

Submitted to ECS Proceedings - Multiscale Simulations of Electrochemical Systems - Computational Aspects, Fall, 2005

Computational Modeling of the Stability of Crevice Corrosion of Wetted SS316L

Fushuang Cui, Francisco J. Presuel-Moreno, Robert G. Kelly
University of Virginia, Department of Materials Science and Engineering
116 Engineer's Way, P.O. Box 400745, Charlottesville, VA 22903

ABSTRACT

The stability of localized corrosion sites on SS 316L exposed to atmospheric conditions was studied computationally. The localized corrosion system was decoupled computationally by considering the wetted cathode and the crevice anode separately and linking them via a constant potential boundary condition at the mouth of the crevice. The potential of interest for stability was the repassivation potential. The limitations on the ability of the cathode that are inherent due to the restricted geometry were assessed in terms of the dependence on physical and electrochemical parameters. Physical parameters studied include temperature, electrolyte layer thickness, solution conductivity, and the size of the cathode, as well as the crevice gap for the anode. The current demand of the crevice was determined considering a constant crevice solution composition that simulates the critical crevice solution as described in the literature. An analysis of variance showed that the solution conductivity and the length of the cathode were the most important parameters in determining the total cathodic current capacity of the external surface. A semi-analytical equation was derived for the total current from a restricted geometry held at a constant potential at one end. The equation was able to reproduce all the model computation results both for the wetted external cathode and the crevice and give good explanation on the effects of physiochemical and kinetic parameters.

Keywords: Localized corrosion, modeling, stainless steel, atmospheric corrosion, repassivation potential

INTRODUCTION

Corrosion resistant materials such as stainless steels or nickel-based alloys may be subject to crevice corrosion initiation under atmospheric exposures at inherent geometrical crevices and other occluded geometries induced by oxide scales and precipitates which promote formation of aggressive chemistry. However, in order for such crevice corrosion to cast a structural integrity challenge, it must stabilize. Stability can only be maintained if the conditions within the occluded region remain sufficiently aggressive as to keep at least a portion of the crevice corroding actively. Not only must

the anodic kinetics within the crevice be sufficiently fast that the occluded solution remains a concentrated metal chloride solution despite diffusion and migration out of the crevice, but also the external cathode must be sufficiently robust in order to consume electrons generated by the anodic reactions. Obviously, ionic and electrical connectivity between anode and cathode must be maintained as well. [1-3]

Historically, crevice corrosion modeling has assumed a constant potential at the crevice mouth [4-6]. In some cases, the external cathode and the crevice have been modeled simultaneously in one code [7-9]. The former method sets a potentiostatic condition that is unrealistic in practice, due to the limitations in throwing power of a wetted (rather than immersed) surface [10]. The latter method makes separation of the effects of the crevice versus the external cathode more difficult. An alternative approach is to computationally separate the external cathode and the anode (the crevice), model them individually, and then link them through a common fixed potential at the crevice mouth. Such a separation allows in-depth study of parameters characteristic to cathode and anode respectively. Indeed, using this approach, effects of physiochemical and kinetic parameters on the cathodic current limitation of wetted SS 316 at 25°C has been studied and meaningful insights of practical significance were obtained [10]. The reported repassivation potential of the crevice was used as it represents a critical point of stability.

As for the previous study [10], CREVICER, an object-oriented code, was extended to study the thin electrolyte system serving as the cathode as well as the anodic crevice. Unlike many published models which assume linear or simple Tafel electrochemical boundary conditions [11-13], this model uses polarization curves constructed based on experimental data. Detailed description of this model can be found elsewhere. [10]

The present study had two objectives. The first objective was to quantify the effects of temperature on the limitation of wetted SS 316L to act as a cathode, extending the previous work at 25 °C. [10] The second objective was to demonstrate an approach to estimating crevice corrosion stability for cases where there are cathode limitations. To do so, preliminary calculations on the demands of a crevice of SS 316L at 25°C (termed I_{LC}) were also performed. As a first approximation to a stable crevice, the crevice in this work was assumed to contain the critical crevice solution (CCS) throughout, and that this solution composition remained constant. This represents a worst case scenario for stabilizing a crevice as in reality only a portion of the crevice would be active.

The total net cathodic current I_{net} that the cathode can support and the total anodic current I_{LC} within the crevice were selected as output parameters of interest. The effects of kinetic and physiochemical parameters on I_{net} were studied while the effect of crevice gap size on I_{LC} was explored as well. The projected I_{net} and I_{LC} at 25°C were then compared to determine stability of the crevice. In addition, an attempt was also made to advance understanding on the observed effects of various parameters on I_{net} . A semi-analytical equation was consequently derived which projected identical I_{net} to computation results and rationalizes the observed effects of the parameters of interest.

MODEL DESCRIPTION AND BOUNDARY CONDITIONS

The model shown in Figure 1.a was used to simulate the atmospheric exposure of a SS 316L substrate covered by a layer of electrolyte thin film and containing a creviced region. The wetted surface (cathode) was assumed to have a varying length of L_c and the crevice (anode) was assumed to have a constant depth of 1 cm. It was assumed that both the wetted cathode surface and crevice had a constant width of 10 mm (an arbitrarily-picked value; the choice of this value has no effect on results). The surfaces were, as illustrated in Figure 1.b, simulated with meshes generated by ANSYS®. The concentration of elements, as illustrated in Figure 1.b, was highest close to the crevice mouth where the potential/current density gradients were expected to be highest. The electrolyte thin film was assumed to be homogeneous (constant conductivity) and have a constant thickness of WL while the crevice was assumed to have a uniform gap size and a homogeneous solution (assumed to be the critical chemistry). As stated earlier, the cathode and anode were modeled separately.

The Cathode—The External Wetted SS 316L Surface

A full description of the FEM model used to study wetted SS316L surface at 25 °C has been presented elsewhere ^[10], and the present study used the same model to investigate the system at 95 °C. The increase of temperature brings changes in conductivity, oxygen solubility and diffusion coefficient, and kinetic parameters (E_{rp} , $E_{o,c}$, $i_{o,c}$, E_{corr} , β_c , and i_p). Realistic values of these parameters were chosen based on a literature search. ^[14-23] For example, the conductivity of the same solution at 95°C was estimated to be 30% higher than at 25°C ^[14], while O_2 diffusion coefficient was estimated to be $5.5 \cdot 10^{-5} \text{ cm}^2/\text{s}$ at 95°C (at room temperature, $D_{O_2} = 1 \cdot 10^{-5} \text{ cm}^2/\text{s}$ was used). ^[15]

The model outputted potential (E) and net cathodic current density ($i_{net} = i_c - i_p$) distribution profiles. A total net cathodic current I_{net} , the cathodic current that the thin-electrolyte cathode can use to support a localized corrosion site, was calculated by integrating the net cathodic current over all of the elements.

A full 3^3 factorial design of water layer (WL), conductivity (κ) and length of cathode (L_c) was performed to explore the possible effects of these parameters as well as their possible interactions. Table 1 lists the parameter values used.

Table 1. Values of WL, conductivity and L_c used in a full factorial design

WL (μm)	$\kappa (\Omega \cdot \text{m})^{-1}$	L_c (cm)
10; 25 ; 200	0.0126; 0.632; 11.22	0.25; 1 ; 10

For these calculations (base cases), the same kinetic parameters were used as shown in Table 2. Figure 2 shows the schematic of corresponding polarization curves: the oxygen reduction reaction (i_c , empty squares) in an electrolyte film with $WL = 10 \mu\text{m}$ and $\kappa = 11.22 (\text{ohm} \cdot \text{m})^{-1}$; the passive behavior of the stainless steel (i_p , solid vertical line) and

the summation of the two ($i_c - i_p$) (thick solid line, which overlaps with i_c at potentials well below E_{cor}). When the WL increases, the limiting current density decreases significantly due to the increase in the effective boundary layer thickness, as shown in Figure 2. However, as highlighted by the shaded zone, the SS 316L is expected to be under activation control in the range of potentials of interest of this study. Also shown in this figure is the $i_c - i_p$ (filled triangles) of an electrolyte film with $WL = 10 \mu\text{m}$ and $\kappa = 11.22 (\text{ohm}\cdot\text{m})^{-1}$ at 25°C . Raising temperature has a significant impact on the electrochemical kinetics of SS 316 for the reduction of oxygen.

Table 2. Values of kinetic parameters used in the base cases at 95°C

$E_{o,c}$ V	E_{rp} V	E_{cor} V	i_p A/cm ²	$i_{o,c}$ A/cm ²	i_{lim} A/cm ²	β_c V/dec
-0.05	-0.40	-0.15	10^{-7}	10^{-8}	$\frac{4FDC}{WL}$	0.1

The effects of each kinetic parameter (E_{rp} , i_p , $i_{o,c}$, and β_c) were studied by performing full factorial designs of L_c and κ shown in Table 3. To save calculation time, however, only $WL = 25 \mu\text{m}$ was considered, and yet the number of calculations still amounted to 99 ($= 11 \times 9$).

Table 3. Values of parameters used to examine their effects on total net cathodic current, I_{net} , at 95°C

E_{rp} (V)	i_p (A/cm ²)	$i_{o,c}$ (A/cm ²)	β_c (V/dec)
-0.3, -0.4, -0.5	$10^{-6}, 10^{-7}$	$10^{-7}, 10^{-8}, 10^{-9}$	0.06, 0.1, 0.13

* For each parameter, full factorial design of L_c and κ was used while WL was fixed at $25 \mu\text{m}$

The Anode—The 316L Within The Crevice

In the present study the anode was modeled by a crevice with the crevice mouth held at the repassivation potential. Figure 3 shows a polarization curve from which the electrochemical kinetics used were abstracted [24]. Salamat et al. [24] studied the kinetics of SS 316L in solutions designed to mimic the critical crevice composition as had been determined by ionic analysis of solutions extracted from active crevices. The anode (crevice) was $L = 1 \text{ cm}$ deep. Three gap (G) sizes were investigated ($G = 1, 10$ and $25 \mu\text{m}$), the solution had a conductivity equivalent to 5 M NaCl , and a pH of 0.75. The potential at the crevice mouth was $E_{rp} = -0.35 \text{ V}_{SCE}$ which was based on the literature. [17] Table 4 shows the values of kinetic parameters used in the base cases. The calculations did not consider chemical composition changes within the crevice. They thus represent a first-order estimate of the current demand of a crevice at the repassivation potential containing the assumed critical chemistry.

Table 4. Values of kinetic parameters used in computation of crevice current

E_{cor} V	E_{rp} V	$i_{o,a}$ A/cm ²	β_a V/dec	E_{aSS}	$i_{o,c}$ A/cm ²	β_c V/dec	E_{cHER}
-0.357	-0.35	10^{-6}	0.06	-0.825	10^{-8}	0.160	0.0975

The output of interest was the total current demand from the crevice which was obtained by integrating the calculated current density profile over the length of the crevice.

RESULTS

The Cathode—The External Wetted SS 316L Surface

Typical Current And Potential Distribution. Figure 4 shows typical potential and corresponding net cathodic current density distributions calculated from the model. As expected, the potential of cathode interface increased away from E_{rp} towards the E_{cor} of the cathode with increasing distance from the crevice, while the corresponding net cathodic current i_{net} decreased simultaneously.

Base Cases. A 3^3 full factorial design of water layer thickness (WL), length of cathode (L_c) and chloride concentration (κ) was performed. A standard analysis of variance [25] was performed on the results from the full factorial design of WL, L_c and κ , and the sum of squares was normalized with respect to the sum of square of WL. Table 5 lists results of the analysis, showing that WL, L_c , κ , as well as the interactions of WL x L_c , and L_c x κ are of significance. The effects of interactions of WL x κ and WL x L_c x κ were very small. The interactions of WL x L_c and κ x L_c can be seen in Figure 5. For example, when κ was $0.0126 \text{ (ohm-m)}^{-1}$, the effect of increasing L_c was negligible as I_{net} remained essentially constant; however, when κ was $11.22 \text{ (ohm-m)}^{-1}$, I_{net} increased from 7.0×10^{-9} to 1.95×10^{-8} A when L_c increased from 0.25 cm to 10 cm. In addition, this figure also suggests that I_{net} saturates as L_c increases. This issue will be addressed in more detail in the Discussion section.

Effects of Kinetic Parameters ($i_{o,c}$, E_{rp} , β_c , i_p). To quantify the effects of kinetic parameters ($i_{o,c}$, E_{rp} , β_c , and i_p) on total net cathodic current I_{net} , the following ratios were defined:

$$\begin{aligned} R_c &= I_{net}(i_{o,c}=10^{-7} \text{ or } 10^{-8}) / I_{net}(i_{o,c}=10^{-9}), \\ R_{E_{rp}} &= I_{net}(E_{rp}=-0.4 \text{ or } -0.5) / I_{net}(E_{rp}=-0.3), \\ R_{\beta_c} &= I_{net}(\beta_c=0.13 \text{ or } 0.1) / I_{net}(\beta_c=0.06), \text{ and} \\ R_a &= I_{net}(i_p=10^{-6}) / I_{net}(i_p=10^{-7}), \end{aligned}$$

where the units for the parameters are A/cm^2 for $i_{o,c}$ and i_p , V (vs SCE) for E_{rp} , and V/dec for β_c respectively. In general, a ratio that significantly deviates from 1 ($>>1$ for R_c and $R_{E_{rp}}$ and or $<<1$ for R_{β_c} and R_a) suggests a considerable effect of the corresponding parameter.

These ratios were calculated and both the magnitudes of the ratios and their dependences on L_c were very similar to those observed at 25°C [10]. E_{rp} and i_c had significant impact on I_{net} (values of R_c and $R_{E_{rp}}$ were significantly larger than 1) whereas the values of R_{β_c} are always smaller than 0.2. For example, increasing $i_{o,c}$ by a factor of 10 resulted in an increase of I_{net} by a R_c between 4 and 11. In addition, L_c and κ have significant impacts on the effect of these kinetic parameters ($i_{o,c}$, E_{rp} and β_c) respectively. Despite the large variation with κ at smaller L_c , however, the ratios (R_c , $R_{E_{rp}}$, and R_{β_c}) tended to reach constant values as L_c increased. For example, $R_{E_{rp}}$ was 9.35, 7.05 and

3.59 for $\kappa=11.22, 0.632, 0.0162 \text{ (ohm-m)}^{-1}$ respectively at $L_c=0.2 \text{ cm}$ ($WL = 25 \text{ microns}$, $E_{rp} = -0.4 \text{ V(SCE)}$), . These values gradually decreased with increasing L_c and eventually reached a constant value (3.45) at $L_c = 10 \text{ cm}$. The passive current density i_p was found to have an extremely small impact on I_{net} in the tested range. At 25°C , i_p had no measurable effect, whereas at 95°C , a change of i_p by a factor of 10 (from 10^{-7} to 10^{-6} A/cm^2) resulted in a small change ($\sim 5\%$, $R_a \sim 0.95$) in I_{net} .

Effect of Temperature. The ratio $R_T = I_{net}(T=95^\circ\text{C})/I_{net}(T=25^\circ\text{C})$ was used to quantify the effect of temperature on I_{net} . Increasing the temperature from 25 to 95°C , I_{net} increased by a factor between 6 and 30, and it was found that κ , WL and L_c all have some interaction with temperature. For example, for a case with the highest conductivity ($11.22 \text{ (ohm-m)}^{-1}$) and a cathode of 1 cm length, the R_T was as high as 21, whereas this R_T decreased to 6.5 for the same cathode with the lowest conductivity ($0.0162 \text{ (ohm-m)}^{-1}$). Despite the large variation of R_T with κ as well as WL at smaller L_c , it nevertheless reached an essentially constant value (~ 6.50) as L_c increased to 10 cm (a value large enough so that I_{net} saturated).

The Anode-The 316L within the Crevice

Typical Current and Potential Distributions. The potential and current distribution results from the computational modeling are shown in Figure 6. As expected, the potential falls monotonically with increasing distance into the crevice. High current densities are observed over up to 1 mm in from the mouth with the current density decreasing deeper into the crevice. The rate of decay of the current density depended strongly on the crevice gap, with larger gaps exhibiting higher currents deeper into the crevice.

Effect of Gap. Nobler potentials are observed deeper for the higher gap cases in Figure 6, *i.e.*, as the gap decreases, the potential profile becomes steeper over initial distances into the crevice, and then flattens out at deeper distances. In all three cases the potential at the tip (farthest in) of the crevice was at or very close to the open circuit potential (OCP), hence the small currents at the corresponding depths. Figure 7 shows the total current demand of the crevice, I_{Lc} , as a function of gap, along with the results of power law fits to the results. The power law fits the data very well, with the exponent of 0.48. Figure 8 shows the effect of temperature on the sensitivity of a cathode to increases in WL . Higher temperatures lead to larger increases in I_{net} with increasing WL .

DISCUSSION

Effects of Parameters on the Current from a Wetted Cathode

For a wetted cathode coupled to a localized corrosion site, the current and potential distribution along it as well as the total net cathodic current I_{net} are affected by many physicochemical and kinetic parameters such as water layer thickness (WL), size of cathode (L_c), κ , temperature (T), anodic and cathodic behavior of the cathode (i_p , $i_{o,c}$, β_c), and repassivation potential (E_{rp}). In a previous study on a wetted SS 316 cathode exposed

at room temperature 25°C^[10], the effects of WL, L_c and κ were studied using a full factorial design using I_{net} as the characteristic of interest. The effects of kinetic parameters were also explored by parameterizing each parameter while holding the rest at base values. In this study, the same approach was used to characterize the effects of these parameters as well as increased temperature (95°C).

The effects of temperature on I_{net} were found to depend on the values of L_c, κ, and WL. The ratio of net currents for a given cathode case ranged from 6 to 30 depending upon the values of the physical parameters. The larger ratios occurred at smaller cathode lengths, and as the cathode reached a length that led to the saturation of I_{net} (cf. Figure 5), the increase in I_{net} upon an increase in temperature from 25°C to 95°C became approximately 6.5, independent of the values of the other parameters. Additional effects of temperature would be through effects on oxygen solubility, oxygen diffusion coefficient, and the kinetic parameters.

Based on the magnitude of normalized sum of squares listed in Table 5, the effects of these five parameters at 95 °C follows the ranking: κ > L_c > L_c x κ > WL > WL x L_c. This order represents a slight change from that observed at 25 °C^[10], where L_c had the largest effects. At both temperatures, the effect of WL is rather small and this is likely because the SS 316L is under activation control in the range of potentials of interest and change in WL consequently has little effect on the corresponding cathodic reaction rate. If the potentials of interest were in the diffusion limited control regime, WL would be expected to have more impact.

Table 5. Analysis of Variance for the full factorial design of WL, L_c, and κ at 95 °C

Source of Variance	WL	L _c	κ	WL x L _c	WL x κ	L _c x κ	WL x L _c x κ
Ratio to WL	1	1.97	4.74	0.60	0.24	1.28	0.36
Ratio to WL (25°C)	1	5.19	3.85	0.74	0.18	2.46	0.24

As observed at 25°C, simple linear regression of the results does not lead to acceptable abstraction. Linear regression using the five factors of significance identified by the analysis of variance results in the following expression:

$$I_{net} = 2.85 \cdot 10^{-12} \cdot WL + 6.74 \cdot 10^{-9} \cdot \kappa - 7.32 \cdot 10^{-10} \cdot Lc + 1.10 \cdot 10^{-11} \cdot WL \cdot Lc + 2.94 \cdot 10^{-9} \cdot \kappa \cdot Lc + 3.35 \cdot 10^{-9} \quad R^2=0.80 \quad (1)$$

The correlation coefficient is similar to that found using a similar approach at 25°C using five factors. The relatively poor performance of the linear regression can be attributed to the lack of inclusion of the effects and interactions with the kinetic parameters as well as the restriction to linear terms.

Saturation of Cathodic Current I_{net}

Figure 5 shows that I_{net} saturates (reach a maximum value, called I_{max} hereafter) when L_c exceeds a critical value. This phenomenon was observed at 25°C as well^[10]. The

origin of this saturation can be ascribed to the fact that i_{net} ($i_c - i_p$) diminishes with distance to the crevice and eventually become zero when the open circuit potential of cathode is reached at a critical distance.

Figure 5 also shows that the I_{max} and corresponding L_c at which I_{max} is observed significantly increases with κ . For example, I_{max} was reached when L_c was as small as 1 cm for a case with the lowest conductivity, whereas I_{max} was only reached when L_c was 15 cm for a case with the highest conductivity. This is due to the increase of conductivity. Computations on cases with fixed $WL=10$ or $200 \mu\text{m}$ as well as fixed 0.001 or 1 M Cl^- were also performed and a similar saturation behavior of I_{net} was observed.

Table 7 Projected saturation limit for I_{net} at 95°C

WL μm	10			25			200		
$\kappa (\text{ohm-m})^{-1}$	0.0162	0.632	11.22	0.0162	0.632	11.22	0.0162	0.632	11.22
$L_c (\text{cm})$ needed for 98% I_{max}	0.25	1	4	0.25	4	10	1	10	15
98% I_{max} (10^{-8}A)	0.066	0.46	1.92	0.102	0.73	3.04	0.265	1.87	7.5

* Choice of kinetic parameters is listed in Table 2.

As discussed above and in an earlier report ^[10], the determination of I_{max} and the smallest cathode size at which I_{max} is realized are of practical importance, offering significant information to answer two important questions to atmospheric systems which often have patches of electrolytes rather than contiguous thin electrolyte films: (a) what size patch of electrolyte could support a sustained localized corrosion site; (b) how fast such a site could corrode. Because I_{max} is approached asymptotically, 98% I_{max} was used to determine required minimum L_c for current saturation and the results are summarized in Table 7. This type of table allows the determination of a practice maximum size of cathode. Further increase of cathode will not provide significant extra cathodic current (<2%). Such a table can also be used to determine stability of a localized corrosion site by coupling with the Galvele criterion ^[27] or using the approached discussed later.

Semi-Analytical Expression of Current Capacity from a Restricted Geometry

In addition to the computational characterization, we have attempted to abstract our results into an equation that incorporates all the parameters of interest and rationalizes the modeling experimental observations. The approach has been to consider the restricted geometry of the wetted cathode and to introduce the concept of an equivalent cathode length, L_c , to account for the distribution of current along the cathode, as well as the introduction of the kinetics via a determination of an equivalent, or average, current density.

For a cathode with the same geometry considered in this study (Figure 1), assume

$$I_{\text{net}} = i_{\text{eq}} \cdot L_{\text{eq}} \cdot W \quad (\text{assumption 1}) \quad (2)$$

where L_{eq} is the equivalent length of the cathode, W is the actual width of the cathode, i_{eq} is the equivalent current density, and I_{net} is the total net cathodic current

$$i_{eq} = \frac{\int_{E_L}^{E_{rp}} (i_c - i_p) \cdot dE}{E_L - E_{rp}} = \frac{\int_{E_L}^{E_{rp}} (i_c - i_p) \cdot dE}{\Delta E} \quad (3)$$

where E_L is the potential of the cathode edge which has the largest distance to the crevice mouth. It is apparent that if the cathode has a constant net cathodic current density along its length, then $L_{eq} = L_c$ and $i_{eq} = i_{lim} - i_p$

Assume that the electrolyte on the cathode surface acts as an ideal resistor with resistance R ,

$$R = \frac{L_{eq}}{C \cdot \kappa \cdot WL \cdot W} \quad (\text{assumption 2}) \quad (4)$$

so that the potential drop across the cathode can be estimated by

$$\Delta E = E_x - E_{rp} = I_{net} \cdot R = \frac{I_{net} \cdot L_{eq}}{C \cdot \kappa \cdot WL \cdot W} \quad (\text{assumption 3}) \quad (5)$$

where κ is the conductivity of the electrolyte (assumed to be constant throughout the restricted geometry), and C is a geometric correction factor. This correction is needed as the electrolyte layer is by no means a simple resistor which would have

$R = \frac{L_c}{\kappa \cdot WL \cdot W}$. In the case of the wetted cathode, the electrolyte layer acts as a distributed resistor due to the interfacial current along its length.

Solve 5 for L_{eq} and substitute the result into equation 2

$$I_{net} = W \cdot \sqrt{C \cdot \Delta E \cdot \kappa \cdot WL \cdot i_{eq}} \quad (6)$$

and replace i_{eq} with equation 3

$$I_{net} = W \cdot \sqrt{C \cdot \kappa \cdot WL \cdot \int_{E_L}^{E_{rp}} (i_c - i_p) \cdot dE} \quad (7)$$

Definition and Validation of a Value for C . The constant C characterizes the effects of the interfacial reactions on the effective resistance. To determine its value, the entire set of results was considered. When the square of I_{net} is plotted *versus* the product of W , WL , σ , and the integral, an excellent linear relationship was observed. The slope of the line was 2.0, with a correlation coefficient of 1.0. Thus,

$$I_{\text{net}} = W \cdot \sqrt{2 \cdot \kappa \cdot WL \cdot \int_{E_L}^{E_p} (i_c - i_p) \cdot dE} \quad (8)$$

In addition, equation 8 also successfully reproduced the observed effects of temperature (changing temperature will result in change of σ and kinetic parameters) and all the kinetic parameters including i_{oc} , E_{rp} , b_c and i_p . Table 6 lists the projections from equation 8 compared to the model outputs for selected cases with different temperature and kinetic parameters. In all cases, equation 8 yielded near identical results (error less than 0.4%) to the full model computation for the individual cases. Gartland^[26] found a similar value of C for the case assuming a region of constant current density within a crevice, as can be easily derived. A more detailed of the dependency of C on geometry and cathodic kinetics will be the subject of future work.

Table 6 Comparison of I_{net} projected by Equation 8 and the model computation for selected cases with various kinetic parameters or temperatures.

	95°C					25°C
	Base case	$i_{oc}=10^{-9}$ A/cm ²	$E_{rp}=-0.3$ V vs SCE	$\beta_c=0.06$ V/dec	$i_p=10^{-7}$ A/cm ²	Base case ^[10]
I_{net} (A/cm ²) projected by Equation 8	$7.312 \cdot 10^{-9}$	$2.196 \cdot 10^{-9}$	$2.197 \cdot 10^{-9}$	$3.785 \cdot 10^{-9}$	$6.836 \cdot 10^{-9}$	$1.131 \cdot 10^{-9}$
I_{net} (A/cm ²) projected by Model Computation	$7.314 \cdot 10^{-9}$	$2.188 \cdot 10^{-9}$	$2.190 \cdot 10^{-9}$	$3.790 \cdot 10^{-9}$	$6.839 \cdot 10^{-9}$	$1.129 \cdot 10^{-9}$
Error %	0.03%	0.36%	0.32%	0.13%	0.04%	0.18%

* All cases have 0.05M Cl⁻, $L_c=10\text{cm}$, $WL=25\mu\text{m}$

For the use of equation 8, one challenge is the determination of E_L , the potential of the cathode edge furthest from the crevice mouth (*i.e.*, at L_c). In general, E_L increases with increasing L_c until the open circuit potential of the cathode, E_{oc} , is reached. In this way, the effect of L_c is thus implicitly considered by this equation. Though in most cases estimation of E_L is not straightforward (in this study, values of E_L were determined from potential profiles outputted by the model calculations), its value is limited in that it can never exceed the open circuit potential of the cathode E_{oc} . Thus, equation 8 can be used to estimate the current limitation of cathodes by using E_{oc} for E_L . It should be noted that the electrochemical kinetics of the cathodic reaction are required to use equation 8. That is, the polarization behavior ($i(E)$) has an influence on the cathode capacity. That said, the spatial current distribution is not required, only the polarization behavior and the two potential limits for the integration.

Figure 8 shows the effect of temperature on the cathode capacity to support localized corrosion. I_{net} is plotted as a function of $WL^{1/2}$ for both temperatures. The primary difference is in the slope of the line. As shown in equation 8, the slope of such a plot would be affected by the conductivity, cathodic kinetics, and choice of potential limits. The slopes in Figure 8 differ by a factor of almost 6.5, showing that at the higher temperature, increasing the WL has a much larger effect on the I_{net} than occurs at 25 °C.

Whereas equation 8 was derived in the context of the current capacity of the external, wetted cathode, it can also be directly applied to the case of a crevice, if the same conditions are operable. In the calculations presented here, these conditions (*i.e.*, constant conductivity, constant geometry, constant potential at the crevice mouth) are

operable. In the case of the crevice, the WL in equation 8 would be replaced by the gap, G , and the current being calculated would be that demanded by the crevice, I_{Lc} . Thus, one would obtain the following:

$$I_{Lc} = W \cdot \sqrt{2 \cdot \kappa \cdot G \cdot \int_{E_L}^{E_p} (i_c - i_p) \cdot dE} \quad (9)$$

Equation 8 represents a power law with respect to the gap G , all else being equal. Thus, it would predict that a plot of $\log I_{Lc}$ versus $\log G$ would result in a straight line with a slope of $1/2$. Figure 9 shows such a plot for the data generated, and an excellent straight line is observed with a slope very close to $1/2$.

These two abstractions can serve as the foundation for the estimation of crevice corrosion stability under atmospheric exposure conditions. For a given set of values of the physical parameters and electrochemical kinetics, the current capacity of the cathode, I_{net} , can be compared to the current demand from the crevice, I_{Lc} . If the former is equal to or exceeds the latter, the crevice can be stabilized by that cathode.

While the calculations for both the cathode and anode assume steady state conditions and uniform conductivity, they do represent a reasonable approach to abstracting the key parameters into a form that allows a first-order estimate of crevice stability. With time, the chemical conditions at the cathode will change and likely decrease the current capacity. Similarly, as the chemical conditions inside the crevice evolve, it is likely that the current demand will decrease, although as the crevice corrodes, the increase in surface area could lead to increased current demand.

Stability of Localized Corrosion

For systems under natural conditions, the stability of localized corrosion requires a cathode which can supply a cathodic current (I_{net}) that matches or exceeds the anodic current within the crevice (I_{Lc}). The anodic current demand is determined by the need to maintain a solution with a sufficiently aggressive composition that repassivation is prevented. The aggressiveness of the occluded solution is determined by the competition between dissolution and subsequent metal ion hydrolysis within the crevice and the dilution of the occluded solution via mass transport of the high concentrations of chloride and hydronium ion out of the crevice.

Experimentally, this stability condition can be measured by determination of the repassivation potential of the crevice. Sridhar and colleagues^[17,28,29] have shown that, when properly determined, E_{rp} can be used as a criterion for crevice stability. If the mouth of the crevice is held at or above E_{rp} , the crevice remains in an active state, whereas below E_{rp} , the crevice eventually repassivates. However, determination of E_{rp} is done under conditions of full immersion and potentiostatic control, which supplies as much current as the anode demands. In natural systems, the role of the potentiostat is replaced by the external cathode. For conditions of full immersion in highly conductive

solutions, increasing the cathode size linearly increases the current the cathode can supply.

For localized corrosion systems under atmospheric conditions, the restricted geometry of a wetted cathode limits the ability of the external cathode to provide current to the crevice at and above the repassivation potential. Although more positive potentials stabilize the crevice, increasing the potential of the cathode decreases the current it can supply. This limitation leads to an inherently increased instability for localized corrosion in atmospheric exposure. The work presented here provides a means to quantitatively assess the level of that instability. By determining I_{\max} and comparing it to I_{Lc} , the stability of coupled localized corrosion site can be assessed. An application of this approach is showcased below considering a localized corrosion of SS 316L under atmospheric exposure at 25 °C. Calculations from previous work with a cathode at 25 °C^[10] are connected to the calculations reported for the anode here.

It is important to point out that the assumption of constant, spatially homogeneous chemistry for the crevice should only be viewed as a gross first approximation for an active crevice. In reality, there are strong chemical gradients within the crevice which are time-dependent. These chemical gradients and their effects on the polarization behavior of the material locally are of critical importance to accurate determination of crevice stability. However, while there exists some information regarding the critical crevice chemistry for different alloys under given experimental conditions, very little detail exists that would allow the time-dependence of polarization behavior of the material inside the crevice on the local chemistry to be captured in a model, although work is ongoing in that area. Similar arguments can be made for the external cathodic surface at which the pH will tend to rise and precipitates will form, likely slowing the cathodic reaction rates.

In the absence of such information, the assumption of a crevice filled with the critical crevice chemistry connected to a time-independent cathode surface allows the illustration of a framework for understanding the stability of localized corrosion under atmospheric conditions. It can be viewed as a zero-order estimate of what combinations of cathode parameters (e.g., WL, solution conductivity, kinetic parameters, L_c) and crevice parameters (e.g., gap) are compatible. It approximately represents the conditions at the initiation of crevice corrosion when the crevice has been activated (and hence contains the critical crevice solution over some portion of its length). If the cathode cannot meet that current need, stabilization of the crevice will not be possible, as the current demand from the crevice will likely rise with time.

Figure 9 represents an example of the application of this framework for crevice stability. The current demand from a 1-cm long crevice is shown as a function of gap, assuming that the mouth is at the repassivation potential ($E_{rp} = -0.35$ V(SCE)). The dotted horizontal lines represent the maximum currents available from an external wetted cathode (I_{\max}) assuming different WL values, but having the same solution composition ($\kappa = 11.22$ (ohm-m)⁻¹, equivalent to 1 M NaCl). Thus, if the WL was 200 microns thick, a crevice with a gap of 2.3 microns could be supported, and decreasing the WL to 25 microns decreases the maximum gap that can be stabilized to 0.4 microns. Further decreasing the WL to 10 microns leads to a reduction in the maximum gap to 0.14 microns. The value of 2.3 microns for the critical gap for a 200 micron WL seems reasonable when compared to the 4 microns predicted by Lee and Kain^[30] using the model of Oldfield and Sutton^[31] for the critical gap for full immersion in seawater.

Such abstractions have utility not only in the design of experiments relevant to localized corrosion under atmospheric conditions, but also in the prediction of cathode/anode combinations that should be avoided to assure long-term integrity of a structure.

CONCLUSIONS

Crevice corrosion of SS 316L exposed to atmospheric conditions was studied by computational study of the external cathode and crevice separately. Effects of physiochemical and kinetic parameters on the total net cathodic current I_{net} and the effect of crevice gap size on the total anodic current I_{Lc} were explored. The I_{net} and I_{Lc} were used to determine stability of crevice corrosion. The following conclusions can be drawn:

For the cathode:

1. WL, Lc and κ , as well as the interactions of Lc and WL, and Lc and κ have significant impact on the total net cathodic current I_{net} . An analysis of variance showed that the effects of these factors decrease in the following order: $\kappa > \text{Lc} > \text{Lc} \times \kappa > \text{WL} > \text{WL} \times \text{Lc}$.
2. Temperature (95 vs 25 °C) was found to have a significant effect on I_{net} with the increase in I_{net} ranging from a factor of 6 to a factor of 30, the value of which was dependent on the values of the other physical parameters. At large cathode sizes, I_{Lc} , the effect of temperature became independent of the other parameters and approached a value of 6.5.
3. Cathodic kinetic parameters, E_{rp} , $i_{\text{o,c}}$, and β_{c} , were found to have significant effects on I_{net} , whereas i_{p} in the cases of studied had little effect on I_{net} .

As with all analyses based on statistics, these analyses are strictly applicable only within the range of parameter values investigated.

4. A semi-analytical equation was derived for the total current from a restricted geometry held at a constant potential at one end. The equation was able to reproduce all the model computation results both for the wetted external cathode and the crevice and give good explanation on the effects of physiochemical and kinetic parameters.

For the anode (25°C):

1. The total anodic current I_{Lc} was calculated for crevice assuming constant crevice chemistry.
2. In accord with the semi-analytical expression described above, I_{Lc} was found to increase in proportion to the square root of the crevice gap.

For the conditions considered in this study, the concept of localized corrosion stability projects that crevices at 25 °C can stabilize only if the crevice gap is smaller than 5 μm , with the exact value depending upon the physical parameters of the cathode.

ACKNOWLEDGEMENTS

This work was supported by the Office of Science and Technology and International of the United States Department of Energy (DOE) and carried out as part of the DOE Multi-University Corrosion Cooperative under Cooperative Agreement DE-FC28-04RW12252. The funding agency is gratefully acknowledged.

REFERENCES

1. M.G. Fontana, Corrosion Engineering, 3rd Edition, 1986: p.53
2. H.W. Pickering, Corrosion 42, 3(1986): p. 125
3. R.K. Dayal, "Crevice Corrosion of Stainless Steel," in Corrosion of Austenitic Stainless Steel, Ed. By H.S. Khatak and B. Raj, 2002: p. 106
4. Y. Xu, H.W. Pickering, *J. Electrochem. Soc.* 140, 3(1993): p. 658
5. J. S. Lee, M. L. Reed, R. G. Kelly, *J. Electrochem. Soc.* 151, 7(2004): B423-B433
6. K.C. Stewart, Ph.D. Dissertation, Department of Materials Science and Engineering, University of Virginia, Charlottesville, VA (1999)
7. J.W. Oldfield and W.H. Sutton, *British Corrosion Journal* 15, 1(1980): p. 31
8. P.O. Gartland, in Proceedings of Corrosion/96 Research Topical Symposia, 311, NACE International, Houston, TX (1996)
9. R.W. Evitts, M.K. Watson and J. Postlethwaite, "Numerical Simulation of Crevice Corrosion of Titanium: Effect of Bold Surface" *Corrosion* 96, 1996:P.121/1-121/10.
10. F. Cui, F. J. Preseul-Moreno, R. G. Kelly, *Corrosion Science*, 47 (2005): 2987-3005.
11. E. McCafferty, *J. Electrochem. Soc.* 124 (1977) 1896
12. P. Doig, P.E.J. Flewitt, *Philosophical Magazine B*, 38 (1978) 27
13. R. Morris, W. Smyrl, *J. Electrochem. Soc.* 135 (1988) 723
14. Y Zheng and J A Robers, *J. Phys: Condens. Matter* 8 (1996): p.8089
15. B. Case, *Electrochimica Acta* 18, 1973: p. 293
16. Kazuya Ohkubo, *Kenkyusho Kenkyu Hokoku*, 3 (2001): p. 2
17. D.S. Dunn, G.A. Cragolino, N. Sridhar, *Corrosion* 56, 1(2000): p. 90
18. G.A. Cragolino, D.S. Dunn, N. Sridhar, "Environmental Effects on Stress Corrosion Cracking of Type 316L Stainless Steel and Alloy 825 as High-Level Nuclear Waste Container Materials, CNWRA 94-028, 1994
19. Radoslav Adzic, "Recent Advances in the Kinetics of Oxygen Reduction", in *Electrocatalysis*, Edited by Jacek Lipkowski and Philip N. Ross, Wiley-VCH 1998: p. 236
20. S.J. Clouser, J.C. Huang, E. Yeager, *Journal of Applied Electrochemistry*, 13(1993): p. 597
21. R. Biswas, S.N. Lvov, Z. Ahmad, Digby D. Macdonald, "Electrode-Kinetic And Corrosion Measurements in High Temperature Aqueous Environments", in proceedings of the symposium on Electrode Materials and Processes For Energy Conversion and Storage IV, edited by J. McBreen, S. Mukerjee, S. Srinivasan, 1997: p. 340
22. Private communication with N. Sridhar at South West Research Institute, 2005

23. N. Sridhar and G.A. Cragnolino, Corrosion 49, 11 (1993): p. 885
24. G. Samalat, G.A. Juhl, and R.G. Kelly, Corrosion 51,11,p832 1995
25. D.C. Montgomery, Design and Analysis of Experiments, 4th Edition, John Wiley & Sons, Inc. New York, NY 1997, p.441
26. P. O. Gartland, in Life Prediction and Crevice Corrosion, Research Topical Symposium/96, NACE International (1996): p. 311.
27. J.R. Galvele, J. Electrochem. Soc., 123 (1976): p. 464
28. N. Sridhar, C.S. Brossia, D.S. Dunn, A. Anderko, Corrosion 60, 10(2004): p. 915
29. A. Anderko, N. Sridhar, D.S. Dunn, Corrosion Science 46, (2004): p. 1583
30. T. S. Lee, R. M. Kain, Paper 69, Corrosion/83, NACE, Houston (1983).
31. J. W. Oldfield, W. H. Sutton, British Corrosion Journal 13, (1978): p. 104

NOTATIONS

D_{O_2}	bulk diffusivity of oxygen (cm^2/s)
E	potential of interface (V_{SCE})
E_{cor}	corrosion potential (V_{SCE})
E_L	potential at point of cathode farthest from crevice mouth
E_{rp}	repassivation potential (V_{SCE})
$E_{o,c}$	reversible oxygen reduction potential (V_{SCE})
E_{aSS}	reversible potential for active stainless steel dissolution (V_{SCE})
E_{cHER}	reversible potential for hydrogen evolution inside crevice (V_{SCE})
F	Faraday's constant (10^5 C/g.eq.)
G	crevice gap (μm)
i	current density (A/cm^2)
i_c	cathodic current density (A/cm^2)
i_a	anodic current density (A/cm^2)
i_{eq}	equivalent current density (A/cm^2)
$i_{o,c}$	exchange current density for O_2 reduction (A/cm^2)
$i_{o,a}$	exchange current density for anodic dissolution (A/cm^2)
i_p	passive current density (A/cm^2)
i_{lim}	limiting current (A/cm^2)
I_{net}	net current sustained by the cathode (A)
L_C	length of cathode (cm)
L_{eq}	equivalent length of cathode (cm)
n	number of electrons transferred in reaction (g. eq./mol)
R	Resistance of electrolyte layer (Ω)
R_c	Ratio of I_{net} for changing $i_{o,c}$ relative to base case
R_{Erp}	Ratio of I_{net} for changing E_{rp} relative to base case
$R_{\beta c}$	Ratio of I_{net} for changing β_c relative to base case
R_a	Ratio of I_{net} for changing i_p relative to base case
R_T	Ratio of I_{net} for changing temperature relative to base case
T	temperature (K)
WL	electrolyte layer thickness (μm)

Greek Symbols

β	Tafel slope (V/dec)
κ	conductivity of the electrolyte ($\Omega\text{-cm}$) ⁻¹

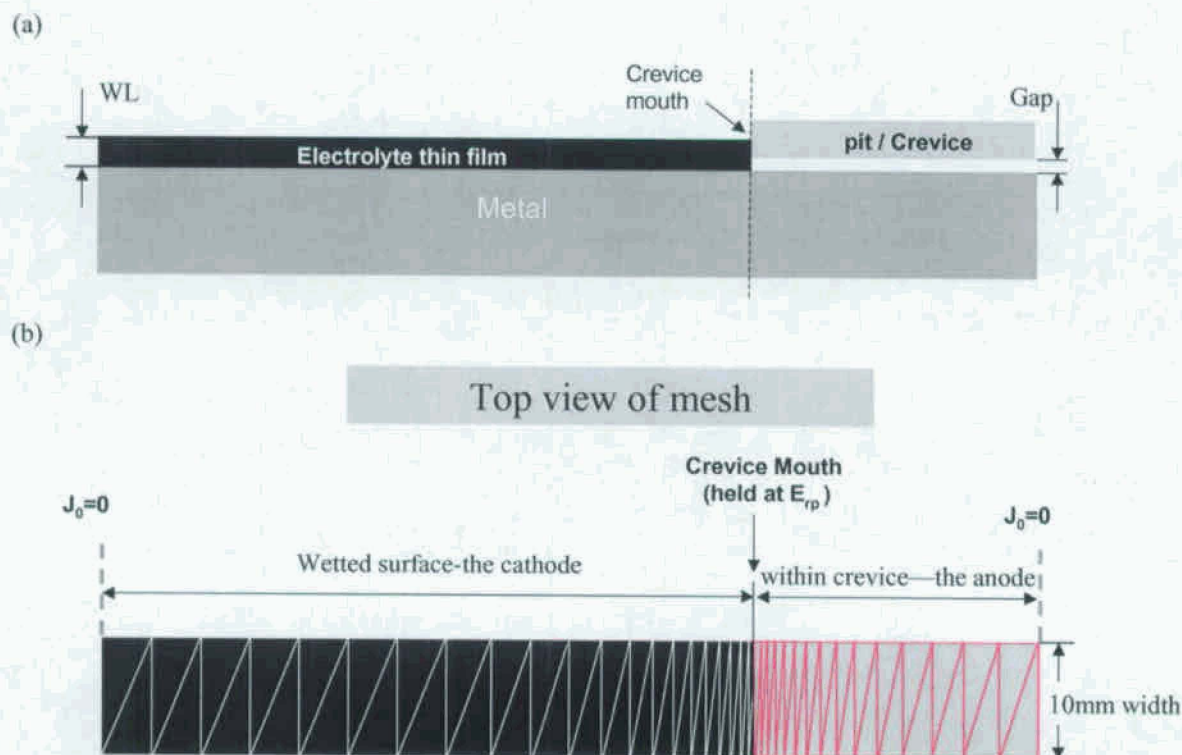


Figure 1. Schematic of the system modeled: a) a typical crevice corrosion system for atmospheric exposure; b) Top view of the mesh. The cathode and anode was separated and modeled individually. The two were linked by holding a common fixed potential E_{tp} (repassivation potential) at the junction point (crevice mouth).

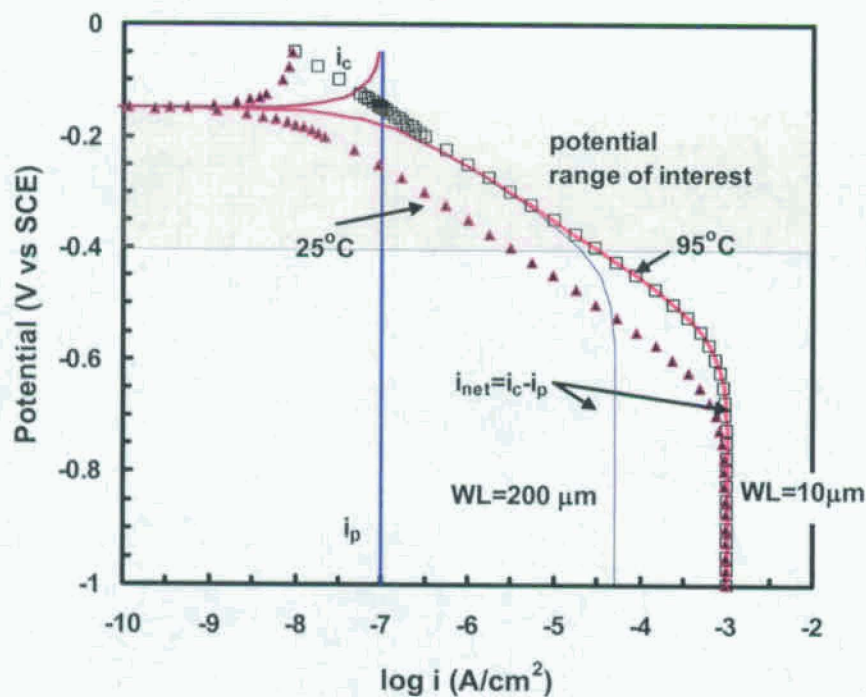


Figure 2. Cathodic and anodic kinetics in base cases at 95°C. Cathodic kinetics are shown for two different WL. Anodic kinetics are described by the passive current density, i_p , which is independent of potential. Shaded area represents range of potentials at which the mouth of the crevice was assumed to be held.

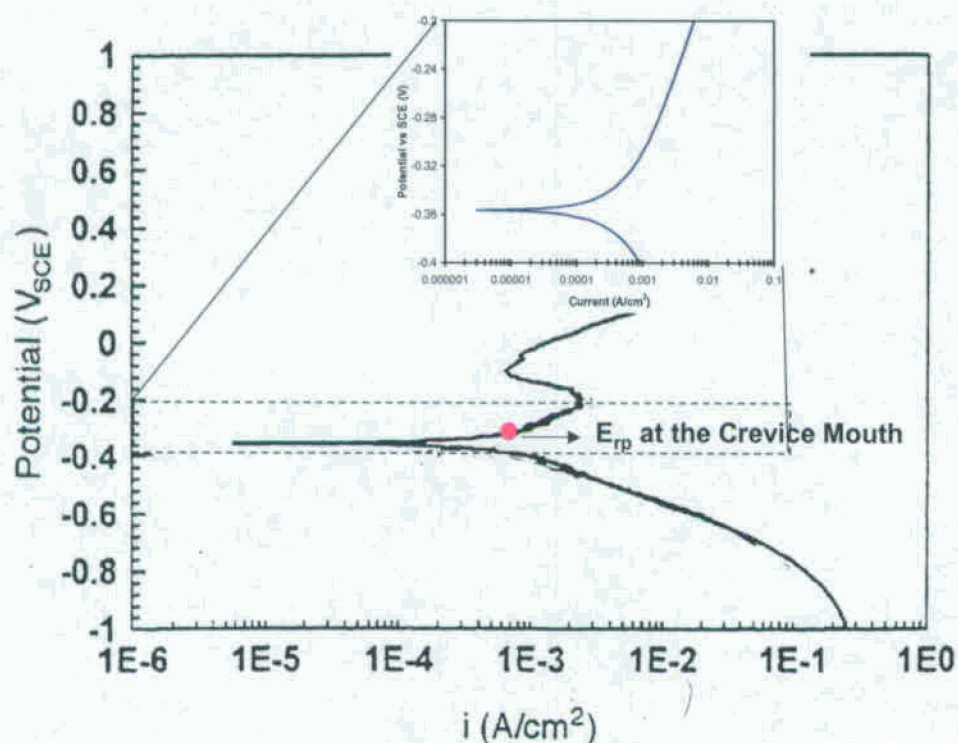


Figure 3. Polarization behavior for 316L in its Critical Crevice Solution (CCS) as determined experimentally by Salamat et al. [24]. Insert shows data close to E_{corr} . These data were used as the basis for the anode kinetics used in the model of the crevice.

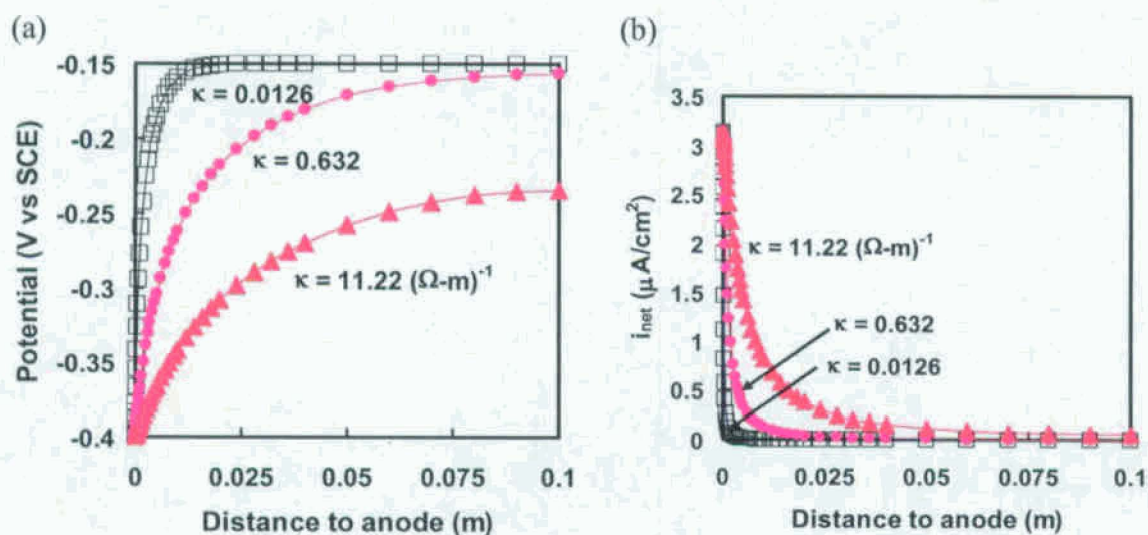


Figure 4. Typical model outputs for the cathode. Potential increased and i_{net} decreased with distance to anode. Elements near to the anode had the highest Potential/ i_{net} , and κ apparently had significant impact on the potential/current density distribution. (Base cases, $WL=25 \mu\text{m}$, $L_c=10\text{cm}$).

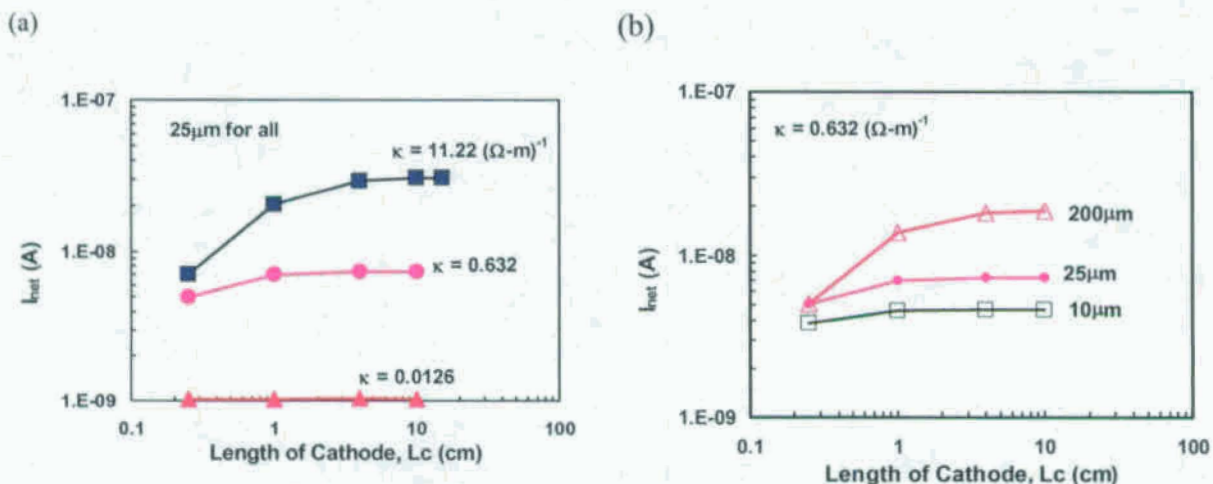


Figure 5. Interaction between parameter (base cases): (a) effect of L_c varies with κ ; (b) Effect of L_c varies with WL . i_{net} gradually saturated as L_c increased, and the speed of saturation depends on κ and on WL . (Extra calculations for selected cases with $L_c=4$ or 15 cm, were performed to reveal the saturation phenomenon.)

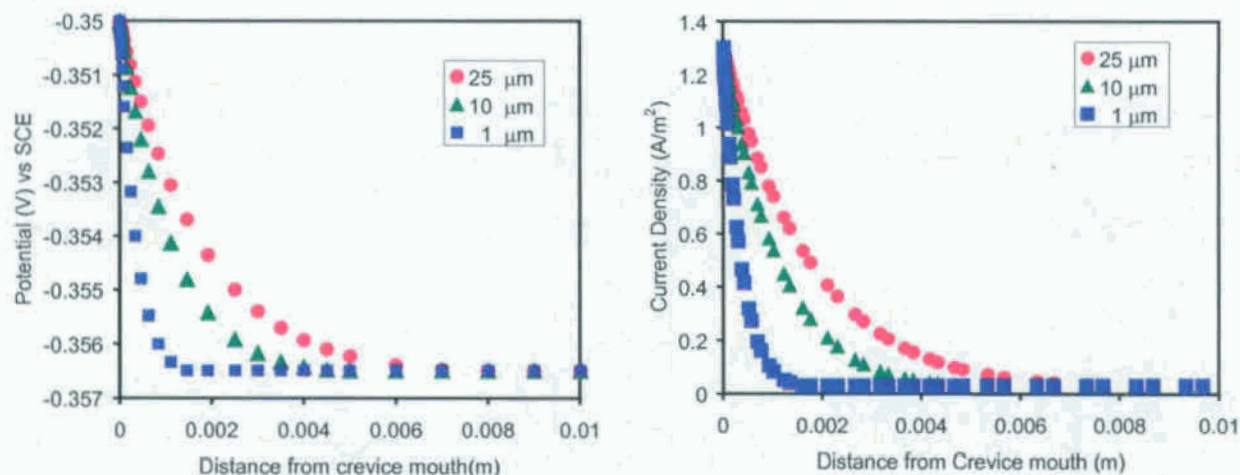


Figure 6. Typical potential and current output for crevice. Base case: $E_{o,c}=-0.05$ V, $E_{rp}=-0.4$ V, $E_{cor}=-0.15$, $i_p=10^{-7}$ A/cm², $i_{o,c}=10^{-8}$ A/cm², $\beta_c=0.1$ V/dec, i_{lim} =by formula, see Table 2.

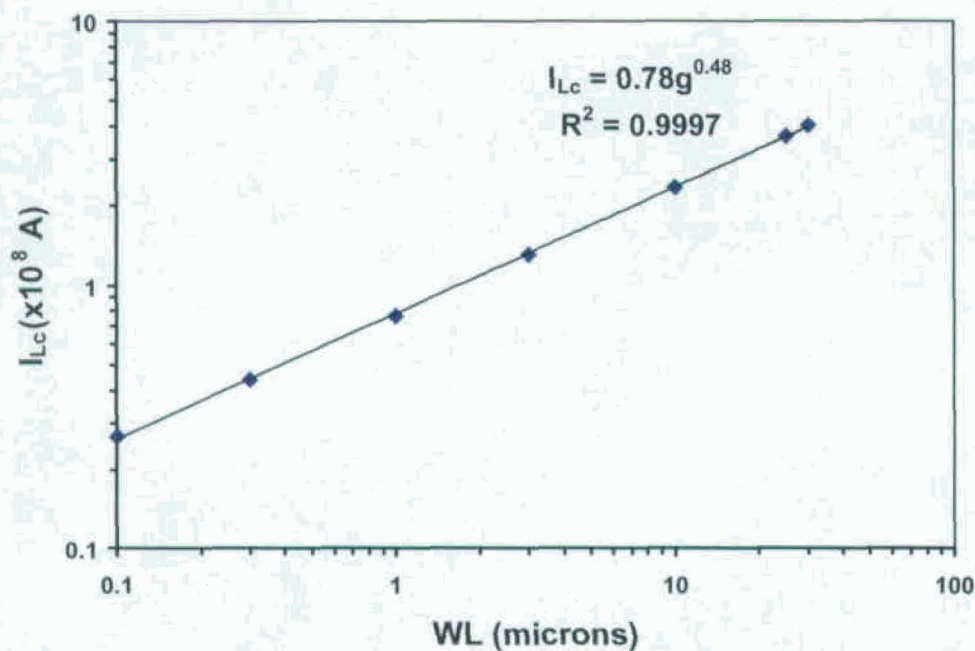


Figure 7: Dependence of I_{net} on water layer thickness. Note the linear relation on the log-log scale. The slope is 0.5. Data points are from several different sets of conditions.

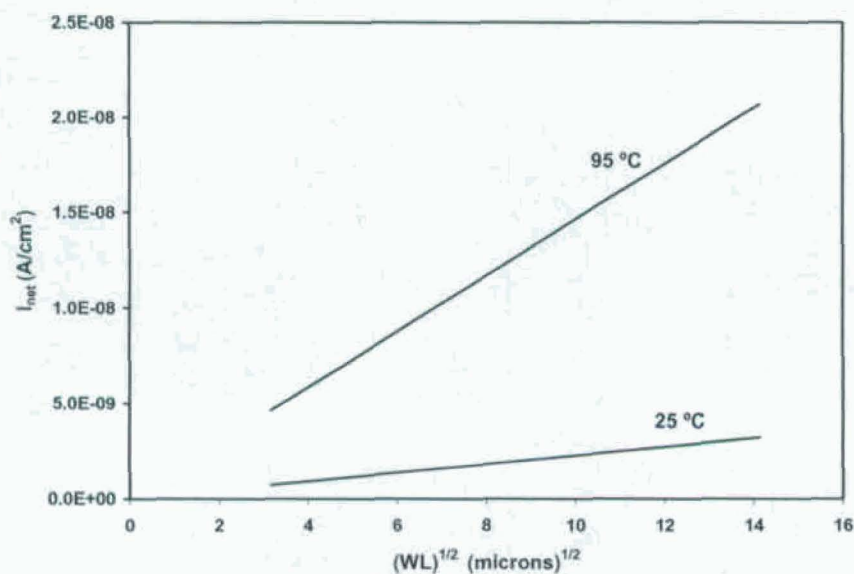


Figure 8. Comparison of calculated I_{net} values for two temperatures. In both cases, the expected linear dependence on the square root of the WL is observed, but the increased conductivity and more rapid cathodic kinetics observed at 95 C produce a larger slope.

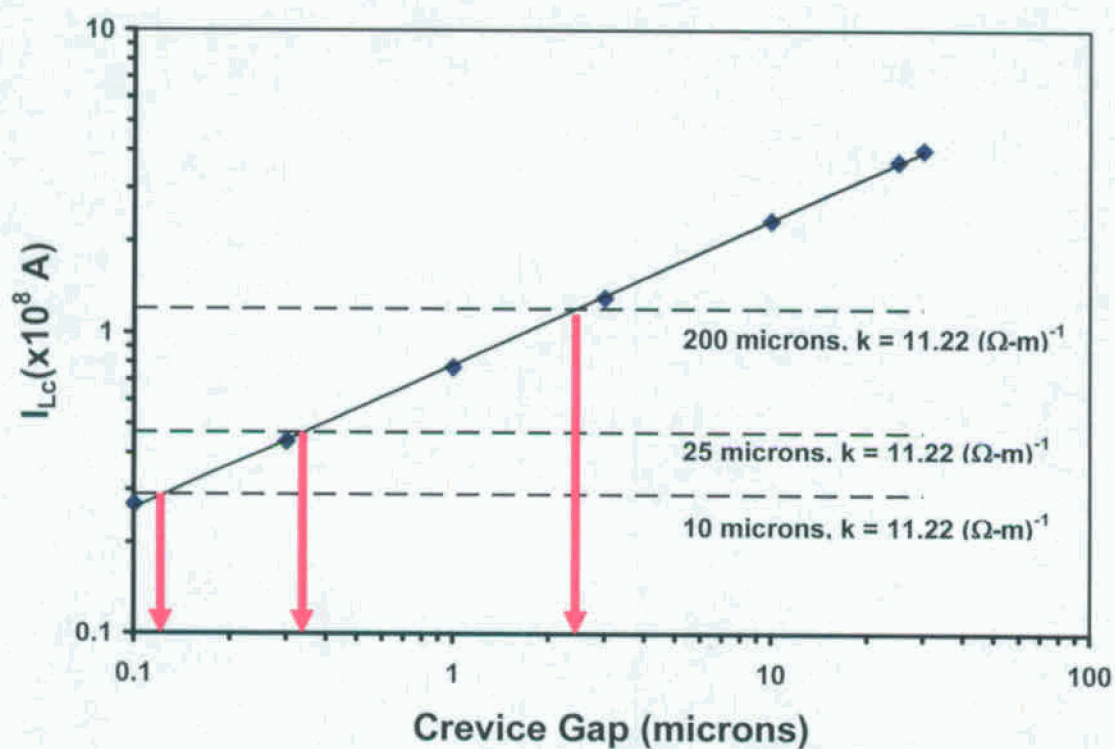


Figure 9. Stability of crevices linked to wetted external cathode. Total current demand of anode is related to the crevice gap via a power law with an exponent of 0.48. The dotted lines represent the maximum current from wetted external cathodes with different water layer thicknesses and a constant solution composition. Only crevices with gaps $< 10 \mu m$ can be stabilized by such cathodes. Conditions: $E_{rp} = -0.35 V$, $T=25^\circ C$, cathodic maximum currents occurred at 15 cm and 30 cm for 10, 25, and 200 microns, respectively.