The stable growth of corrosion pits requires the presence of an aggressive chemistry at the corroding surface as characterized by a high metal chloride concentration and low pH. The conditions leading to the maintenance of such chemistry were mathematically considered by Galvele through an investigation of the steady state relationship between metal dissolution and mass transport out of a one-dimensional (1-D) pit. For the case of a 1-D pit, it was theoretically demonstrated that a minimum critical value of cation flux — expressed as the product of the current density and the pit depth, \( i \cdot x \) — was necessary for the pit to maintain a critical chemistry and thus stably corrode. As such, should the product of the current density and the pit depth fall below this critical value, repassivation would set in due to the loss of the aggressive chemistry. Subsequent studies on stainless steel pitting referred to this parameter and equivalent relationships for other pit geometries as the pit stability product. Critical pit stability product (denoted \( (i \cdot x)_{\text{stability}} \)) was employed as the anodic stability parameter to determine the maximum pit size that can be attained on a particular metal surface in a given corrosive environment.

Experimental results obtained using the artificial pit or lead-in-pencil electrode can be directly used to quantify 1-D dissolution kinetics because the construction of this electrode results in inert walls surrounding a single active surface corroding under a precipitated salt film upon the application of high anodic potential in corrosive solution. The presence of the salt film results in diffusion-limited dissolution conditions that permit the study of the corroding system in a quasi-steady state. The pit stability product under a salt film, \( (i \cdot x)_{\text{saltfilm}} \), can then be extracted from measuring the diffusion-limited current density at different depths. The critical pit stability product can then be expressed as a fraction of this measured pit stability parameter \( (i \cdot x)_{\text{saltfilm}} \).

Pit stability data collected from experiments at shallow pit depths may possess three-dimensional characteristics due to the influence of the external hemispherical boundary layer at the pit mouth. The value of high-throughput artificial pit techniques in accessing a wide range of pit depths to obtain kinetic data and therefore avoid this problem has been previously reported. It is necessary to consider in detail the dependence of measured current on geometric variables in order to ensure that pit stability data extracted from artificial pit experiments does indeed correspond to true 1-D transport. An analysis of this nature would assist in judicious selection of the experimental parameter space (pit diameter, pit depth, concentration of bulk electrolyte) within which pit stability data can be properly collected and interpreted.

The utilization of finite element modeling permitted the rapid generation of flux characteristics by varying specific geometric parameters of a 1-D pit, similar in approach to the work performed on hemispherical pits by Harb and Alkire. A systematic treatment of the flux response to pit geometry in this manner evaluated the minimum depth that had to be attained in order to obtain artificial pit data truly representative of 1-D mass transport. Furthermore, the data from deep pits reflected pit stability kinetics isolated from effects of the bulk chloride environment, thus affording better agreement of experimental measurements with the theoretical basis of the Galvele stability criterion. Finally, the results of this study provide a scientifically defendable rationale for the empirical observation of a plateau in the measured repassivation potential for deep pits, thereby assisting in the development of a quantitative framework that connects electrochemical parameters critical to both pit stability and repassivation.
in the simulations, which was two orders of magnitude larger than the deepest pit simulated.

- An initial linear concentration gradient was considered inside the pit, i.e., $C(z, t = 0) = C_{\text{sat}} \frac{z}{Z}$.
  The walls of the pit were considered to be inert, i.e., the flux across these boundaries was set to zero for all time.

- A constant diffusion coefficient $D$ was assumed; the value used was $8.24 \times 10^{-6}$ cm²/s as employed by Gaudet et al.\textsuperscript{14} based on FeCl\textsubscript{2} diffusion in 1 M HCl. This value is a reasonable approximation because it is within the range of the values of $7 \times 10^{-6}$ cm²/s to $1 \times 10^{-5}$ cm²/s reported for $D$ in other 1-D pit studies in the literature.\textsuperscript{26-27,29,36} Also, the assumption of constant diffusivity has been shown by Gaudet et al.\textsuperscript{14} to effectively approximate the combined effects of variable diffusivity and electromigration on the cation flux.

Accounting for variable $D$ and electromigration would be more representative of actual mass transport conditions, but the effects of these individual variables tend to counter each other, resulting in a situation where their net influence on the flux is approximated within an error of 10% by assuming a constant value for $D$.\textsuperscript{14} Moreover, Steinsmo and Isaacs provided evidence that calculating the diffusion coefficient based on activity coefficients results in a value much higher than attributed to by experimental observations.\textsuperscript{37} Furthermore, Ernst and Newman,\textsuperscript{29} Jun et al.,\textsuperscript{36} and Woldemedhin et al.\textsuperscript{37} have shown that modeling the transport characteristics of the 1-D pit corroding under a salt film purely as a diffusion-limited process with the value for $D$ as reported by Gaudet et al.\textsuperscript{14} approximates the experimentally observed results closely, particularly for bulk $[\text{Cl}^-]$ lower than 4 M. Ernst and Newman\textsuperscript{29} have noted that salt solubility affects mass transport more than $D$ until the bulk $[\text{Cl}^-]$ reaches 4 M; beyond this value, viscosity effects on $D$\textsuperscript{19} are likely to influence mass transport synergistically with cationic chloride solubility. As for the effects of electromigration, the ohmic drop for a 1 mm deep pit corroding under a salt film ($l_L = 0.1$ A/cm², average resistivity 6.7 Ω·cm) is calculated to be 67 mV. The ohmic drop in a 1-D pit corroding under a salt film has been shown by Laycock and Newman\textsuperscript{30} to be independent of pit diameter. Also, studies by Novakovski and Sorokina,\textsuperscript{38} and later by Isaacs\textsuperscript{18} have shown that the majority of this potential drop occurs across the salt film, and the current in the pit is primarily regulated by diffusion. Therefore, in order to parse the effect of pit geometry on cation flux, diffusion has been considered independent of electromigration in this study.

The steady-state flux data for this system were extracted by integrating the individual flux elements along the $z$-direction and dividing by the cross-sectional area of the pit. This provides an average value of the flux across the corroding surface. Simulations were run until differences in calculations from consecutive iterations as determined by the built-in $a posteriori$ error estimation capability of the software decreased to less than the threshold tolerance of 0.1%.

**Artificial pit experiments.**—The 1-D artificial pit (lead-in-pencil) electrode was constructed using 316L stainless steel wire (California Fine Wire Company, Grover Beach, CA) of diameter 50.8 μm cast in epoxy. The composition of the wires used is shown in Table I. The electrode surface was polished to a surface finish of 320 grit with SiC abrasive paper and placed upright in a test cell containing unbuffered 0.6 M NaCl solution. The exposed area of the electrode was 2.03 \( \times 10^{-5} \) cm². A saturated calomel reference electrode (SCE) and a platinum mesh counter electrode were utilized for all the tests. All electrochemical testing was carried out at an average ambient temperature of 22°C using a Bio-Logic SP-200 (Bio-Logic SAS, Claux, France) potentiostat.

Pitting was initiated by applying a potential of +750 mV\textsubscript{SCE} for a short duration (2 to 5 minutes) and then propagated to various depths by applying a lower potential of +450 mV\textsubscript{SCE} for different periods of time. This sequence was followed by a rapid cadic polarization scan at 5 mV/s to a final potential of −100 mV\textsubscript{SCE} in order to obtain an estimate of the diffusion-limited dissolution current density $i_L$. Variants of this procedure to measure $i_L$ have been employed in other pitting studies as well.\textsuperscript{27,28} This dissolution current density was converted to a flux value $J$ as shown in Equation 1.

$$J = \frac{i_L}{\pi F} = \frac{D \Delta C}{d} = \frac{D(C_{\text{sat}} - C_{\text{pit mouth}})}{d} \Rightarrow J \propto \frac{1}{d} \tag{1}$$

where $z$ is the number of electrons transferred during the oxidation reaction (2.2), $D$ is the diffusion coefficient of the cation species

| Alloy | C   | Mn  | P   | S   | Si  | Cr  | Ni  | Mo  | N   | Cu  | Fe  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 316L  | 0.019 | 1.356 | 0.030 | 0.0287 | 0.406 | 17.07 | 10.66 | 2.16 | 0.0499 | 0.232 | 67.98 |

\textsuperscript{a}OLI Analyzer System 9.3 software (OLI Systems, Inc., Cedar Knolls, NJ) was used to calculate the average resistivity as the arithmetic mean of solutions corresponding to mixture of cationic chlorides at 100% saturation and the bulk solution 0.6 M NaCl. The cationic chloride solution at 100% saturation considered included FeCl\textsubscript{2}, CrCl\textsubscript{3}, NiCl\textsubscript{2} following the proportion determined by Isaacs et al.\textsuperscript{36}
(8.24 \times 10^{-6} \text{ cm}^2/\text{s}), and \( F \) is Faraday’s constant (96,485 C/mol-equivalent). One-dimensional mass transport with the pit depth as the diffusion length would therefore be indicated as a straight line on a plot of \( J \) versus \((1/d)\).\(^{14,18,25,28}\) These values have been taken from several sources in the literature on stainless steel dissolution in chloride media.\(^{14,25,26,28,29,36}\) The pit depth \( d \) was calculated by converting the charge density passed during the potentiostatic hold and the polarization scan using Faraday’s law, as indicated in similar experiments reported in the literature.\(^{27,28}\)

\( \Delta C \) is the change in concentration of the cation across the pit depth. Following the literature on stainless steel pitting using this equation, the cation concentration at the pit base is considered to be at the saturation concentration of either a stoichiometric combination of the chlorides of Fe\(^{2+}\), Cr\(^{3+}\), and Ni\(^{2+}\); or only FeCl\(_2\); the cation concentration at the pit mouth is considered to be zero.\(^{3,13,14,25,29,35}\)

A separate set of artificial pit experiments as described above were also performed on the sample with the exposed surface facing downward, in both quiescent and stirred 0.6 M NaCl solution. The stirring rates employed were 75 rpm (low) and 300 rpm (high). These configurations were employed to study the effect of boundary layer thickness on the kinetics of the system due to either natural or forced convection.\(^{39,40}\) The experimental procedure described was also performed on a separate sample with the exposed surface facing upward in quiescent 0.6 M HCl solution (measured pH = 0.58) which would prevent the precipitation of any corrosion product at the pit mouth (as predicted using thermodynamic modeling by the OLI Analyzer Studio 9.2 software (OLI Systems, Inc., Cedar Knolls, NJ)). This latter test served to observe what effects, if any, the possible deposition of corrosion products at the pit mouth\(^{41}\) may have had on the mass transport of the system in the neutral, unbuffered chloride solution.

### Results

Figure 2 plots the numerically simulated flux as a function of pit depth for two different pit diameters. The slopes of the curves as pit depth increases provide a preliminary idea about the nature of mass transport for the two cases. The decrease in flux is very steep for the 50 \( \mu \text{m} \) diameter pit as it approaches a depth of 500 \( \mu \text{m} \), indicating that analytically determined 1-D Fickian mass transport based on the pit depth as the diffusion length closely approximates the simulated value beyond this depth. For the 1 mm diameter pit, the overall flux across depths is low and a distinct transition as seen for the 50 \( \mu \text{m} \) pit is not apparent from the figure.

Figure 3a shows a plot of the numerically simulated flux results versus the reciprocal of the pit depth for three different pit diameters. These results were obtained by performing the simulation on the geometry described previously using values of 5.02 M for \( C_{\text{sat}}\) and 8.24 \times 10^{-6} \text{ cm}^2/\text{s} \) for \( D\).\(^{13,14}\) In Figure 3a, these simulations are compared with the analytically determined expectation of 1-D Fickian flux, calculated using the same values for \( C_{\text{sat}}\) and \( D\). A linear relationship between flux and the reciprocal of the pit depth is expected in the case of 1-D transport, as indicated in Equation 1; this is the line that describes the analytical 1-D flux in Figure 3. It is evident from the plot that the numerically simulated flux deviates from the analytical calculation for shallow pits. This deviation decreases as the pit depth increases – pits of diameter 50 \( \mu \text{m} \) begin converging with the analytical 1-D flux for pits deeper than 300 \( \mu \text{m} \) and are indistinguishable from the latter once pits of depth close to 1000 \( \mu \text{m} \) are

\[ \frac{\Delta C}{D} \frac{1}{C_{\text{sat}}} \quad \text{versus} \quad \frac{1}{d} \]
attained. A similar trend is observed for a pit diameter of 90 \( \mu \text{m} \) – the convergence to the theoretical line begins around depths of 400 \( \mu \text{m} \) and the simulated and analytical fluxes coincide for pit depths in the vicinity of 1000 \( \mu \text{m} \). However, for the larger pit diameter of 1 mm, the simulated flux deviates greatly from the analytical calculations and begins to converge only once depths of nearly 5 mm are attained.

Figure 3b illustrates this difference even more starkly with the simulated concentration profiles plotted along the pit depth for two 1 mm deep pits of different diameters. The numerically simulated result for the 50 \( \mu \text{m} \) diameter pit agrees very well with the analytical line, with the concentration at the pit mouth approaching zero. However, for the 1 mm diameter pit, the simulated results show that the concentration at the pit mouth has dropped to only around 30% of saturation (\( \approx 1.5 \text{ M} \)), and therefore deviate from analytically expected behavior at these depths.

Figure 4 shows that the experimental fluxes obtained from 50 \( \mu \text{m} \) diameter artificial pits of up to 500 \( \mu \text{m} \) deep match the analytical expectations closely, even for shallow depths around 100 \( \mu \text{m} \). In order to ensure that experimental conditions did not cause mass transport restrictions, the effects of convection and possible corrosion product deposition on the flux were explored. These results are shown in Figures 5 and 6, respectively, and indicate that the flux is not affected significantly by either of these modifications to the experimental conditions for the pit diameter studied here, with the results bounded by the simulations on the lower end and the theoretical line on the upper end. In each of these experiments, it is observed that as pits grow deeper, the experimentally observed flux converges to the theoretical estimate.

In Figure 7, published high-throughput artificial pit experimental data\(^28\) for 50 \( \mu \text{m} \) diameter artificial pits are juxtaposed with the numerically simulated flux as well as two analytically determined flux lines. The analytical Fickian calculations differ only in terms of the value of \( C_{\text{sat}} \) used. The line with the higher slope utilizes the value of 5.02 \text{ M} \) that results from observations by Isaacs et al.\(^35\) based on the stoichiometric dissolution of the individual components of 18–8 stainless steel (\( \text{Fe}^{2+}, \text{Cr}^{3+}, \text{and Ni}^{2+} \)), whereas the line with the lower slope adopts 4.2 \text{ M} as \( C_{\text{sat}} \) reported by Gaudet et al.\(^14\) as well as by Ernst and Newman.\(^29\) Based on the assumption that saturated FeCl\(_2\) approximates the behavior of the concentration at the pit base. The experimental data are observed to span the region between the simulated flux and the theoretical flux based on 5.02 \text{ M} for shallow pits, and converge to the analytical line for deep pits (\( \approx 400 \mu \text{m} \)). It is seen that analytical calculations using \( C_{\text{sat}} \) data from stoichiometric dissolution bound the experimental data for 316L stainless steel better than if only FeCl\(_2\) were considered. This result concurs with previous work\(^28\) on the dissolution kinetics of 316L and 17–4 PH stainless steel artificial pits, indicating the \( C_{\text{sat}} \) value used in calculations needs to be based on stoichiometric dissolution. The experimental data obtained in this study from the different configurations considered were also found to be contained within the limits of scatter of the high-throughput data at all depths.

**Discussion**

This work presents a combined experimental and computational analysis of the effects of the pit depth on the measurement and evaluation of the pit stability parameter from artificial pit experiments from the perspective of 1-D mass transport. Possible effects of convection and corrosion products on the 1-D flux are taken into account, before parsing the results to elucidate the effects of the external boundary layer on mass transport with pit depth and diameter. Artificial pit data...
in the literature are considered to rationalize the effect of bulk [Cl\(^-\)] on pit stability in addition to pit depth. Finally, the observed behavior of repassivation potential on pit depth is quantitatively explained in the context of steady state 1-D transport, using the results of this study.

**Mass transport is unaffected by bulk convection and corrosion products at pit mouth.**—The results of artificial pit experiments performed with configurations designed to examine the effects of both natural and forced convective flow, demonstrated that these modifications had no substantial effect on the flux, as shown in Figure 5. Work on rescaled crevices by Lee et al.\(^{42}\) was leveraged to ensure that effects due to gravity were countered by capillary forces and did not lead to momentum transfer within the pit. These calculations applied the Young-Laplace equation for hydrostatic equilibrium, considering the solution within the pit as a cylinder, as shown in Equation 2:

\[
\gamma \sin \theta - \rho g \pi \delta^3 / 4 = \frac{D \Delta C}{d + \delta}
\]

where \(\gamma\) is the average surface tension (\(= 78 \text{ dyne/cm}\)) and \(\rho\) is the average density (\(= 1.2 \text{ g/cm}^3\)) of the pit solution (considered the arithmetic mean of the solution of cationic chlorides at 100% saturation and 0.6 M NaCl, as mentioned previously), calculated using OLI Analyzer Studio 9.3. \(d\) and \(\delta\) are the pit depth and diameter respectively, and \(\theta\) is the contact angle between the solution and the pit wall. These calculations are plotted in Figure 8 for \(\theta = 45^\circ\); using the entire range of the cosine function would yield similar results for the capillary force, i.e. three orders of magnitude greater than the weight of the solution.

The results shown in Figure 5 were consistent with the interpretation provided in published hydrodynamic studies on pitting\(^{33,44}\) that external fluid flow has little effect on narrow cavities as opposed to shallow ones. The possibility of mass transport effects due to corrosion product precipitation (which may be likely in the neutral chloride solution when the cations encounter a higher p\(\text{H}\) at the pit mouth) can be rejected for the pit diameters studied based on the results shown in Figure 6. These results demonstrated that performing the same experiment in media in which the bulk p\(\text{H}\) would be too low for such corrosion products to precipitate does not lead to a considerable change in flux. On the basis of these results, mass transport effects observed in the system can therefore be examined solely on the basis of a dependence on pit depth.

**External hemispherical boundary layer affects mass transport of shallow pits.**—The deviation from linearity at shallow pit depths displayed by the numerically simulated flux results can be attributed to the effect of the external hemispherical boundary layer on the total diffusion length.\(^{31}\) The deviation from the analytical Fickian expectation therefore occurs because the pit depth alone does not approximate the total diffusion length for shallow pits. The hemispherical boundary layer influences the mass transport because the cation concentration outside the pit does not immediately vanish at the pit mouth. Instead, this change in concentration occurs across a finite length; for shallow pits, this additional length is comparable to and sometimes much larger than the pit depth, as shown in Figure 9.

The consequence of this effect is that the mass transport follows a behavior expressed in terms of a modified version of Equation 1:

\[
J = \frac{i_L}{zF} = \frac{D \Delta C}{d + \delta} = \frac{D(C_{\text{sat}} - C_{\text{pitmouth}})}{d + \delta} \Rightarrow J \propto \frac{1}{d + \delta}
\]

where \(\delta\) represents the effect of the boundary layer on the overall diffusion length. The value of \(\delta\) can be calculated using Equation 3 from the numerically simulated data. As Figure 9a indicates, \(\delta\) is dependent only on the pit diameter and does not change as the pit depth increases. When normalized in terms of the pit diameter \(\phi\), \(\delta\) assumed relatively constant values equal to approximately 40% of the pit diameter across the range of pit depths studied (Figure 9b). Finally in Figure 9c, when visualized as a fraction of the pit depth, it is abundantly clear that for the larger pit diameter, the effect of the boundary layer is massive for shallow pits. At these depths, \(\delta\) contributes disproportionately to the overall diffusion length because it is nearly three orders of magnitude greater than the pit depth. Conversely, as pits grow deeper, the effect of \(\delta\) on the overall diffusion length diminishes greatly, as is made distinctly apparent in the figure. In fact, at pit depths where the numerically simulated flux is seen to converge with the analytical calculations, \(\delta\) is less than 2% of the pit depth. Therefore, for deep pits, the relative influence of \(\delta\) vanishes and utilizing the pit depth alone serves as a good approximation for the overall diffusion length.

The effect of \(\delta\) on the observed mass transport of the system can also be examined in terms of the change in concentration from the pit base to the pit mouth. Figure 10 displays the concentration change...
Figure 9. Effect of the boundary layer $\delta$ on the overall diffusion length across pit depths for pits of different diameters. (a) Absolute value of $\delta$ across pit depths. Note the logarithmic scale on the ordinate – the dependence of $\delta$ on pit diameter is evident in this comparison. (b) Effect of the boundary layer on the overall diffusion length interpreted in terms of a generalized geometry – $\delta$ has been normalized as a ratio of pit depth plotted versus pit depth normalized over diameter. This plot shows that $\delta$ is always virtually the same fraction of the pit diameter and independent of pit depth itself. (c) Influence of the boundary layer on affecting the overall diffusion length in relation to the pit depth. Note how the contribution of $\delta$ to the overall diffusion length ($d + \delta$) decreases with increasing pit depth, and that for the pit of smaller diameter, $\delta$ is always less than $d$, with a maximum value of only around 30% of the pit depth.

across the model domain using a set of concentration profiles (similar to Figure 3b). As is evident upon comparing Figures 10a and 10b, the concentration profile of the pit of smaller diameter is closer to the theoretical basis of $\Delta C = (C_{\text{sat}} - 0) = 5.02$ M than that of the pit of larger diameter. This result implies that the concentration gradient for the smaller diameter is steeper than that of the larger diameter because both these pits are of the same depth. In order to interpret these data in terms of a generalized geometry, the cation concentration at the pit mouth as estimated by the simulations is plotted as a fraction of the concentration at the pit base ($C_{\text{sat}} = 5.02$ M) against pit depth normalized by the pit diameter ($d/\phi$) in Figure 11. As can be seen in this plot, the data obtained based on different pit diameters collapses on to a single curve, indicating that the concentration of the pit mouth approaches zero only when pit depths close to 10 times the pit diameter are attained.

**Bulk $[\text{Cl}^-]$ affects pit stability product measurement for shallow pits**—Prior work has shown that the pit stability product is affected by bulk electrolyte chemistry.\(^{27,29,36,44}\) Figure 12a reproduces the plot of $(i \cdot x)_{\text{saltfilm}}$ versus bulk $[\text{Cl}^-]$ from the work of Woldemedhin et al.\(^{27}\) In this plot, the y-intercept provides the value of pit stability product under a salt film isolated from the effects of bulk $[\text{Cl}^-]$ (i.e., at a bulk $[\text{Cl}^-] = 0$).

This value is the true measure of the anodic stability parameter because it reflects a zero cation concentration gradient at the pit mouth, which is the theoretical basis of the Galvele formulation.\(^3\) The resulting expression is similar in form to Equation 1 and is expressed below, and is also noted similarly in the literature:\(^{25,27,28,34}\)

$$\frac{i_L}{zF} = \frac{D\Delta C}{d} = \frac{D(C_{\text{sat}} - C_{\text{pitmouth}})}{d}$$

$$\Rightarrow i_L \cdot d = zFC_{\text{sat}} = (i \cdot x)_{\text{saltfilm}}$$  \hspace{1cm} [4]

As the bulk $[\text{Cl}^-]$ increases, $C_{\text{pitmouth}}$ increases, and the corresponding change in measured $(i \cdot x)_{\text{saltfilm}}$ is mapped by the slope of the linear fit in Figure 12a.

From Figure 12b, the slopes of the linear fits for the experimental data obtained at shallow pits are lower than those for the deep pits.
Furthermore, the scatter (indicated by the $R^2$ value) is lower for deep pits than for shallow pits. The $\lambda_{x,salt,m}$ value of 0.9031 obtained for deep pits is in good agreement with the value of $\lambda_{x,salt,m}$ isolated from the effects of bulk $[\text{Cl}^-]$ (y-intercept in Figure 12a). Figure 13 shows the apparent cation concentration at the pit mouth as a fraction of $C_{sat}$ mapped against the bulk $[\text{Cl}^-]$, calculated from the experimental $(i-x)_{salt,m}$ versus bulk $[\text{Cl}^-]$ data,27 assuming a constant value of $D$. It is evident that as the bulk $[\text{Cl}^-]$ increases, the cation concentration of the pit mouth increases. This result therefore implies that as the bulk $[\text{Cl}^-]$ rises, the assumption that the cation concentration at the pit mouth is zero breaks down, i.e., $\Delta C$ is no longer equal to $C_{sat}$. This result may be reflective of the fact that viscosity effects on physicochemical parameters play an increasingly important role in determining mass transport as the bulk chemistry becomes more concentrated in chloride, as reported in the literature.19,29,36,44 Such effects on solution properties may have an impact on both $D$ as well as $C_{sat}$, the latter being influenced by the common ion effect from the bulk electrolyte as has been discussed in other studies.29,36,44 In toto, the results shown in Figures 9 through 13 demonstrate that it is imperative to account for the effects of both pit depth as well as bulk electrolyte chemistry during measurement and analysis of artificial pit studies to obtain accurate estimates of pit stability parameters.

**Saturation based on stoichiometric dissolution correctly represents analytical Fickian 1-D flux.**—The influence of pit depth and bulk electrolyte concentration also impacts the value of $C_{sat}$ considered when calculating the analytically determined Fickian 1-D flux. This point is made particularly evident when the experimental data from Gaudet et al.14 is considered (reproduced in Figure 14). At pit depths of $\approx400 \mu m$, the experimental values (data points) appear to converge to the analytical expectation (dashed line) calculated using the saturation concentration of $\text{FeCl}_2$ in 1 M HCl (4.2 M).35 However, the results from this study show that the experimental data converge with the analytical calculations with low scatter only when the depth is greater than about 8 times the diameter (Figure 7). Therefore, for a pit diameter of 1 mm, deviation between experiment and theory would be expected to disappear only beyond a depth of 8 mm, in contrast to 400 $\mu m$ as observed. When 5.02 M, the value obtained from in situ X-ray measurement of the stoichiometrically dissolved 18–8 stainless steel in chloride solution,35 is used for $C_{sat}$ instead, it is observed that the experimental data now indeed deviate from the analytical prediction (solid line) at $\approx400 \mu m$. It must also be noted that the experimental data of Gaudet et al.,14 although convergent at $\approx400 \mu m$ to the analytical expectation assuming a surface concentration of 4.2 M $\text{FeCl}_2$, begin to deviate from that line towards the line describing a surface concentration of 5.02 M as deeper pits are approached, as can be observed in Figure 14.

The observed agreement of the experimental data with the analytically determined calculations based on $C_{sat}$ of 4.2 M can be rationalized with analysis based on the data from Figures 12 and 13. The experimental data of Gaudet et al. were reportedly obtained in a solution with a concentration of approximately 1 M $[\text{Cl}^-]$. Substituting this value for $[\text{Cl}^-]$ in Equation 4, a value of 0.79 A/m for $(i-x)_{salt,m}$ is obtained, which in turn results in a value of 4.52 M for $C_{sat}$, which is in good agreement with the value of 4.2 M used by Gaudet et al.14 with a relative error of only around 7.6%. This deviation was within the error of the linear regression for $(i-x)_{salt,m}$ in Figure 12a. These...
results reinforce the necessity of data collection from deep pits. The lack of data from sufficiently deep pits (d/φ ≈ 8) indicates that the experimental values in the Gaudet et al. obtained are not isolated from the effects of bulk [Cl\(^{-}\)]. The depressed value of (i\(\cdot\)x\(_{\text{saltfilm}}\)) that is obtained as a result yields a \(C_{\text{sat}}\) estimate which is lower than the actual value for 18–8 stainless steel, but fortuitously agrees with the value for FeCl\(_2\) in 1 M HCl. Consequently, the perceived agreement of the Gaudet et al. experimental data with the analytical predictions at depths shallower than expected from this study emerges because a lower value of \(C_{\text{sat}}\) based on FeCl\(_2\) solubility rather than stoichiometric dissolution of the stainless steel was used.

Effect of pit depth on 1-D transport rationalizes repassivation behavior.—The results in this study can also be used to examine the impact of pit depth on the critical surface concentration associated with repassivation. Several studies have shown that a salt film is not critical for stable pit growth\(^{13,29,46}\) and that pit stability ought to be examined in the context of repassivation.\(^{10,28,30}\) This latter idea implies that the minimum critical conditions for stable pit growth also characterize pit repassivation. Figure 15a shows that even when the surface concentration at the pit base is diluted to lower fractions of the concentration at saturation, the numerically simulated flux continues to converge towards the analytically determined flux at pit depths which are approximately eight to ten times the pit diameter. Suzuki and Kitamura\(^{47}\) reported that for 316L in chloride solution, activated pits that were about ten times as deep as their diameter registered a critical potential for repassivation similar to activated crevices. In their study, the dissolution current density was monitored versus time at progressively lower applied potentials. The critical potential in their study was defined as the lowest potential at which this dissolution could not be sustained upon prolonged holding (≈ 20 h). The results of the present study provide quantitative support to the notion that it is only upon attaining depths about ten times the diameter that sufficient

Figure 12. Effect of the bulk [Cl\(^{-}\)] on the pit stability data from artificial pit experiments. (a) Replotted data from Woldemedhin et al.\(^{27}\) indicating linear dependence of (i\(\cdot\)x\(_{\text{saltfilm}}\)) on bulk [Cl\(^{-}\)]. (b) Data from Srinivasan et al.\(^{28}\) replotted to highlight the difference in slopes at shallow and deep pits. Pit diameter = 50 \(\mu\)m.

Figure 13. Apparent cation concentration at the pit mouth as a function of bulk [Cl\(^{-}\)], calculated from the (i\(\cdot\)x\(_{\text{saltfilm}}\)) data of Woldemedhin et al.\(^{27}\) assuming a constant value of \(D\). Pit diameter = 50 \(\mu\)m.

Figure 14. Effect of utilizing different values of \(C_{\text{sat}}\) (based on stoichiometric dissolution of 18–8 stainless steel or only FeCl\(_2\)) on interpretation of experimental data from 1-D pits of large diameter. Experimental data are replotted from Gaudet et al.\(^{14}\) (pit diameter = 1 mm).
mass transport restriction results for 1-D pits to sustain the steady-state concentration necessary to corrode stably with a film-free surface. For shallower 1-D pits, the diffusion out of the pit would overwhelm the rate of metal dissolution, leading to repassivation.

The view that restricted mass transport impedes repassivation has been substantiated by Sridhar and Cragonlino,24 as well as Srinivasan et al.,30 who have shown that crevice formation in large-area samples can lead to the measurement of more active repassivation potential values even when the charge density passed is low. Finally, studies using artificial pits27,28,30 have shown that the depth at which the measured repassivation potential approaches a plateau is approximately eight to ten times the pit diameter, as can be seen in the data reproduced in Figure 15b. These latter results lend credence to the proposition that at this pit depth, a critical steady state concentration (lower than 100% saturation)30,32,34 is attained at the pit base, with equal rates of both metal dissolution and diffusion out of the pit, thus marking the transition between pit stability and repassivation.

Conclusions

This study employed artificial pit experiments as well as finite element modeling to elucidate the effects of pit depth on the flux emanating from 1-D pits, providing commentary on proper collection, analysis, and interpretation of pit stability data from artificial experiments. For shallow pits, the hemispherical boundary layer at the pit mouth significantly affected the flux characteristics. It was only once such pits had attained depths of around eight times the diameter that the overall diffusion length could be approximated well by the pit depth alone. The examination of results from artificial pit experiments reinforced the importance of obtaining data from deep pits so that pit stability parameters extracted not only reflected true 1-D mass transport based on the pit depth, but also were not affected by the bulk electrolyte. Artificial pit experiments performed in several configurations ruled out the influence of convective transport and the precipitation of corrosion products on the mass transport in pits of small diameter. The trends observed in published experimental data were also explained by the inferences of bulk electrolyte effects obtained from this work. Finally, the results of this investigation were also used to rationalize the observed dependence of repassivation potential on pit depth, thereby providing a quantitative connection between pit stability and repassivation studies.

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Figure 15. Implications of pit depth on measured repassivation parameters and critical conditions for pit stability. Pit diameter = 50 μm. (a) Comparison of fluxes obtained from the analytical solution and the numerical solution mapped across pit depths with successive dilutions of cation concentration at the corroding surface. The dashed lines represent the flux determined from the analytical solution and the connected symbols denote the numerical simulations. (b) Observed behavior of repassivation potential with pit depth from artificial pit experiments on stainless steels in chloride media. The shaded region signifies the depths at which the \(E_{rp}'\) saturates’ or approaches a plateau – at around 400 to 500 μm, these depths are approximately 8 to 10 times the pit diameter. Data for NaCl and FeCl₃ are reproduced from Srinivasan et al.²⁸ and Woldemedhin et al.,²⁷ respectively.
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