Evaluation of the Maximum Pit Size Model on Stainless Steels under Thin Film Electrolyte Conditions

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This paper presents the experimental evaluation of a recently developed model for predicting the maximum pit size possible on a stainless steel surface under a certain set of atmospheric conditions. Prediction of the maximum pit size possible on 304L and 316L was accomplished by coupling the maximum cathode current available from a thin film of ferric chloride covering the steel’s surface to the minimum current needed by a growing hemispherical pit. The experimental validation involved exposure tests of 304L and 316L steel samples covered by thin film of ferric chloride solution at a relative humidity of 97% with a loading density of 400 μg cm−2. Evaluation of the maximum pit size model was done by comparing the pit size from the model with the pit size obtained from exposure tests at the same atmospheric conditions. The model was found to bound all of the experimental data for both alloys if it was assumed that the critical pit solution was between 60% and 80% of the saturation concentration.

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The passive oxide layer covering stainless steel samples reduces the rate of corrosion when the materials are exposed to the atmosphere. That said, the presence of aggressive halide ions like chloride will lead to pitting corrosion. Pits can serve as fatigue crack initiators, undermining the strength of the alloy which is used in components undergoing cyclic service, such as landing gear and engine compressor blades. Such cracking results in high economic costs due to service downtime and repair, as well as posing significant safety hazards. Structural integrity calculations are used by engineers to predict cracking based on a starting crack size. However such calculations usually do not account for damage accumulation from corrosion and hydrogen uptake, which could lead to underestimation of the potential damage or gross conservatism if a large initial crack size is assumed. One of the input parameters to account for corrosion under atmospheric conditions is pit size.

Knowledge of the maximum pit sizes formed under such atmospheric conditions where the material is covered by a thin layer of electrolyte would be of great use in corrosion damage prediction. Power laws, of the form shown in equation 1, are one of the empirical models used for predicting maximum pit sizes under atmospheric conditions. Generally, power laws extrapolate corrosion data from short-term atmospheric exposures to predict maximum pit size for a certain set of material and atmospheric exposure conditions and exposure time

\[
d_{\text{pit}} = At^m \tag{1}
\]

where \(d_{\text{pit}}\) is the maximum pit depth, \(t\) is the exposure time, while \(A\) and \(m\) are constants that are specific to material and exposure condition.\(^5\) Muto et al.\(^5\) reported the maximum pit sizes of four steel samples, Fe-11Cr, 430, 304 and Fe-25Cr-13Ni-0.8Mo, exposed to severe marine, industrial and hot spring environmental conditions and fitted the data to power laws for each environment. The reported pit sizes on the steel samples were correlated with exposure time in severe marine exposure site, but the correlation of the pit sizes with time on samples retrieved from a hot spring exposure site gave a power law exponent of close to zero, i.e., the pit size reached a maximum threshold even for exposure times of over 10 years. This result shows that the power law works well in predicting pit sizes for certain material and atmospheric exposure conditions, but it cannot be extended to other material/environment systems. Instead of extrapolating empirical power laws for predicting pit sizes it is preferable to calculate the maximum pit size possible for certain material under a certain atmospheric condition. In fact, closer inspection of the data of Muto et al.\(^5\) shows that under all of the exposure conditions used, there appears to be a maximum pit size that is not exceeded even after long times (10 yrs).

The work of Muto et al.\(^5\) is not unique. Atmospheric exposure tests of stainless steels at different locations have consistently shown a limiting pit size, Nakata et al.\(^6\) reported the pit depth observed on 304 and 316 stainless steel samples from exposure tests for 13 years. The pit depth on the two steels reached a limiting value within 4–5 years of exposure, the size of which depended on the details of the exposure environment.

The observed limiting values in pit depth on stainless steels under atmospheric conditions can be rationalized by consideration of the galvanic couple involved in the pitting corrosion process. The two components of the galvanic couple in pitting corrosion are the actively dissolving pit and the cathode area covered by a thin film of electrolyte surrounding the pit as shown in Figure 1.

By first considering the anode and cathode separately, one can then couple their behavior in order to estimate a maximum pit size. The anode will be considered in terms of the minimum current needed (referred to as the anode current demand, \(I_{\text{anode}}\)) to maintain the aggressive chemistry required within the pit. The cathode will be analyzed in terms of the maximum amount of cathodic current that the surrounding surface could provide (referred to as \(I_{\text{inj, max}}\)) under optimal conditions. These two parameters are described in more detail below.

Anode current demand (\(I_{\text{anode}}\)).— The anode current demand of an actively dissolving pit is determined based on the work of Galvele\(^7\) for a one-dimensional pit with an active base surface and passive walls. Anodic metal dissolution at the active base of the pit produces metal cations. Subsequently, the metal cations undergo hydrolysis and produce metal hydroxide and hydrogen ions which result in an aggressive pit solution with low pH and high chloride concentration due to the need for electroneutrality.

\[
M \rightarrow M^{n+} + ne^- \tag{2}
\]

\[
M^{n+} + nH_2O \leftrightarrow M(OH)^{(n-1)+} + H^+ \tag{3}
\]

The anodic pit must dissolve rapidly enough to preserve the critical aggressive pit solution within the pit against dilution via diffusion in

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order to continue growing. Dilution of the aggressive pit solution will lead to repassivation of the pit. The depth of the one dimensional pit represents the diffusion barrier. Thus, in order for the pit to remain active, the rate of dissolution of the metal at the active base surface and the subsequent hydrolysis reaction of the metal cation must exceed the rate of diffusion out of the pit that could lead to dilution of the aggressive pit chemistry and eventual pit repassivation.

The anodic current demand \( I_{\text{anode}} \) is given by the pit stability product \( (i \cdot x) \),\(^{5-15} \) where \( i \) is the anodic dissolution current density from an active pit surface and \( x \) is the pit depth of a one dimensional pit. There is a critical value for the pit stability product for each material/bulk environment that must be continually exceeded for the pit to continue to grow. The pit stability product gives information about the anodic current \( i \) needed for stability of a one dimensional pit of depth \( x \). Thus, deeper pits can survive with smaller anodic current density compared to shallower pits for pit growth. The \( (i \cdot x) \) value for a one dimensional pit growing in its diffusion controlled state (due to the presence of a salt film on the dissolving surface) can be measured using the artificial pit technique:\(^{12-15} \)

\[
(i \cdot x)_{\text{salt film}} = \frac{nFD \Delta C}{2} = i_d
\]  

where \( i_d \) is the diffusion limited current density, \( d \) is the depth of the pit, \( n \) is the number of electrons transferred (based on stoichiometric compositions of the alloys \( n = 2.30 \) for 304L and 2.245 for 316L), \( F \) is Faraday’s constant, \( D \) is the diffusion coefficient and \( \Delta C \) is the difference in concentration of metal cations between the surface of the pit and the bulk solution.

For a two-dimensional hemispherical pit, the pit stability product becomes, via geometry, \( Ir \) where \( I \) is the anodic current and \( r \) is the pit radius. The relation between \( Ir \) and \( (i \cdot x) \) is shown in the derivation below. The concentration gradient between the pit surface and bulk solution of a hemispherical pit is given by:\(^{16} \)

\[
\Delta C = \frac{2\pi}{3nFD} \frac{Ir}{r}
\]  

Rearranging equation 5:

\[
\frac{Ir}{r} = \frac{3nFD\Delta C}{2\pi}
\]  

But the anodic current density \( i \) is ratio of the absolute current \( I \) and the surface area of hemispherical pit:

\[
I = \frac{I}{2\pi r^2}
\]  

Substituting equation 7 in equation 6 and solving for \( Ir \):

\[
\frac{I}{r} = 3nFD\Delta C
\]

Combining equation 4 and 8 yields:

\[
\frac{I}{r} = 3ix
\]

Thus, the critical anode current need \( I_{\text{anode}} \) can be determined experimentally by the artificial pit method for a given material and bulk environment. If the critical condition for pit stability is the presence of a salt film, then the artificial pit measurement provides the critical value of \( (Ir)_{\text{salt film}} \) directly. If concentrations less than saturation are required, the critical \( Ir \) can be scaled accordingly.

Cathode current supply.— The cathode, the area around the pit covered with a thin electrolyte film, must provide sufficient cathodic current to support the growth of a pit. However, the cathodic current that can be supplied by the cathodic area is limited due to the inherent interfacial kinetics and the ohmic resistance of the thin electrolyte film. This limit on the cathode current supply to a growing pit puts a limit on the pit size possible under a given set of atmospheric conditions. Figure 1 schematically shows the potential and cathodic current profile starting from the pit mouth. The potential on the external cathode increases from repassivation potential \( (E_{\text{rp}}) \) at the pit mouth to the open circuit potential \( (E_{\text{corr}}) \) at some distance away from the pit, with the cathode current density decreasing with distance from the pit as the potential becomes more positive. For all distances beyond the point at which the potential reaches the open circuit potential, the cathode cannot supply any cathodic current to support pit growth because all the cathode current generated is used locally to support the local passive current. The repassivation potential is used as the potential at the pit mouth because it has been shown that when properly measured, \( E_{\text{rp}} \) represents the lowest potential at which pits can propagate.\(^{17} \) This lower limit for the potential is important, as the lower the potential, the higher the cathodic current on the surrounding surface, and thus the larger the pit that can be supported.

The maximum cathode current \( I_{\text{cath,max}} \) supplied from the area of the cathode between the pit mouth and the point at which the potential reaches the corrosion potential, is given in equation 10 from the work of Chen and Kelly:\(^{18} \)

\[
\ln I_{\text{cath,max}} = \frac{4\pi kW \Delta E_{\max}}{I_{\text{cath,max}}} + \ln \left[ \frac{\pi r^2}{\Delta E_{\max}} \int_{E_{\text{corr}}}^{E_{\text{rp}}} (i_c - i_p) dE \right]
\]

where \( k \) is the conductivity of the thin film electrolyte, \( W \) is the water layer thickness, \( \epsilon \) is Euler’s number (2.718), \( i_c \) is the cathodic current density, \( i_s \) is the passive current density of the surrounding surface and \( \Delta E_{\max} = E_{\text{corr}} - E_{\text{rp}} \) is the maximum potential difference possible between the mouth of the pit and the point on the cathode surrounding the pit at which the potential reaches the corrosion potential.

Because the main goal is to determine the total current that can be delivered from a cathode area covered by a thin film of electrolyte knowledge of the spatial distribution of potential and current is not required. In such a case the real cathode can be replaced by an equivalent cathode. The equivalent cathode has the same spatial integration of the current density as the real cathode, but has a current density that is constant with position, and is referred to as the equivalent current density, \( i_{eq} \), as shown in Figure 1. The equivalent cathodic current density is the average current density over the potential difference between the mouth of the pit and some distance away from the pit at which the potential reaches the open circuit potential:

\[
i_{eq} = \frac{E_{\text{rp}} - E_{\text{corr}}}{\Delta E_{\max}} \int_{E_{\text{corr}}}^{E_{\text{rp}}} (i_c - i_p) dE
\]
Considering a circular cathode geometry, the maximum cathode current can be related to the equivalent cathode current density as:

$$i_{eq} = \frac{i_{cath, max}}{A_{eq}} = \frac{i_{cath, max}}{\pi r_{eq}^2} \quad [12]$$

where $A_{eq}$ is the area of equivalent cathode and $r_{eq}$ is the radius of the equivalent cathode.\(^{18}\)

Each of the variables in Eqn. 10 can be either calculated from thermodynamic physical chemistry data or measured in electrochemical experiments. Thus, calculating the anode current demand ($i_{anode}$) and the maximum cathodic current ($i_{cath, max}$) delivered from the cathode to the pit separately would enable one to calculate the maximum pit size possible under atmospheric conditions as the pit size at which the maximum cathode current ($i_{cath, max}$) is equal to the minimum anode current demand ($i_{anode}$). At larger pit sizes, the anode would require more current than the cathode could give even under the optimal conditions, and thus continued hemispherical pit growth would not be possible. Although it is theoretically possible that a pit could maintain its critical current density by decreasing its active area, such a pit is outside the considerations of this model.

In this work experimental validation of the computational model recently developed by Chen and Kelly\(^{18}\) in predicting the maximum pit size on stainless steels under atmospheric conditions is presented. The electrolytes used are ferric chloride formed as thin films on stainless steel surfaces. Ferric chloride is widely used as an accelerated test medium for localized corrosion of stainless steels.\(^{19}\) As will be shown, the reduction of ferric ions closely approximates the constant current density of an equivalent cathode, and the high chloride concentrations lead to a negligibly short initiation time. This combination allows for a rigorous test of the validity of the approach to predicting maximum pit sizes under thin film electrolyte conditions.

### Experimental

**Conductivity and water layer thickness.—** Accurate calculation of the deliquescence properties of the salt solution is important in predicting the pit sizes on corroding samples using equation 10. Chemical modeling of the deliquescence parameters of ferric chloride salt, the salt used for accelerated pitting corrosion exposure tests in this work was accomplished using OLI Systems Analyzer Studio 3.1 (OLI Systems Inc, Whippany, NJ) software. The software uses a mixed-solvent electrolyte thermodynamic model\(^{20–23}\) that is able to predict the properties of electrolyte solutions up to the fused salt limit. Speciation, such as ion pairing, acid-base reactions, and complexation accounts for the nonideality of concentrated electrolyte solutions and can have effects on phase equilibria and salt solubility, both of which can impact the size to which a pit can grow.\(^{20,21}\)

The relative humidity determines the equilibrium concentration of salt in solution through the deliquescence behavior of the salt(s) of interest.\(^{24}\) The water layer thickness is related to the loading density (LD, the amount of salt per unit surface area), specific density ($\rho_{sp}$) of the electrolyte, molecular weight (M), and equilibrium concentration ($C_{eq}$) of the salt as:

$$WL = \frac{LD \rho_{sp}}{MC_{eq}} \quad [13]$$

Because the density and equilibrium concentration are dependent on the RH, the WL is also a function of RH as shown previously by Chen et al.\(^{25}\)

**Anode kinetics parameters.—** The pit stability product ($j \cdot \Delta x$) and repassivation potential ($E_{rp}$) of the two stainless steels, 304L and 316L, were determined in ferric chloride solution using the artificial pit electrode technique. Wire samples of 50 $\mu$m diameter were embedded in epoxy and ground with a 600 grit silicon carbide paper. The exposed area of the wire was then rinsed with distilled water and dried with nitrogen gas. The exposed area was then mounted upright in an electrochemical cell containing 0.4 M ferric chloride solution which corresponds to 97% relative humidity. The electrochemical experiment started by potentiostatically applying $+0.75$ mV vs. SCE for 5, 10, 15, 20, 30, 45, 60 or 120 minutes in order to grow one-dimensional pits of different depths. After each potentiostatic hold the potential was scanned at a rate of 1 mV s$^{-1}$ in the cathodic direction starting from $+0.5$ V vs. SCE to $-0.5$ V vs. SCE. In this way, the pit stability product and the repassivation potential could be determined in the same experiment.\(^{26,27}\)

**Cathode kinetics parameters.—** To quantify the cathodic kinetics required in Eqn. 10, cathodic polarization scans at a rate of 1 mV s$^{-1}$ starting from $+100$ mV vs. OCP to $-750$ mV vs. SCE were carried out on 304L and 316L samples in 0.2 M chloride-free ferric sulfate solution instead of ferric chloride to assess the cathode kinetics of the ferric to ferrous reduction on unpitted surfaces of 304L and 316L. SEM micrographs in Figure 2 of 304L and 316L after cathodic polarization scans reveal the pitting effect of ferric chloride in comparison to the corresponding surface in ferric sulfate. The ferric sulfate solution was prepared in a concentration matching the ferric ion used for the determination of the anode kinetics. The sample surfaces were cleaned with distilled water, ethanol, and acetone. Finally, the sample surfaces were cleaned with an oxygen plasma from a March Model PX250 plasma cleaner, using a power of 150 W to remove dirt and organic matter from the surface to improve its wettability.

**Computational prediction of maximum pit size.—** The required input parameters for the maximum pit size modeling, such as conductivity, water layer thickness, corrosion potential, and repassivation potential, were determined from the previously described chemical modeling, anode kinetics, and cathodic scans. These data were used to calculate the $i_{cath, max}$ at 97% RH and 400 $\mu$g cm$^{-2}$ loading density as function of pit radius using equation 10. By coupling $i_{cath, max}$ with the pit stability product for hemispherical pit as a function of pit radius, the maximum pit size possible on 304L and 316L stainless steels samples at 97% RH and 400 $\mu$g cm$^{-2}$ loading density was determined. The pit radius at which the cathodic current ($i_{cath, max}$) is equal to the anodic current demand ($i_{anode}$) is taken as the maximum size of a hemispherical pit that can grow on the steel surface for the atmospheric conditions under consideration.

**Laboratory exposure tests.—** The laboratory exposure tests were done using a thin film of ferric chloride covering the steel surface. In order to cover the samples with a uniform aqueous thin film, the samples’ surface needs to be free from any hydrophobic contaminants. The procedure to achieve such a surface starts by cleaning the steel surface, which were polished using 800 grit silicon carbide paper, with soapy water followed by sequential rinses in tap water, distilled water, ethanol, and acetone. Afterwards the samples’ surface were cleaned with oxygen plasma, March PX250, using 150 W power for one hour to remove any contaminants that might decrease the wettability of the samples’ surface. The cleaned samples’ surface were then covered by a thin film of ferric chloride with loading density of 400 $\mu$g cm$^{-2}$ and placed in a chamber in which the RH was controlled to 97% by the presence of a saturated salt solution of potassium sulfate for 6, 12, 24, 48 or 168 hours.

The plasma cleaning created a stainless steel surface that could be fully wetted by the ferric chloride solution, thus creating a thin, uniform film for comparison to the model results. After the plasma cleaning, the ferric chloride solution was immediately placed on the surface. The differences in wetting can be seen in Figure 3. Pitting corrosion damage to the samples’ surface was evaluated by a HIROX laboratory exposure tests using multi-focus synthesis in which a sequence of images from the lowest focal plane at the bottom of the pit to the surface of the sample are collected and combined. The three dimensional images were then analyzed using Mountains Map Imaging Topography 6.0 surface.
analysis software to determine the pit diameter and depth. The radius of the pit is taken by dividing the measured pit diameter by 2. Ratio of the pit radius to the pit depth was used to determine the morphology of the pits.

Results and Discussion

Chemical modeling.— Figure 4 shows the results from chemical modeling of the deliquescence behavior of ferric chloride calculated using OLI Systems Analyzer Studio 3.1 software. The deliquescence properties of ferric chloride were determined between the deliquescence relative humidity (DRH) of ferric chloride (40% RH) and 100% RH. As seen in the figure, the values of all of the properties of interest of ferric chloride solution decreased with increasing relative humidity. The equilibrium concentration of ferric chloride decreases from a saturation concentration of 6 mol kg$^{-1}$ at the DRH to 0 mol kg$^{-1}$ of pure water. Likewise the density decreases from 1513 kg m$^{-3}$ at the DRH to the density of pure water, 997 kg m$^{-3}$ at 25°C and RH = 100%. Increasing the relative humidity above the DRH will result in the dilution of the saturated salt solution and a gradual decrease in the conductivity of ferric chloride solution. The conductivity with concentration behavior shown in Figure 4a and 4c is typical of salts with moderate solubility. For highly soluble salts such as ammonium nitrate the conductivity initially increases before going through a maximum value, and then starts to decrease with further increase in concentration of the solution.$^{28,29}$ The oxygen solubility in ferric chloride solutions decreases with increasing RH and hence concentration in accordance with Henry’s law. This trend is opposite to the oxygen solubility data in sodium chloride solutions.$^{30-32}$

Anode kinetics parameters.— Polarization scan results from artificial pits after different depths of potentiostatic pit growth for 304L and 316L SS in 0.4M FeCl$_3$ solution (which corresponds to RH = 97%) are shown in Figure 5a and 5b, respectively. The plateau current density in Figure 5 is the diffusion limited current density of the dissolution of the material in a saturated pit solution. It was used to determine the pit stability product from the slope of $i_L$ vs $d^{-1}$ based on equation 4. Figure 6 shows such a plot for 304L and 316L in 0.4M ferric chloride solution.

The linear relationship between the limiting current density and the inverse of the pit depth for both materials in 0.4M ferric chloride
solution confirms the process is diffusion controlled as shown by Laycock et al.\textsuperscript{14}

The pit stability product is simply the slope of Figure 6 which is 0.83 A m\(^{-1}\) for both steels in 0.4M ferric chloride solution. Based on this value, the pit stability product for a hemispherical pit \((I/r)_{\text{saltfilm}}\) of 304L and 316L in 0.4M ferric chloride solution in the presence of salt film would be 2.49 A m\(^{-1}\).

The other parameter determined from the same polarization curve is the repassivation potential, \(E_{\text{rp}}\). The repassivation potential is the minimum potential that can sustain pit growth. It was determined from the polarization curves in Figure 5 by taking the potential at which the current changes its polarity, which is likely conservatively low. The repassivation potentials from successive polarization scans at different pit depths for 304L and 316L in 0.4M ferric chloride solution are plotted as a function of the charge density consumed during pit growth in Figure 7. The plateau potential of \(-264\) mV and \(-230\) mV vs. SCE for 304L and 316L, respectively, is taken as the repassivation potential of each steel samples in 0.4M ferric chloride solution. These values were used in calculating the maximum cathode current possible using equation 10 at RH = 97%. Calculations of the
maximum cathode current at other RH would require determination of the $E_{rp}$ in the solution representative of the RH of interest because it is known that the $E_{rp}$ depends on the environmental factors such as chloride concentration.\(^{33}\)

Cathode kinetics parameters.— The cathodic polarization scans that characterize the cathode kinetics of the reduction of ferric ion in chloride-free ferric sulfate solutions on the surface of 304L and 316L are shown in Figure 8. In both materials a very high diffusion limited current density for ferric ion reduction is recorded. Equation 10 requires calculation of the area under the i-E curve between the corrosion potential ($E_{corr}$) and repassivation potential ($E_{rp}$) to quantify the integral term in equation 10.

Pit size prediction using the maximum pit size model.— Once the input parameters for anode and cathode kinetics were determined as shown above, the maximum pit size possible under a certain set of atmospheric conditions was predicted using the model of Chen and Kelly.\(^{18}\) Results from such pit size predictions for 304L and 316L samples at RH = 97% and LD = 400 $\mu$g cm\(^{-2}\) ferric chloride salt are shown in Figure 9. The plot shows current versus pit radius. The curved line is the maximum cathodic current calculated using equation 2 for both samples as a function of pit radius, whereas the linear lines are the pit stability product of a hemispherical pit for different levels of saturation within the pit. Gaudet et al.\(^{35}\) showed that stable pits on stainless steel can continue to grow if the surface solution composition

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**Figure 6.** $i_L$ vs. $d^{-1}$ for 304L and 316L in 0.4 M ferric chloride solution.

**Figure 7.** Repassivation potentials collected at different pit depths from cathodic polarization scans in 0.4M ferric chloride solution after potentiostatic pit growth as a function of the charge density consumed to grow the pits on 304L and 316L stainless steel samples.

As shown in Figure 7, the repassivation potential decreases with increasing charge density (and hence pit depth) before it attains a plateau value in a similar way to the work from Dunn et al. on alloy 825 at 95°C.\(^{34}\)

**Figure 8.** Cathodic polarization scans of 304L & 316L samples in 0.2M ferric sulfate solution.

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**Figure 9.** Maximum cathodic current and anode current demand at three levels of metal chloride saturation for 304L and 316L samples at RH = 97% and LD = 400 $\mu$g cm\(^{-2}\).
was between 60–80% of the saturation concentration of the metal chlorides associated with the alloy composition. The intersection of the maximum cathodic current with the linear anode current demand will give the predicted pit size at different levels of saturation within the pit. As shown in Figure 9 saturation levels lower than 100% result in higher values for the predicted pit radius.

![Optical profilometry images of 304L and 316L after exposure tests of 6, 12, 24, 48 and 168 hours long at RH = 97% and LD = 400 μg cm⁻² of thin film ferric chloride.](image)

**Figure 10.** Optical profilometry images of 304L and 316L after exposure tests of 6, 12, 24, 48 and 168 hours long at RH = 97% and LD = 400 μg cm⁻² of thin film ferric chloride.

**Pit size predicted with model versus pit size measured from exposure tests.** — Optical profilometry images in Figure 10 show the maximum pit size observed on the surface of 304L and 316L after exposure at RH = 97% and LD = 400 μg cm⁻² where the pits were hemispherical as assumed in the model. A comparison of the maximum pit size predicted using the maximum pit size model to the
maximum pit size measured after laboratory controlled atmospheric exposures over times of up to 7 days (168 h) is given in Figure 11. It can be seen in Figure 10 that the small pits on 304L are approximately hemispherical (their diameters are approximately twice their depth), whereas the large pits on both 304L and 316L appear to be more shallow. Apparent deviations from the hemispherical shape are predominantly due to the limitations of the line-of-sight optical profilometry on the deeper pits. The pit to the right for the 304L after 6 hrs and the pit to the left for the 304L after 48 hrs show the hemispherical shape. The profilometer cannot access the bottoms of the deeper pits and thus the bottoms show up as black on the views shown in Figure 10. In cross-section, the limit of the profilometry manifests itself as a flat-bottomed pit.

The data points with error bars are average maximum pit radii from two exposure tests carried out on 304L and 316L samples at RH = 97% and LD = 400 μg cm$^{-2}$. The horizontal lines represent the maximum pit size predicted for the different levels of saturation within the pit. As shown in Figure 11, the observed pit size data from exposure tests are well-bounded by the 60% and 80% saturation line for 316L and 304L, respectively. From these experiments the maximum pit size model was able to predict the maximum pit size possible under thin film conditions using a reasonable minimum for pit stability.

It is of interest to note that the maximum pit sizes measured on 304L were smaller than 316L despite the fact that 304L is more susceptible to pitting corrosion than 316L. This observation can be explained based on the pit density (i.e., the number of pits per unit area), within the cathode area. The 304L showed a much higher pit density than 316L as shown in Figure 12. The pits counted for comparison have pit diameters greater or equal to 50 microns and within 4 mm and 3 mm radial distance, (representing the equivalent cathode radii) of 304L and 316L, respectively, from the widest pit respectively for 304L and 316L. After one week of exposure at RH = 97% 42 pits were observed on 304L which is almost four times that of 11 pits observed on 316L. The difference in pit density will have an impact on the amount of cathodic current available to any single growing pit assuming that more than one pits grows simultaneously. The sharing of the available cathode current by the higher number of pits on 304L than 316L resulted in smaller pit size on 304L despite the fact that 304L is more susceptible to pitting corrosion than 316L.

**Summary**

The maximum pit model has been validated experimentally under controlled laboratory conditions. Chemical modeling of ferric chloride using OLI software gave some of the input variables needed for the calculation of the maximum cathodic current available from the surface of 304L and 316L covered with a thin film of ferric chloride to a growing pit. Electrochemical characterization of the cathodic kinetics of ferric to ferrous reduction on the steel surface was generated by cathodic polarization scans in 0.4M ferric sulfate. The area under the cathodic polarization curve between the corrosion and repassivation potentials was the second important input needed for calculating the $I_{\text{cath,max}}$. Anode kinetics from the dissolution of 304L and 316L in 0.4M FeCl₃ were generated using the artificial pit electrode method. The repassivation potential and pit stability product were the two important kinetic parameters obtained from anode kinetics experiments. Prediction of the maximum pit size that could grow on the surface of 304L and 316L at RH = 97% and LD = 400 μg cm$^{-2}$ was accomplished by coupling the cathode kinetics and anode kinetics in one plot. The intersection point between the $I_{\text{cath,max}}$ and the pit stability product in the plot of current versus pit radius gave the maximum pit size.
size possible on the steels surface. Validation of the maximum pit size model was accomplished by comparing the predicted pit size with the pit size obtained from exposure tests. Assessment of the corrosion damage to the steels' surface after exposure for a period of up to one week was done using optical profilometry. From the optical profile it was shown above that the maximum pit size model developed by Chen and Kelly was able to bound the maximum pit size observed from the exposure tests by assuming 60% and 80% level of saturation within the pits of 316L and 304L respectively. Such a level of saturation is consistent with the work of Gaudet. Despite the fact that 304L is more susceptible to pitting corrosion than 316L, smaller pits were observed on 304L compared to the pits on 316L. However, the pit density around the biggest pit within the cathode area of 304L is almost four times that of 316L. This difference in pit density resulted in the sharing of available cathode current available to growing pits which resulted in smaller pit sizes on 304L.

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