹¹⁻¹⁵

Oxidant-induced termination of crevice corrosion.—At an arbitrary time during the initial stable crevice corrosion (see Fig. 4 to 8), electrolyte containing an oxidant concentration was added to the crevice, effectively replacing the deaerated crevice electrolyte, in order to determine the effect of the oxidant on destabilizing crevice corrosion. It was found that when the deaerated crevice electrolyte was replaced with O₂-saturated electrolyte, sudden termination of the crevice corrosion process occurred in crevices with gap openings of $a \leq 0.25$ mm. This role of crevice opening dimension, a , or aspect ratio, L/a , in determining the effectiveness of the oxidant in terminating the crevice corrosion process is shown in Table I. In the O₂ column in Table I, termination of crevice corrosion occurred for the smaller a values (as indicated by the x symbols in the O₂ col-

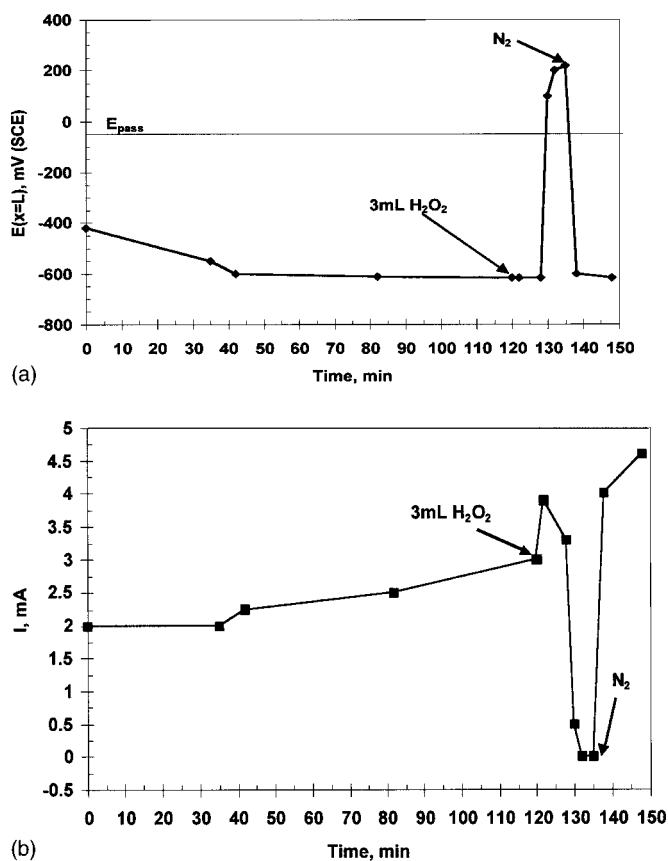


Figure 6. (a, top) $E_{x=L}$ and (b, bottom) I transients show immediate crevice corrosion of iron, whereas upon adding H_2O_2 solution to the crevice electrolyte at 120 min, crevice corrosion abruptly stopped after a few minutes of gas bubble formation and fluctuation of $E_{x=L}$ and I and then was re-established upon adding a N_2 -saturated electrolyte (at 135 min).

umn) when O_2 -saturated electrolyte was added to the crevice, but not for the larger a values (as indicated by the o symbols in the O_2 column).

Representative abrupt changes in ionic current, I , and potential, $E_{x=L}$, showing this effect of O_2 in suddenly destabilizing crevice corrosion, are given in Fig. 4. In this experiment, 20 mL of an O_2 -saturated electrolyte was added to the top opening of the crevice at the 140 min mark of stable crevice corrosion. For this oxygen level and gap opening ($a = 0.10$ mm with $L = 10$ mm), sudden deactivation of the on-going crevice corrosion process occurred. The potential at the crevice bottom, $E_{x=L}$, which is maintained by the large IR voltage (~ 1.45 V), shifted within (tens of) seconds to a value above E_{pass} , i.e., from $E_{x=L} \approx -0.65$ V_{SCE} to within a few tens of millivolts of $E_{x=0} = 0.800$ V_{SCE}. However, to show the rapidity of this transition in the experiments, more data points are required in Fig. 4-8. This new $E_{x=L}$ value at a few tens of millivolts below $E_{x=0} = 0.800$ V_{SCE} means that the IR voltage is much smaller (tens of millivolts), as a result of the much reduced I that is associated with O_2 reduction occurring at or close to the anodic sites on the crevice wall. Thus, the simultaneous decrease in the measured I to nearly zero, is commensurate with the electrode potential at the bottom of the crevice, $E_{x=L}$, now having a more positive value in the passive, rather than active, region. Thus, the entire crevice wall, as well as the outer surface of the iron sample, are in the passive region of the polarization curve.

Beyond the 140 min mark in Fig. 4, the passive state continued for the remaining several hours of these experiments, i.e., long after the added oxygen should have been consumed; this indicates that

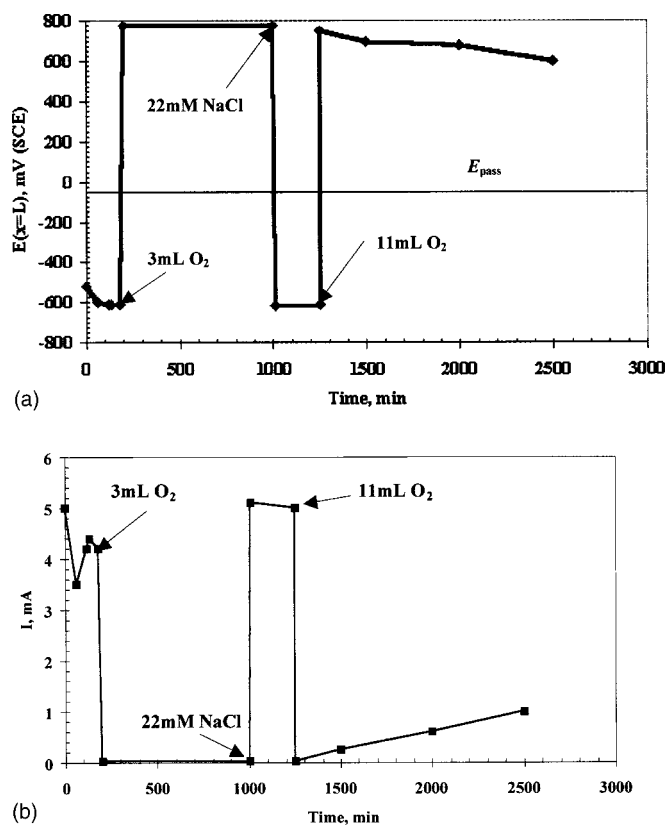


Figure 7. $E_{x=L}$ (a, top) and I (b, bottom) transients show that after terminating crevice corrosion with O_2 -saturated electrolyte at 200 min, reinitiation occurred upon the addition to the crevice electrolyte of 10 mL of bulk electrolyte which was 22 mM in NaCl (at 1000 min), followed again by termination when the O_2 -saturated electrolyte was added at 1250 min.

reinitiation was more difficult than was the original initiation of crevice corrosion. The time needed for the depletion of oxygen from the crevice can be calculated from the equation, $t = nFCa/i_{pass}$, where n is the number of equivalents per mole for oxygen reduction, F is the Faraday constant, C is the saturation concentration of oxygen for water in contact with air at room temperature, a is the gap opening dimension of the crevice (thickness of the crevice electrolyte), and i_{pass} is the passive current density on the crevice wall.² Using $C = 2 \times 10^{-7}$ mol cm⁻³ (Ref. 2) and $i_{pass} = 10^{-5}$ A/cm² (Fig. 2), the calculated times for consumption of the oxygen are $t = 80$ to 200 s for $a = 0.01$ to 0.025 cm. This calculation assumes that oxygen will arrive at the surface as fast as it is needed to satisfy the anodic current, $i_{pass} = 10^{-5}$ A/cm². This assumption is validated by calculating the time for oxygen to diffuse to the surface from the maximum distance, $a = 0.01$ to 0.025 cm, using the mean square displacement equation, $t = x^2/2D$, and $D = 10^{-3}$ cm²/s. These times were 2.5 and 15 s.

Thus, reactivation of this passive crevice wall was more difficult than the original initiation of crevice corrosion with the crevice wall in the active state. This is a consequence of the fact that the passive current on the crevice wall produced a much smaller I flowing through the crevice electrolyte than the initial active currents produced. Hence, the IR voltage within the crevice electrolyte was also much smaller for the passive crevice wall. Thus, it is not surprising that the passive state with only a negligibly small passive current and a measured potential well in the passive region at the bottom of the crevice, $E_{x=L} \leq 0.80$ V_{SCE}, remained in this state rather than reverting back to the active state after depletion of the added O_2 in the crevice electrolyte. This result (no reactivation of crevice corro-

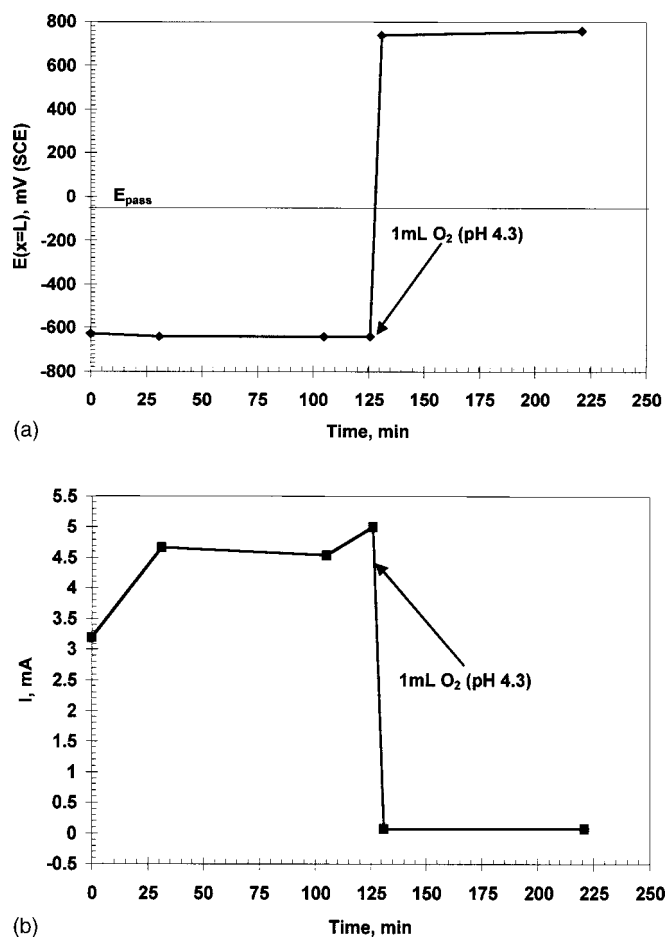


Figure 8. $E_{x=L}$ (a, top) and I (b, bottom) transients show crevice corrosion of iron from 0 to 120 min, whereas upon adding O₂-saturated solution of pH 4.3 to the crevice electrolyte, crevice corrosion stopped abruptly with the passive state persisting on the crevice wall to the end of the experiment.

sion after depletion of the dissolved O₂) was observed in several experiments with different gap dimensions, $0.10 < a \leq 0.25$ mm, for which crevice corrosion had been terminated by the O₂ addition to the crevice.

To study the effect of increasing oxidant concentration on the stability of crevice corrosion, bulk electrolytes saturated with N₂, air, or O₂ were added in succession to a crevice with a gap opening of 0.25 mm, Fig. 5 and Table I. At 250 min of stable crevice corrosion, 2.6 mL of a N₂-saturated electrolyte were added to the crevice electrolyte. After minor disturbances in $E_{x=L}$ and I , both remained at their original (crevice corrosion) values, *i.e.*, $E_{x=L} \approx -0.65$ V_{SCE} and $I \approx 2$ mA, as shown in Fig. 5. Then (at 295 min), 2.6 mL of air-saturated electrolyte were added to the crevice. Again, essentially no change occurred in the $E_{x=L}$ and I values. Thus, neither the deaerated nor the air-saturated solution was able to destabilize the crevice corrosion process. This was expected since crevice corrosion originally started in an air-saturated crevice electrolyte when the outer surface of the sample was initially polarized into the passive region at $E_{x=0} = 0.800$ V_{SCE}.

Finally, the addition of 4.2 mL of an O₂-saturated electrolyte to the crevice (at 330 min) caused sudden destabilization of the crevice corrosion process, as revealed by the sharp decrease of I to a stable, nearly zero value, and increase of the potential at the bottom of the crevice to a stable $E_{x=L} \approx 0.750$ V_{SCE}. The O₂ addition also terminated crevice corrosion when there were no prior additions of N₂

Table I. Effect of N₂, air, O₂, or H₂O₂ additions to the crevice electrolyte on terminating or reinitiating crevice corrosion. Substances that were added have either an o, x, y, or z in the column for the given a value, where o is corrosion continued, x is corrosion stopped, y is no reinitiation, and z is corrosion reinitiated. Additions were made sequentially from left to right. No entry (blank) means that substance was not added.

Gap size a (mm)	Effect of additions to crevice				
	N ₂	air	O ₂	H ₂ O ₂	N ₂
0.1			x		
0.2			x		y
			x		y
0.25			x		
			x		
			x		
	o	o	x		
	o	o	x		
0.3				x	
				x	z
				x	z
		o	o		
0.35		o	o	x	z
			o		
			o		
0.4				x	y
0.5			o	x	
0.6			o	x	y

and air, as described above for the experiment in Fig. 4 and in other experiments with $0.1 \leq a \leq 0.25$ mm in Table I.

The explanation of the destabilization of the crevice corrosion process shown in Fig. 5, is the same as for Fig. 4: With the replacement of the original crevice electrolyte with electrolyte of higher oxygen content, *i.e.*, stronger oxidizing power, sufficient cathodic reaction occurred inside the crevice at the anodic sites to significantly reduce I (flowing out of the crevice) and the IR voltage. Thus, at $x = L = 10$ mm the potential, $E_{x=L}$, is now more positive and in the passive region. Subsequently, after the oxidant is depleted, the small passive current on the crevice wall produces small I and IR values, so that $E_{x=L}$ is stabilized by a small IR voltage (tens of millivolts) at a value only slightly less positive than the applied $E_{x=0} = 0.800$ V_{SCE}.

As the gap opening increased to $a > 0.25$ mm, the ability of the O₂-saturated electrolyte to destabilize the crevice corrosion process significantly decreased. In several experiments, the addition of O₂-saturated electrolyte to crevices with gap openings of $a = 0.3$ - 0.6 mm could not destabilize the crevice corrosion process (Table I). Two contributing factors are the dilution effect of the larger volume of crevice electrolyte and the premature reduction of the oxygen before it arrives at the deeper location of the active region on the crevice wall for the more open crevices. Experiments were then performed using an electrolyte with more oxidizing power.

Figure 6 shows typical $E_{x=L}$ and I responses when 1 mL of a 3% hydrogen peroxide (H₂O₂) solution was added to the crevice electrolyte. During the initial minutes following addition of the H₂O₂ to the crevice, some gas bubbles formed, presumably from the decomposition of H₂O₂ to water and oxygen, while fluctuations of the potential, $E_{x=L}$, and current, I , occurred. Then, destabilization of the crevice corrosion process was indicated by a sudden increase in $E_{x=L}$ from -0.65 to 0.25 V_{SCE} (with fluctuations occurring between ~ 0.11 and ~ 0.19 V_{SCE} within the passive region); simultaneously, I decreased from 3.2 to 0.2 mA. These passive $E_{x=L}$ and I values,

however, were not indicative of a strongly passive state. $E_{x=L} = 0.25 \text{ V}_{\text{SCE}}$, is only 0.30 V above $E_{\text{pass}} (= -0.05 \text{ V}_{\text{SCF}})$. Also, $E_{x=L}$ is 0.55 V below the crevice mouth's $E_{x=0}$ value ($=0.800 \text{ V}_{\text{SCE}}$), meaning $\text{IR} = 0.55 \text{ V}$ from the crevice opening, $x = 0$, to the $L = 10 \text{ mm}$ depth of the passive crevice wall. This $\text{IR} (=0.55 \text{ V})$ voltage is less than the critical $\Delta\phi^*$ voltage needed for maintaining crevice corrosion, where $\Delta\phi^* = E_{x=0} - E_{\text{pass}} = 0.800 - (-0.05) = 0.85 \text{ V}$.¹¹ Thus, although the $\text{IR} = 0.55 \text{ V}$ was significant in amount, it was not large enough to keep the bottom of the crevice in the active region, *i.e.*, only the passive region of the polarization curve exists on the crevice wall. It is not clear what role the oxygen gas bubbles played during the several minutes prior to termination of the crevice corrosion process by the added H_2O_2 , or why the current did not decrease to a more typical passive value (*i.e.*, 0.2 mA, rather than on the order of $<0.1 \text{ mA}$ typically obtained with O_2 -saturated electrolyte). This general behavior was also observed in the other experiments using H_2O_2 that are indicated in Table I.

Re-initiation of crevice corrosion.—It was reported above for the experiment in Fig. 4 that after termination of crevice corrosion by the O_2 addition, the passivity of the crevice wall was maintained for the hours-long duration of the experiment *i.e.*, long after the added oxygen should have been consumed. To determine if crevice corrosion might resume in the H_2O_2 experiments where the $E_{x=L} (=0.25 \text{ V}_{\text{SCF}})$ value is only 0.3 V from the system's E_{pass} value and $I = 0.2 \text{ mA}$ is a relatively high passive current (Fig. 6), a de-aerated electrolyte was added to the crevice in an attempt to remove any remaining H_2O_2 . This caused an immediate decrease of the potential from $E_{x=L} = 0.25$ to $-0.63 \text{ V}_{\text{SCE}}$ and increase of the current from $I = 0.2$ to 4.7 mA, signifying the reactivation of crevice corrosion. Presumably, the current (I) flowing through the crevice electrolyte increased as a result of removing the remaining H_2O_2 still available for reduction on the crevice wall, with the result that the IR value increased to greater than $-\phi^*$. Thus, in this case of a marginal passive condition, removal of the H_2O_2 provided the increased I that was needed to generate the required IR voltage in order to reactivate and stabilize crevice corrosion in this experiment. The rapidity of the transition also shows that other changes in solution composition were not involved in the reactivation process. This is in accord with other data which show that only a sufficient IR voltage is required to initiate crevice corrosion in iron,^{11,12} nickel,^{13,14} and stainless steel,¹⁵ when an active peak exists in the system's polarization curve and the aspect ratio is greater than the critical aspect ratio.¹⁰

Role of chloride ion and acidification.—In another experiment, after terminating the crevice corrosion process and passivating the crevice wall using an O_2 -saturated electrolyte, the addition of 10 mL of bulk electrolyte containing 22 mM NaCl to the crevice electrolyte immediately reactivated the crevice corrosion process (Fig. 7); whereas the same amount of electrolyte with a lower concentration of NaCl (9 mM) did not immediately reactivate crevice corrosion. Reactivation is attributed to the significantly higher passive current in the polarization curve caused by the increasing Cl^- ion concentration in the bulk solution; the increasing Cl^- ion concentration had no effect on the size of the active peak.¹⁷ When O_2 -saturated (chloride-free) electrolyte was subsequently added to the crevice electrolyte, the entire crevice wall repassivated, *i.e.*, $E_{x=L}$ suddenly changed to a more positive value than E_{pass} and the current immediately fell to near zero. This was followed by a gradual increase in I as the O_2 became depleted in the (residual chloride containing) crevice electrolyte.

The pH of the crevice solution was measured with pH paper during crevice corrosion and found to be dependent on the gap opening dimension of the crevice. The pH within the crevice decreased during crevice corrosion from a bulk value of about pH 6 to

4.5 as the gap opening dimension was decreased from $a = 0.50$ to 0.10 mm. The decrease in pH within the crevice during a stable crevice corrosion process demonstrates that the crevice electrolyte changed in composition during the course of the stable crevice corrosion process, in particular, for the smaller gap dimensions for which convective mixing was less than adequate for maintaining the composition of the crevice electrolyte within 0.5 pH of the bulk solution achieved under the best of conditions.¹³⁻¹⁵

An experiment was run using an O_2 -saturated electrolyte with a more acidic pH 4.3, similar to the lowest pH 4.5 measured during crevice corrosion in the tightest ($a = 0.10 \text{ mm}$) crevices. A pH 4.3 bulk electrolyte that was saturated with O_2 was added to the crevice during stable crevice corrosion (at 125 min in Fig. 8). The electrode potential at the bottom of the crevice suddenly increased from $E_{x=L} = -0.64$ to $0.72 \text{ V}_{\text{SCE}}$ and I decreased from 5.0 to 0.1 mA. This shows that in a more aggressive crevice electrolyte containing an accumulation of H^+ ions, the oxygen content in an O_2 -saturated electrolyte is still able to destabilize crevice corrosion for these experimental conditions despite the relatively high acidity and the fact that H^+ ions are known to increase the susceptibility of iron to crevice corrosion by decreasing the $\Delta\phi^*$ value.^{11,12} This result clearly shows that the measured transitions in I and $E_{x=L}$ in Fig. 4-8 are the result of the addition of the oxidant to the crevice electrolyte, and not due to a change in pH. Furthermore, the transition times are much too short in Fig. 4-8 for there to be a role of other changes in concentration of the crevice electrolyte during the transitions. It would require a much longer time (than the transition time) for the mass transport of species into the crevice by diffusion and migration from the bulk electrolyte.

Critical oxidizing power or oxidant concentration.—The above results show that initiation of crevice corrosion in this system is immediate when the iron surface is polarized into the passive region of the system's polarization curve, even in the presence of a significant oxidant concentration (*e.g.*, air saturation) in the crevice electrolyte, as found also for other spontaneously active systems.^{11,13-15} Consequently, a stronger oxidant or higher concentration of oxidant in the crevice electrolyte (*e.g.*, O_2 -saturated electrolyte is a stronger oxidant than an air-saturated electrolyte) needs to be added to the crevice electrolyte with $E_{x=0} = 0.800 \text{ V}_{\text{SCE}}$ in order to terminate the on-going crevice corrosion process in these experiments. These observations are in accord with IR theory, and its application to crevice corrosion. Related modeling¹² shows the parameters which are important for determining the susceptibility of a crevice to IR -induced crevice corrosion or, conversely, for determining the stability, or lack thereof, of an on-going crevice corrosion process. This model assumes that all of the I that results from metal dissolution according to the anodic polarization curve, flows through the crevice electrolyte to the cathodic reaction which occurs at the counter electrode (during potentiostatic polarization) or at the outer surface of the sample (during open circuit corrosion). These parameters are the same as those that determine whether or not some portion of the active peak of the crevice system's polarization curve will be present on the crevice wall for the given conditions.^{10,12,15,18} Thus, in principle, one can determine if crevice corrosion will occur for a given oxidizing power or amount of oxidant in the crevice electrolyte or, conversely, how strong an oxidant has to be added to the crevice electrolyte, in order to terminate an on-going, IR -stabilized crevice corrosion process.

These parameters¹² are the (i) crevice depth, L , for a given (gap) opening dimension, a , or aspect ratio where the aspect ratio L/a for a rectangular crevice,¹⁸ (ii) resistivity of the crevice's electrolyte, (iii) anodic polarization curve with an active/passive transition for the metal in the crevice electrolyte, and (iv) electrode potential, $E_{x=0}$, at the outer surface. The reduction of oxidants on the crevice wall mainly modifies parameter (iii) in that something less than the total possible ionic current from the anodic reaction (polarization curve) on the crevice wall flows out of the crevice. The model¹²

assumes that there are no reduction reactions (other than hydrogen evolution) occurring inside the crevice. In this case, all of the metal dissolution current represented by the polarization curve on the crevice wall is converted to ionic current flowing out of the crevice. In contrast, the reduction of oxidants at the anodic sites on the crevice wall reduces the magnitude of I .¹⁸ Thus, something less than the largest possible IR voltage is generated when oxidant reduction occurs inside the crevice. Carrying this to the limit, when all of the anodic reaction on the crevice wall is satisfied by the reduction of oxidant at these anodic sites on the crevice wall, no ionic current flows out of the crevice (*i.e.*, there is no separation of the anodic and cathodic reactions),¹⁸ and hence, the IR voltage is zero. Thus, the entire crevice wall is at the same potential in the passive region as the outer surface, *i.e.*, $E_{x=L} = E_{x=0}$ ($=0.800 \text{ V}_{\text{SCF}}$ for the experiments in this paper). Thus, to the extent that oxidants are present and undergo reduction inside the crevice, they decrease the magnitude of this I , which in turn decreases the size and gradient of the IR voltage. Consequently, at some decreasing value of I due to more and more oxidant reduction on the crevice wall, the condition, $\Delta IR \geq \Delta \phi^*$, needed to maintain $E_{x=L}$ in the active region as described elsewhere,^{10-15,18,19} is not met and termination of the crevice corrosion process occurs.

Thus, one observes that the initial area of active metal dissolution on the crevice wall decreases as reduction of oxidant increases at the anodic sites on the crevice wall, *i.e.*, the x_{pass}^o boundary (the initial location of the passive/active transition on the crevice wall) corresponding to E_{pass} of the crevice polarization curve, shifts deeper into the crevice. Along with x_{pass}^o the critical depth, L_c , and critical aspect ratio, AR_c , also increase.^{9,10,15,19} Thus, at some point of increasing oxidizing power in the crevice electrolyte and decreasing I and IR, the criterion, $L_c < L$ or $AR_c < AR$ corresponding to $IR \geq \Delta \phi^*$,¹⁸ for stability of crevice corrosion in a spontaneously active system is not met, and instead one has the criterion for termination of crevice corrosion, $L_c > L$ or $AR_c > AR$ corresponding to $IR \geq \Delta \phi^*$. Thus, L_c has increased to a value which is larger than the depth, L , of the crevice, so that an on-going crevice corrosion process terminates.

Open circuit corrosion (OCC).—One can ask whether the immediate onset of crevice corrosion that occurs in the above potentiostatic experiments is possible in the case of OCC in a spontaneously active system, where the oxidant concentration initially is the same in the crevice electrolyte as everywhere else and is the only source of the cathodic reaction, *e.g.*, an air saturated solution. In this case, there initially is no separation of the anodic and cathodic reactions, *i.e.*, the anodic reaction initially is everywhere compensated by the oxygen reduction reaction occurring at the same site.¹⁸ In this case crevice corrosion can not occur by the IR mechanism until some oxygen depletion occurs inside the crevice electrolyte, thereby providing for some separation of the anodic and cathodic reaction sites. Once the oxygen is partially or fully depleted in the crevice electrolyte, some or all of the cathodic reaction has to occur on the outside surface of the sample where oxygen is more plentiful. This separation of the anodic and cathodic reactions, in turn, establishes the necessary I and $IR \geq \Delta \phi^*$ voltage inside the crevice electrolyte (and $L_c < L$ or $AR_c < AR$) needed to shift $E_{x=L}$ into the active region for a spontaneously active system, as described above and elsewhere,^{11,12,15,19} Thus, for OCC by the IR mechanism, some small induction time (tens of seconds or less) passes before crevice corrosion occurs in a spontaneously active system. This OCC situation is physically different than in a potentiostatic experiment where a constant strong oxidizing power is imposed, in which case crevice corrosion can begin immediately in a spontaneously active system, as has been observed in the above experiments and in the literature.¹¹⁻¹⁵

Conclusions

The principal conclusions of the present work can be summarized in the following points.

If an oxidant is added to the crevice electrolyte, it decreases I that flows out of the crevice. As a result, the gradient of the IR voltage and the tendency for IR-induced crevice corrosion are reduced.

The presence of some oxygen within the crevice electrolyte for externally polarized, spontaneously active systems does not, in general, preclude the onset of immediate IR-induced crevice corrosion, whereas under open circuit conditions, crevice corrosion occurs only after some oxidant depletion occurs in the crevice electrolyte. Thus, the onset of crevice corrosion in spontaneously active systems for both situations requires a certain amount of separation of the anodic and cathodic reaction sites.

The above rapid $E_{x=L}$ transitions from an active to a passive potential (terminations of crevice corrosion), as well as their having been obtained on a time scale too short for accompanying changes in the pH within the crevice electrolyte, provide an additional proof of the IR voltage form of crevice corrosion for spontaneously active systems.

The oxidizing power, *e.g.*, concentration of oxidant in the crevice electrolyte, is the important quantity that either prevents the onset of, or conversely terminates, on-going, IR-induced crevice corrosion. The critical concentration of oxidant depends on the polarization curve of the metal/electrolyte system, $E_{x=0}$, resistivity of the crevice electrolyte, and the dimensions of the crevice, a and L for a rectangular crevice. Thus, in these experiments for the Fe/neutral sulfate system, crevice dimensions, $a = 0.1\text{--}0.6 \text{ mm}$ and $L = 10 \text{ mm}$ and $E_{x=0} = 0.800 \text{ V}_{\text{SCF}}$, the concentration of oxygen in an air-saturated electrolyte did not prevent the immediate onset of crevice corrosion. Similarly, the addition of an O_2 -saturated electrolyte with its higher oxygen concentration than in an air-saturated electrolyte, to a crevice that was undergoing stable crevice corrosion, terminated crevice corrosion in the samples of larger aspect ratio, *i.e.*, $0.10 \leq a \leq 0.25 \text{ mm}$ for $L = 10 \text{ mm}$ (Table I). An even stronger oxidant, H_2O_2 , did the same for the smaller, as well as larger, aspect ratios, *i.e.*, $0.10 \leq a \leq 0.60 \text{ mm}$ for $L = 10 \text{ mm}$.

Reinitiation of crevice corrosion, following termination of a crevice corrosion process, is more difficult than the (first) initiation in a spontaneously active system. Once terminated, all of the crevice wall is in the passive state and the passive current on the wall produces only a modest IR gradient, which may not be able to shift the potential at the crevice bottom, $E_{x=L}$, to the active region of the polarization curve. Addition of chloride ions to the crevice electrolyte promoted reinitiation of crevice corrosion through its effect on increasing the passive current.

The same qualitative behavior (rapid termination of crevice corrosion) was observed when the electrolyte concentration, *e.g.*, pH, had changed during the prior crevice corrosion process. Although acidification produced a more stable crevice corrosion process, the subsequent addition of O_2 -saturated electrolyte of the same pH to the crevice's electrolyte provided a cathodic reduction rate on the crevice wall that was still adequate to terminate the crevice corrosion process.

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