Further Modeling of Chloride Concentration and Temperature Effects on 1D Pit Growth

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The product of diffusion coefficient and saturation concentration of metal ions \((D_{M+} \cdot C_{sat})\) is associated with steady state dissolution of metal in corrosion pits. In our previous paper, \(D_{M+} \cdot C_{sat}\) was modeled for one dimensional (1D) pit dissolution of super 13Cr stainless steel (S13Cr) by taking into account the common ion effect, as well as viscosity and temperature influences. However, the modeled values were only half of the experimentally-measured \(D_{M+} \cdot C_{sat}\), implying that \(D_{M+}\) and/or \(C_{sat}\) were underestimated. To improve the modeling of \(D_{M+} \cdot C_{sat}\), the effects of complexation and electromigration were additionally considered, which led to the definition of effective diffusion coefficient \((D_{eff})\) applicable for the dissolution of metal ionic species under the combined effect of viscosity, temperature and electric field inside a growing 1D pit. The newly modeled \(D_{eff} \cdot C_{sat}\) values were very close to the experimental values, validating the modeling approach described in this paper.

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Dissolution of metal under steady state diffusion can be described by the modified Fick’s first law, which relates the limiting current density \(i_{lim}\) with the product of diffusion coefficient \((D_{M+})\) and concentration difference \((\Delta C_{M+})\) of the metal ion through the diffusion length \((L)\):

\[
\frac{i_{lim} L}{F} = n D_{M+} \cdot \Delta C_{M+} \quad [1]
\]

where \(F\) is the Faraday constant, and \(n\) is the charge of the metal ion. For the dissolution of metal in a one dimensional (1D) pit electrode, the concentration of metal ion outside of the pit is commonly assumed to be zero,1−8 so that \(\Delta C_{M+}\) is simply the concentration of metal ion at the pit bottom \((C_{M+})\). It is also usually supposed that \(L\) is equal to the pit depth \(δ\),9−12 although the diffusion of metal ions may extend out of pit, forming additional layer of hemispherical diffusion and causing \(L\) to be longer than \(δ\).11 The effect of this additional diffusion layer on \(i_{lim}\) was found to diminish as \(δ\) of 1D pit with 1 mm diameter was greater than 0.4 mm (aspect ratio of pit depth/mouth: 0.4) for SS 30411 and super martensitic stainless steel.10 More recent study on 1D pit growth of SS 316L, however, has suggested that the length of additional diffusion layer \((L')\) is approximately 40% of pit diameter, and \(δ\) should be much larger than \(L'\) to apply the \(L \approx δ\) condition for the calculation of \(i_{lim}\).11

In a previous paper, the authors suggested that \(i_{lim}\) in 1D pit electrode of super 13Cr stainless steel (S13Cr) can be related to the sum of \(D_{M+} \cdot C_{sat}\) from each metal component, if the transport of all metal ions is under diffusion control.14 In this case, \(i_{lim}\) can be expressed as:

\[
\frac{i_{lim} L}{F} = 2D_{Fe^{2+}} \cdot C_{Fe^{2+}/pb} + 3D_{Cr^{3+}} \cdot C_{Cr^{3+}/pb} + 2D_{Ni^{2+}} \cdot C_{Ni^{2+}/pb} \quad [2]
\]

where both \(C_{M+}\) is replaced by the concentration of metal ions at the pit bottom \((C_{Fe^{2+}/pb}, C_{Cr^{3+}/pb} \text{ and } C_{Ni^{2+}/pb})\). The content of Mo in S13Cr is small (2 wt% or 1.16 at%), so it was omitted for the calculation of \(i_{lim}\). For Eq. 2, three conditions were postulated: 1) The diffusion coefficients of all metal ions are the same \((D_{Fe^{2+}} = D_{Cr^{3+}} = D_{Ni^{2+}} = D_{M+})\), 2) \(Cr^{3+}\) is the major dissolved species, and the precipitating metal salt at the pit bottom is considered to be FeCl3, at which point the solution is saturated with the metal ions and supporting anion \((Cl^-)\). In situ X-ray analysis of the metal salt precipitated on a dissolving stainless steel found that the precipitated salt was mostly comprised of Fe and Cl.12 Based on this, it is reasonable to assume that the precipitating metal salt is FeCl3. The concentration of \(Fe^{2+}\) for the saturated solution in equilibrium with FeCl2 salt is designated as \(C_{sat}\) (\(C_{Fe^{2+}/pb} = C_{sat}\)). 3) Assuming congruent dissolution, the ratios of \(C_{sat}/C_{Cr^{3+}/pb}\) and \(C_{sat}/C_{Ni^{2+}/pb}\) are identical to the mole fractions of Fe, Cr and Ni \((X_{Fe}, X_{Cr}, X_{Ni})\) in S13Cr, and \(C_{Cr^{3+}/pb}\) and \(C_{Ni^{2+}/pb}\) can expressed in terms of \(C_{sat}\) using \(X_{Fe}, X_{Cr}\), and \(X_{Ni}^{-}\):

\[
C_{Cr^{3+}/pb} = \left(\frac{X_{Cr}}{X_{Fe}}\right) \cdot C_{sat} \quad [3a]
\]

\[
C_{Ni^{2+}/pb} = \left(\frac{X_{Ni}}{X_{Fe}}\right) \cdot C_{sat} \quad [3b]
\]

Using Eqs. 3a and 3b, the sum of \(C_{sat}, C_{Cr^{3+}/pb}\) and \(C_{Ni^{2+}/pb}\) simplifies to:

\[
C_{sat} + C_{Cr^{3+}/pb} + C_{Ni^{2+}/pb} = \frac{C_{sat}}{X_{Fe}} = C_{tot} \quad [4]
\]

where \(C_{tot}\) is the total concentration of metal ionic species at the pit bottom. Note that \(C_{tot}\) here defined by \(C_{tot}/X_{Fe}\) is only applicable for Fe-based alloys where \(X_{Fe}\) is much higher than the fraction of other components \((X_{Cr}\) and \(X_{Ni}\)) so that the congruent dissolution of the alloy would precipitate FeCl3 upon the saturation of \(Fe^{2+}\) \((C_{sat})\). By applying these conditions and Eq. 4 to Eq. 2, Eq. 5 is obtained:

\[
\frac{i_{lim} L}{F} = D_{M+} \cdot C_{sat} \left(\frac{2X_{Fe} + 3X_{Cr} + 2X_{Ni}}{X_{Fe}}\right) = \frac{n D_{M+} \cdot \bar{C}_{sat}}{X_{Fe}} \quad [5]
\]

where \(n\) is the average charge of metal ions dissolving from S13Cr, calculated by adding up the product of charge and mole fraction of metal components \((2X_{Fe} + 3X_{Cr} + 2X_{Ni})\). The composition of S13Cr gives \(X_{Fe} \cdot X_{Cr} \cdot X_{Ni} = 0.81 \cdot 0.14 \cdot 0.05\) without considering Mo, which yields \(n = 2.14\) and \(C_{tot} = 1.23 C_{sat}\). The concentrations of metal ions measured in the saturated pit solution for Fe-18Cr-13 Ni alloy at room temperature resulted in \(C_{tot} = 1.46 C_{sat}\), which is the same value determined by assuming congruent dissolution of the alloy.12 Therefore, the assumption of congruent dissolution, which was also adopted by others,15,16 seems to be reasonable.

Assuming that all of the anodic charge \((Q_a)\) was associated with metal dissolution and a planar electrode assembly, \(δ\) can be calculated from:

\[
δ = Q_a M \frac{M}{\bar{n} F \rho A} \quad [6]
\]

where \(M\) and \(ρ\) are atomic weight and density of S13Cr, and \(A\) is surface area of 1D pit electrode. Combining Eqs. 5 and 6 gives Eq. 7, where both \(i_{lim}\) and \(Q_a\) are experimentally measurable and allow for

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determination of experimental value of \( D_{M^+} \cdot C_{\text{sat}} \):

\[
D_{M^+} \cdot C_{\text{sat}}(\text{experimental}) = \frac{i_{\text{mb}}}{nF} = \frac{i_{\text{mb}}Q_{M}}{n^2F^2\rho A}
\]  

\( D_{M^+} \cdot C_{\text{sat}}(\text{experimental}) \) was found to decrease with increasing concentration of bulk NaCl solution ([NaCl]_b), indicating that increasing [NaCl]_b must decrease \( D_{M^+} \) and/or \( C_{\text{sat}} \). Increasing the concentration of other chlorides such as LiCl and FeCl_3 were also found to decrease experimental \( D_{M^+} \cdot C_{\text{sat}} \) of different stainless steels. If Na+ ions are present at the pit bottom, the common ion effect could decrease \( C_{\text{sat}} \). This effect would be more pronounced as [Na+]_b at the pit bottom ([NaCl]_b) increased. Meanwhile, \( D_{M^+} \) was estimated to decrease with increasing the viscosity of pit solution, the positive correlation of solution viscosity and concentration implies that \( D_{M^+} \) would decrease with increasing concentration of pit solution.

Based on the assumption that increasing [Na+]_b can cause stronger common ion effect and higher viscosity of pit solution to decrease \( C_{\text{sat}} \) and \( D_{M^+} \), our previous paper suggested a modeled \( D_{M^+} \cdot C_{\text{sat}} \) (designated as modeled \( D_{M^+} \cdot C_{\text{sat}} \) in the paper) dependent on the pit chemistry and viscosity. The previous study (including the erratum published after the original publication) showed that the modeled \( D_{M^+} \cdot C_{\text{sat}} \) was about one half of the experimental \( D_{M^+} \cdot C_{\text{sat}} \). A reconciliation of the modeled \( D_{M^+} \cdot C_{\text{sat}} \) with the experimental value is described here, in which the influences of the common ion effect, relative viscosity and electromigration are addressed.

**Modeled Concentration Gradients of 1D pit and \( C_{\text{sat}} \)**

To find the contribution of the common ion effect on \( C_{\text{sat}} \), [Na+]_b was assumed to have two extreme cases: [Na+]_b = 0 (zero [Na+]_b) and the maximum [Na+]_b possible (max. [Na+]_b) that neither precipitates NaCl nor surpasses [Na+]_b, i.e. Na+ concentration of the bulk solution. The modeled concentration gradients of 1D pits associated with these two conditions are shown in Fig. 1. In the modeled gradients, the total concentration of metal ionic species (\( C_{\text{Metal}} \)) is the sum of simple and complexed metal ions and it linearly decreases from the saturation level (\( C_{\text{sat}} \)) at the pit bottom to zero at the pit mouth. On the other hand, [Na+]_b inside the pit decreases from [Na+]_b at the pit mouth to either zero or to the max. [Na+]_b value at the pit bottom. According to these conditions, the concentration profiles for simple/complexed metal ions and Na+ in Fig. 1 can be written as linear functions of distance (x, \( x = 0 \) and \( \delta \) for pit mouth and bottom):

\[
C_{\text{Metal}}(x) = C_{\text{sat}} \left( \frac{x}{\delta} \right) = C_{\text{sat}} \times \text{Me}(\frac{x}{\delta})
\]

\[
C_{\text{Na}^+}(x) = \left( [\text{Na}^+]_b - [\text{Na}^+]_b \right) \left( \frac{x}{\delta} \right) + [\text{Na}^+]_b
\]

The speciation of cations in the pit is crucial to find the total positive charge that determines the gradient of \([\text{Cl}^-] \) for electro-neutrality. Hydrolysis and chloride complexation of metal ions produce different types of metal complexes and \( H^+ \), as follows:

\[
\text{Me}^{n+} + a\text{H}_2\text{O} \rightleftharpoons \text{Me(OH)}_a^{(n-a)+} + a\text{H}^+
\]

\[
\text{Me}^{n+} + a\text{Cl}^- \rightleftharpoons \text{MeCl}_a^{(n-a)+}
\]

where \( n = 2 \) and \( a = 1 \) or 2 for ferrous and nickel ions, \( n = 3 \) and \( a = 1, 2 \) or 3 for chromium ion. In Eq. 10a, the net positive charge on both sides is equal to \( n \), indicating hydrolysis would not change the total positive charge inside the pit. Chloride complexation of metal ions in Eq. 10b, however, decreases the positive charge inside the pit. Chloride complexation of metal ions after chloride complexation is:

\[
n_1(\text{Fe}) = 2 \cdot \left( 1 - \frac{X_{\text{FeCl}^2} + X_{\text{FeCl}}}{} \right) + 0 \cdot X_{\text{FeCl}^2}
\]

\[
n_1(\text{Fe}) = 0.5 \cdot X_{\text{FeCl}^2} - X_{\text{FeCl}^2}
\]

\[
n_1(\text{Fe}) = 0.5 \cdot X_{\text{FeCl}^2} - X_{\text{FeCl}^2}
\]

The effective charge (\( n_{\text{eff}} \)) of metal ions and their chloride complexes can be defined by taking \( X_{\text{FeCl}^2} \), \( X_{\text{NiCl}^2} \), \( X_{\text{CrCl}^2} \) and \( X_{\text{CrCl}^2} \) into account:

\[
n_{\text{eff}} = [0.81 \ 0.14 \ 0.05] \begin{bmatrix} n_{1/Fe} \\ n_{1/Cr} \\ n_{1/Ni} \end{bmatrix}
\]

\[
= [0.81 \ 0.14 \ 0.05] \begin{bmatrix} 2(1 - 0.5X_{\text{FeCl}^2}) \\ 3(1 - 0.33X_{\text{CrCl}^2} - 0.67X_{\text{CrCl}^2}) \\ 2(1 - 0.5X_{\text{NiCl}^2}) \end{bmatrix}
\]

where 0.81, 0.14 and 0.15 in a 1 x 3 matrix account for the concentration ratio of produced Fe^{2+}, Cr^{3+} and Ni^{2+} from congruent dissolution of 513Cr. Note that X_{FeCl}^2, X_{CrCl}^2 and X_{CrCl}^2 are omitted for \( n_{1/Fe}, n_{1/Cr} \) and \( n_{1/Ni} \) in Eq. 12. If metal ions do not form any complexes (i.e. the fractions of all complexes are zero), \( n_{\text{eff}} \) is identical to \( n \). More recently, the speciation of pit ions predicted using OLI software showed...
that the change in pit concentration appeared to influence the fraction of complexation.\textsuperscript{7,23} Nonetheless, here the fractions are postulated to be independent of pit concentration, resulting in an invariable $n_{\text{eff}}$ along the concentration gradient inside the pit. The calculation of $n_{\text{eff}}$ can be further simplified by assuming that the fractions of all metal complexes are equal to $X_{\text{FeCl}_2} = X_{\text{NiCl}_2} = X_{\text{CrCl}_2} = X_{\text{NiCl}_2}^{+}$, which modifies Eq. 12 to:

$$n_{\text{eff}} = 2.14 - 1.28 X_{\text{Cpx}}$$

[13]

The concentration profile of $[\text{Cl}^-]$ ($C_{\text{Cl}^-}(x)$) in Fig. 1 is then written as:

$$C_{\text{Cl}^-}(x) = \left( \frac{n_{\text{eff}} C_{\text{sat}}}{X_{\text{Fe}}} + [\text{Na}^+]_b - [\text{Na}^+]_b \right) \left( \frac{x}{T} \right) + [\text{Na}^+]_b$$

[14]

Note that $[\text{Na}^+]_b$ is used to designate $[\text{Cl}^-]$ of the bulk solution ($[\text{Cl}^-]_b$) in Eq. 14 as $[\text{Na}^+]_b = [\text{Cl}^-]_b$. It is also confirmed that the charge neutrality condition $n_{\text{eff}} C_{\text{Metal}}(x) + C_{\text{Na}}(x) = C_{\text{Cl}^-}(x)$ is valid for Eqs. 8, 9 and 14.

The stoichiometric concentrations of metal and chloride ions to precipitate FeCl\textsubscript{2} were determined using OLI software for zero and max. $[\text{Na}^+]_b$ conditions in different bulk NaCl concentrations, $[\text{NaCl}]_b$. The input for OLI software takes the form of salt concentration,\textsuperscript{26} so that [FeCl\textsubscript{2}], [CrCl\textsubscript{3}] and [NiCl\textsubscript{2}] with the ratio of 0.81:0.14:0.05 were used along with [Na\textsuperscript{+}]\textsubscript{b} input to modify [Na\textsuperscript{+}]\textsubscript{b}. $C_{\text{sat}}$ was defined as the total concentration of ferrous ionic species coexisting with solid FeCl\textsubscript{2} precipitate. Values of $C_{\text{sat}}$ for the zero and max. $[\text{Na}^+]_b$ conditions and $[\text{NaCl}]_b = 0.1 - 3$ M at 85°C are summarized in Table II, and the dependency of $C_{\text{sat}}$ on $[\text{Na}^+]_b$ was approximated by trend line fitting as:

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
[NaCl]\textsubscript{b} (M) & [Na\textsuperscript{+}]\textsubscript{b} (M) & $C_{\text{sat}}$ (M) \\
\hline
0.1 to 3 & (zero) & 4.88 \\
0.1 & 0.07 & 4.83 \\
0.3 & 0.22 & 4.76 \\
1 & 0.72 & 4.52 \\
3 & 0.83 & 4.47 \\
\hline
\end{tabular}
\caption{Predicted $C_{\text{sat}}$ for zero and max. $[\text{Na}^+]_b$ conditions at 85°C in $[\text{NaCl}]_b = 0.1 - 3$ M.}
\end{table}

$$C_{\text{sat}} \left( \frac{[\text{Na}^+]_b}{\text{M}} \right) \approx 4.88 M - 0.5[\text{Na}^+]_b \quad \text{for} 0 M < [\text{Na}^+]_b < 0.83 M, \text{at} 85°C$$

[15]

where $C_{\text{sat}}(\text{Na}^+_b)$ is the value of $C_{\text{sat}}$ decreased by the presence of $[\text{Na}^+]_b$.

The upper limit of $[\text{Na}^+]_b$ is predicted to be 0.83 M because larger values resulted in NaCl precipitation according to the OLI software. The maximum common ion effect would then be possible at $[\text{Na}^+]_b = 0.83 M$, which would decrease $C_{\text{sat}}$ to 4.47 M. This is in agreement with the analysis of $C_{\text{sat}}$ for $[\text{NaCl}]_b = 3 M$ in the previous paper, where the input of $[\text{Na}^+]_b = 3 M$ was estimated to produce 0.83 M of aqueous $[\text{Na}^+]_b$ and 1.9 mol of NaCl precipitates with $C_{\text{sat}} = 4.47 M$, which is the same $C_{\text{sat}}$ obtained here by inputting $[\text{Na}^+]_b = 0.83 M$. The calculations in Table II show that the concentration of metal ions decreases by less than 10% due to the common ion effect.

### Effective Diffusion Coefficient of Metal Ions

The previous analysis\textsuperscript{14} assumed that the diffusion coefficients of Fe\textsuperscript{2+}, Cr\textsuperscript{3+} and Ni\textsuperscript{2+} are equal and have the same dependency on pit concentration. In fact, the self-diffusion coefficients ($D^*$) of metal ions at room temperature are quite similar, 0.71 × 10\textsuperscript{-5} cm\textsuperscript{2} s\textsuperscript{-1} for Fe\textsuperscript{2+}, 27-29 0.6 × 10\textsuperscript{-5} cm\textsuperscript{2} s\textsuperscript{-1} for Cr\textsuperscript{3+}.27-28 and 0.69 × 10\textsuperscript{-5} cm\textsuperscript{2} s\textsuperscript{-1} for Ni\textsuperscript{2+},27-28,30 supporting the validity of modeled concentration profile and further allowing the use of universal $D^*$ for all metal ions ($D_{M_i}$) as previously practiced for 80Ni-20Fe alloy.\textsuperscript{31} A good approximation for $D_{M_i}$ is $0.7 \times 10^{-5}$ cm\textsuperscript{2} s\textsuperscript{-1}. Other studies also used a single value of $D_{M_i}$ for different metal ions to analyze diffusion-controlled metastable\textsuperscript{32,33} and stable\textsuperscript{10,34-38} pit growth.

The effect of temperature on $D_{M_i}$ can be estimated by Eq. 16, based on the Stokes-Einstein equation:\textsuperscript{39}

$$D_{M_i/T} = D_{M_i/298} \times \left( \frac{T}{298} \right) \left( \frac{\eta_298}{\eta_T} \right)$$

[16]

where $D_{M_i/T}$, $D_{M_i/298}$, $\eta_298$ and $\eta_T$ denote the self-diffusion coefficient of metal ions and dynamic viscosity of pure water at an absolute temperature $T$ and 298 K, respectively. At 85°C (358 K), $D_{M_i/298}$ is 3.21 times $D_{M_i/T}$ using $\eta_298 = 0.89$ cp and $\eta_T = 0.333$ cp.\textsuperscript{40}

Diffusion of metal ions in a growing 1D pit deals with complicated conditions including significant change in ionic concentration along with solution viscosity and buildup of potential gradient,\textsuperscript{20} which suggests that the $D_{M_i/T}$ defined for an infinitely-dilute solution will not apply. The approximation of $D_{M_i/T}$ ($D_{M_i}$ at $T$) then needs to incorporate the effect of solution viscosity and electromigration caused by the potential gradient inside the pit.

The effect of viscosity associated with concentration increase can also be predicted using the Stokes-Einstein equation:\textsuperscript{59}

$$D_{M_i/T} = \frac{D_{M_i/T}}{\eta_T} \left( \frac{\eta_298}{\eta_T} \right)$$

[17]

where $D_{M_i/T}$ and $\eta_T$ are the diffusion coefficient of metal ion and dynamic viscosity in the solution with concentration of $C$ at $T$, and $\eta_T$ is relative viscosity at $T$ defined by $\eta_T(C)/\eta_T$. Eq. 17 was previously adopted to calculate $D_{M_i/298}$ for pit diffusion using $D_{M_i/298}$ and $\eta_T$ estimated from the average concentration of pit solution.\textsuperscript{11,20}

The chemistry of pit solution for varying depth can be characterized as the concentration of aqueous solution containing different amounts of metal chlorides and NaCl. Using Eqs. 8 and 9, the amounts of FeCl\textsubscript{2}, CrCl\textsubscript{3}, NiCl\textsubscript{2} and NaCl for different pit distance ($x$) were determined as 0.81×$C_{\text{Metal}}(x)$, 0.14×$C_{\text{Metal}}(x)$, 0.05×$C_{\text{Metal}}(x)$ and $C_{\text{Na}}(x)$, respectively, which were then taken as inputs for OLI software to predict $\eta_{T/298}$. The plots of $\eta_{T/298}$ vs. $x$ shown in Fig. 2 were fitted to quadratic equations (also included in Fig. 2) with good agreement, and the equations were determined to be the functions of $\eta_{T/298}$ and $x$. The average
pit viscosity at 85°C ($\eta_{\text{pit}}$) along the entire pit depth from $x = 0$ to $x = \delta$ can be calculated from:

$$\eta_{\text{pit}} = \frac{\int_0^\delta \eta_{\text{pit}}(x)dx}{\delta}$$  \quad [18]$$

Values of $\eta_{\text{pit}}$ for zero and max. [Na$^+$]$\text{b}$ conditions in 0.1–3 M [NaCl$b$ are summarized in Table III.

Electromigration, another factor that may affect transport, can be addressed by adding the effect of the potential field on the flux of metal ions: 42

$$\frac{i}{nF} = D_{\text{M+}} \left( \frac{dC_{\text{M+}}(x)}{dx} + nC_{\text{M+}}(x) \frac{F}{RT} \frac{d\Phi}{dx} \right)$$  \quad [19]$$

where $C_{\text{M+}}(x)$ is the function of metal ion concentration and $x$, $R$ is the gas constant and $\Phi$ is the solution potential inside the pit. In a growing 1D pit, Cl$^-$ migrates from the bulk solution to the pit bottom to balance the dissolving metal ions, 42 creating a [Cl$^-$] gradient along the entire pit depth from pit mouth to pit bottom.

Figure 2. Predicted $\eta_{\text{pit}}$ profiles of Si13Cr pits and $\eta_{\text{pit}}(x)$ by trend-line fitting in 1 M [NaCl]$b$ for zero and max. [Na$^+$]$\text{b}$ conditions ($x = 0$: pit mouth and $x = \delta$: pit bottom).

Meanwhile, the total amount of Cl$^-$ ($m_{\text{Cl-}}$) in the pit is calculated by multiplying the surface area of 1D pit and integral of Eq. 14 for $x = 0$ to $\delta$:

$$m_{\text{Cl-}} = A \int_0^\delta C_{\text{Cl-}}(x)dx = \left( \frac{\delta}{2} \frac{A}{X_{\text{Fe}}} \right) \left( \frac{n_{\text{eff}}C_{\text{sat}}}{X_{\text{Fe}}} \right) \left[ \text{Na}^+ \right]_{\text{b}} - \left[ \text{Na}^+ \right]_{\text{b}}$$  \quad [22]$$

$J_{\text{Cl-}/\text{net}}$ is the flux contributing to the increase of $m_{\text{Cl-}}$ during pit growth and associated with the time derivative of $m_{\text{Cl-}}$:

$$J_{\text{Cl-}/\text{net}} = \frac{dm_{\text{Cl-}}}{A\delta t} = \left( \frac{1}{2} \frac{n_{\text{eff}}C_{\text{sat}}}{X_{\text{Fe}}} \right) \left( \frac{[\text{Na}^+]_{\text{b}}}{[\text{Na}^+]_{\text{b}} - [\text{Na}^+]_{\text{b}}} \right) \left( \frac{d\delta}{dt} \right)$$  \quad [23]$$

A unitless coefficient ($c_i$) is defined to satisfy $J_{\text{Cl-}/\text{net}} = c_i \cdot J_{\text{Cl-}/\text{diff}}$. Taking the diffusion flux term of Eq. 20 and using Eqs. 21 and 23, $c_i$ can be expended:

$$c_i = \frac{J_{\text{Cl-}/\text{net}}}{J_{\text{Cl-}/\text{diff}}} = \frac{\delta(n_{\text{eff}}C_{\text{sat}}/X_{\text{Fe}} + [\text{Na}^+]_{\text{b}} + [\text{Na}^+]_{\text{b}})(d\delta/dt)}{2D_{\text{Cl-}}(n_{\text{eff}}C_{\text{sat}}/X_{\text{Fe}} + [\text{Na}^+]_{\text{b}} - [\text{Na}^+]_{\text{b}})}$$  \quad [24]$$

Laycock and Newman found that $d\delta/d\delta t$ in 1D pit growth of SS 304 under steady state diffusion is associated with $D_{\text{M+}}$ and $\delta$: 15

$$\frac{d\delta}{dt} \approx c_g \cdot \delta$$  \quad [25]$$

where $\delta/D_{\text{M+}}$ was defined as characteristic time ($\tau$) for metal ions to diffuse out of pit and $c_g$ is a unitless constant associated with the increase of pit depth during $\tau$ and was experimentally determined to be 0.03 (3% increase of pit depth) in 1 M NaCl solution at room temperature. The value $c_g$ is speculated to depend on experimental conditions including temperature, type of metal and the concentration of bulk electrolyte. Rearranging Eq. 25 in terms of $d\delta/d\delta t$ yields:

$$\frac{d\delta}{dt} \approx c_g \cdot D_{\text{M+}}$$  \quad [26]$$

Applying Eq. 26 to $d\delta/dt$ of Eq. 24 gives:

$$c_i = \frac{1}{(n_{\text{eff}}C_{\text{sat}}/X_{\text{Fe}} + [\text{Na}^+]_{\text{b}} + [\text{Na}^+]_{\text{b}})D_{\text{M+}} \cdot \left( n_{\text{eff}}C_{\text{sat}}/X_{\text{Fe}} + [\text{Na}^+]_{\text{b}} - [\text{Na}^+]_{\text{b}} \right)}$$  \quad [27]$$

The self-diffusion coefficient of Cl$^-$ (2 × 10$^{-5}$ cm$^2$/s) is about 2.8 times the predicted $D_{\text{M+}}$ (0.7 × 10$^{-5}$ cm$^2$/s) at 25°C, and assuming this relationship is valid for pit diffusion, $D_{\text{M+}}/D_{\text{Cl-}}$ is approximated to be 0.18. The value of $c_i$ calculated for different [Na$^+$]$b$ and possible $c_g$ (0.02 to 0.08) is plotted in Fig. 3, where the largest $c_i$ is 0.023 for [Na$^+$]$b$ = 3 M and $c_g$ = 0.08, indicating $J_{\text{Cl-}/\text{net}}$ is only 2.3% of

Figure 3. Predicted values of $c_i$ for [Na$^+$]$b$ = 0.1 – 3 M and $c_g$ = 0.02 – 0.08 taking $n_{\text{eff}}$ = 2.14, $C_{\text{sat}}$ = 4.88 M (for zero [Na$^+$]$b$) and $X_{\text{Fe}}$ = 0.81 for calculation.

Table III. Predicted $\eta_{\text{pit}}$ for different [Na$^+$]$b$ and [NaCl]$b$ conditions.

| [NaCl]$b$ (M) | [Na$^+$]$b$ = 0 condition | max. [Na$^+$]$b$ condition |
|----------------|---------------------------|--------------------------|
| 0.1            | 2.51                      | 2.53                     |
| 0.3            | 2.56                      | 2.61                     |
| 1              | 2.7                       | 2.87                     |
| 3              | 3.09                      | 3.24                     |

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where $J_{\text{Cl-diff}}$ at best in the considered conditions. This justifies assuming that $J_{\text{Cl-neg}} \approx J_{\text{Cl-diff}}$ for the balance equation of Cl$^-$ fluxes ($J_{\text{Cl-neg}} = J_{\text{Cl-diff}} + J_{\text{Cl-nod}}$).

Using $J_{\text{Cl-neg}} = J_{\text{Cl-diff}}$, the right side of Eq. 20 becomes zero:

$$D_{\text{Cl}} \left( \frac{dC_{\text{Cl}}(x)}{dx} - C_{\text{Cl}}(x) \frac{F \, d\Phi}{RT \, dx} \right) = 0 \quad [28]$$

Eq. 28 can be rearranged in terms of $d\Phi/dx$:

$$\frac{d\Phi}{dx} = \frac{RT}{\bar{F}} \frac{1}{C_{\text{Cl}}(x)} \left( \frac{dC_{\text{Cl}}(x)}{dx} \right) \quad [29]$$

This electric field ($d\Phi/dx$) acting on Cl$^-$ will also drive the migration of metal ions toward the pit mouth so that Eq. 29 can be applied to Eq. 19 along with $\bar{n}$, $n_{\text{eff}}$, and $C_{\text{M/MX}}$, resulting in Eq. 30, which takes the same form to the flux equation derived by Landolt.

$$\frac{i}{\bar{n}F} = D_{M^+} \left( \frac{dC_{\text{M/MX}}(x)}{dx} + n_{\text{eff}} \frac{C_{\text{M/MX}}(x) \, dC_{\text{Cl}}(x)}{C_{\text{Cl}}(x)} \right) \quad [30]$$

The underlying assumption made for Eq. 30 is that all simple/complexed metal ions share the same diffusion coefficient (written as $D_{M^+}$) so the transport of metal ionic species can be described using single $D_{M^+}$.

The diffusion coefficients of most complexed metal ions are not readily available, but the self-diffusion coefficients of FeCl$^+$, NiCl$^+$, CrCl$^+$ and CrCl$_2^+$ were previously estimated to be $0.8 \times 10^{-3}$ cm$^2$ s$^{-1}$ at room temperature, which is not effectively different from $D_{M^+}$ for Fe$^{2+}$, Cr$^{3+}$, and Ni$^{2+}$ listed earlier in this paper and rationalizes the use of a single $D_{M^+}$ for Eq. 30.

$C_{\text{M/MX}}(x)/C_{\text{Cl}}(x)$ in Eq. 30 is the term assigned for the concentration of simple/complexed metal and chloride ions that are subjected to migration. Using Eqs. 8, 14 and 21, the product of $C_{\text{M/MX}}(x)/C_{\text{Cl}}(x)$ and $dC_{\text{Cl}}(x)/dx$ can be modified to:

$$\frac{C_{\text{M/MX}}(x) \, dC_{\text{Cl}}(x)}{C_{\text{Cl}}(x)} = \frac{(C_{\text{tot}}/X_{\text{Fe}})(x) \, (n_{\text{eff}} \, C_{\text{tot}}/X_{\text{Fe}} + [\text{Na}^+]_{\text{pb}} - [\text{Na}^+]_{b})(1/b)}{(n_{\text{eff}} \, C_{\text{tot}}/X_{\text{Fe}} + [\text{Na}^+]_{\text{pb}} - [\text{Na}^+]_{b})(1/b) + [\text{Na}^+]_{b}} \quad [31]$$

where $k = (n_{\text{eff}} \, C_{\text{tot}}/X_{\text{Fe}} + [\text{Na}^+]_{\text{pb}} - [\text{Na}^+]_{b})$ and has the units of concentration. The averaged concentration gradient contributing to migration ($dC_{\text{M/MX}}/dx$) is calculated from Eq. 31 for the entire pit depth (from $x = 0$ to $x = b$):

$$\frac{dC_{\text{M/MX}}}{dx} = \frac{1}{b} \int_0^b k(C_{\text{tot}}/X_{\text{Fe}}) \, (x/b) \, dx = \frac{C_{\text{tot}}}{k} \frac{\delta \cdot X_{\text{Fe}}}{\delta \cdot X_{\text{Fe}}} \left[ 1 + \frac{[\text{Na}^+]_{b}}{k} \ln \left( \frac{[\text{Na}^+]_{b}}{n_{\text{eff}} \, C_{\text{tot}}/X_{\text{Fe}} + [\text{Na}^+]_{b}} \right) \right] \quad [32]$$

where $a$ is a unitless term. By applying the derivative of $C_{\text{M/MX}}$ (calculated from Eq. 8) and Eq. 32 to Eq. 30, Eq. 33 for $i_{\text{lim}}$ is obtained:

$$i_{\text{lim}} \cdot \frac{\delta \cdot X_{\text{Fe}}}{\delta \cdot X_{\text{Fe}}} = D_{M^+} \left( \frac{C_{\text{tot}}}{X_{\text{Fe}}} \right) \left( 1 + an_{\text{eff}} \right) \quad [33]$$

Using Eq. 17, $D_{M^+}$ can be replaced with $D_{M^+}/\eta_{\text{Fe}}$, where $\eta_{\text{Fe}}$ is defined in Eq. 18. Eq. 33 can then be rewritten as:

$$i_{\text{lim}} \cdot \frac{\delta \cdot X_{\text{Fe}}}{\delta \cdot X_{\text{Fe}}} = D_{M^+} \left( \frac{C_{\text{tot}}}{X_{\text{Fe}}} \right) \left( 1 + an_{\text{eff}} \right) \quad [34]$$

Gaudet et al. used the term ‘effective diffusion coefficient ($D_{\text{eff}}$)’ which incorporates the contribution of solution viscosity and electromigration on the diffusion-based transport of metal ions. The $D_{\text{eff}}$ then can be defined from Eq. 34:

$$D_{\text{eff}} = D_{M^+} \left( 1 + an_{\text{eff}} \right) \frac{1}{\eta_{\text{Fe}}} \quad [35]$$

where the $an_{\text{eff}}$ in the numerator corresponds to the contribution of electromigration on $D_{\text{eff}}$, $an_{\text{eff}}$ is plotted vs. $[\text{Na}^+]_{\text{pb}}$ in Fig. 4 for $[\text{Na}^+]_{\text{pb}} = 0$ at 85°C with varying $X_{\text{Fe}}$, conditions, where the relationship of $n_{\text{eff}}$ and $X_{\text{Fe}}$ is defined in Eq. 13. Electromigration plays a decreasing role as $[\text{Na}^+]_{b}$ increases.

For 1D pit growth in a bulk solution with near-zero concentration, the pit mouth can be considered as a depletion boundary, so the migration factor could be found using $n_{\text{eff}} = n_{\text{eff}}$, which is $n_{\text{eff}}$ for simple/complexed metal and chloride ions. This is in good agreement with the trend that $an_{\text{eff}}$ reduces to $n_{\text{eff}}$ as $[\text{Na}^+]_{b}$ (also $[\text{Cl}^-]$) approaches to zero, predicted by Eq. 32.

However, the value of $an_{\text{eff}}$ is close to zero for $[\text{Na}^+]_{\text{b}}$ higher than 12 M, which is comparable to the concentration of $\text{Cl}^-$ at the pit bottom ([$\text{Cl}^-$]$_{\text{b}}$). Because $[\text{Na}^+]_{\text{b}} = [\text{Na}^+]$, $[\text{Cl}^-]_{\text{b}}$ indicates $[\text{Cl}^-]_{\text{b}}$, where no gradient of $[\text{Cl}^-]$ exists between the pit and bulk solution and thus no $d\Phi/dx$ either. For $X_{\text{Fe}} = 0.1$ and $[\text{Na}^+]_{\text{b}}$ (or $[\text{NaCl}]_{\text{b}}$) = 0.1 M at 85°C, $an_{\text{eff}}$ varies from 1.93 to 1.09, suggesting that electromigration has comparable or greater influence on the transport of metal ions compared to diffusion for this concentration range.

$D_{\text{eff}}$ at 85°C can now be written as Eq. 36, which has the factor of 3.21 on $D_{M^+}$ for the increase in solution $T$ from 298 to 358 K:

$$D_{\text{eff/358}} = 3.21 D_{M^+} \left( 1 + an_{\text{eff}} \right) \frac{1}{\eta_{\text{Fe}}} \quad [36]$$

To estimate the possible range of $n_{\text{eff}}$, two boundary conditions for $X_{\text{Fe}}$ were chosen as $X_{\text{Fe}} = 0$ (no complex formation) and $X_{\text{Fe}} = 0.1$ (10% complexation). The values of $an_{\text{eff}}$, $a$ and $D_{\text{eff/358}}$ for different $[\text{NaCl}]_{\text{b}}$, $[\text{Na}^+]_{\text{b}}$ and $X_{\text{Fe}}$ are summarized in Tables IV and V, where $\eta_{\text{Fe}}$ values are taken from Table III.

At room temperature ($RT$), $D_{\text{eff}}$ was reported to range from $7 \times 10^{-6}$ to $9.2 \times 10^{-6}$ cm$^2$ s$^{-1}$ for diffusion-limited dissolution of pure Fe$^{3+}$ and different stainless steels in acidic and neutral chloride solutions. For the pit dissolution of S13Cr at $RT$, $D_{\text{eff}}$ calculated by Eq. 35 should be close to the reported $D_{\text{eff}}$. To make a fair comparison, the following conditions are considered for the dissolution of S13Cr...
Table IV. Calculated $n_{\text{eff}}, \alpha$ and $D_{\text{eff}/358}$ using $X_{\text{pit}} = 0$ and $D_{\text{eff}/M} = 0.7 \text{ cm}^2 \text{s}^{-1}$ for $[\text{NaCl}]_b = 0.1 – 3 \text{ M}$ and zero or max. $[\text{Na}^+]_b$ conditions at $85^\circ\text{C}$ ($358^\circ\text{K}$).

| $n_{\text{eff}} (X_{\text{pit}} = 0)$ | $[\text{NaCl}]_b$ (M) | $[\text{Na}^+]_b = 0$ condition | max. $[\text{Na}^+]_b$ condition |
|-----------------------------------|-------------------------|---------------------------------|---------------------------------|
|                                   | $\alpha$ | $n_\eta$ | $D_{\text{eff}/358} (10^{-5} \text{ cm}^2 \text{s}^{-1})$ | $\alpha$ | $n_\eta$ | $D_{\text{eff}/358} (10^{-5} \text{ cm}^2 \text{s}^{-1})$ |
| 2.14                              | 0.1     | 0.96    | 2.51                          | 2.74 | 0.96    | 2.53                          | 2.72 |
| 0.3                               | 0.91    | 2.56    | 2.6                           | 0.91 | 2.61    | 2.53                           |
| 1                                 | 0.79    | 2.7     | 2.23                          | 0.78 | 2.87    | 2.09                           |
| 3                                 | 0.56    | 3.09    | 1.6                           | 0.55 | 3.24    | 1.51                           |

Table V. Calculated $n_{\text{eff}}, \alpha$ and $D_{\text{eff}/358}$ using $X_{\text{pit}} = 0.1$ and $D_{\text{eff}/M} = 0.7 \text{ cm}^2 \text{s}^{-1}$ for $[\text{NaCl}]_b = 0.1 – 3 \text{ M}$ and zero or max. $[\text{Na}^+]_b$ conditions at $85^\circ\text{C}$ ($358^\circ\text{K}$).

| $n_{\text{eff}} (X_{\text{pit}} = 0.1)$ | $[\text{NaCl}]_b$ (M) | $[\text{Na}^+]_b = 0$ condition | max. $[\text{Na}^+]_b$ condition |
|---------------------------------------|-------------------------|---------------------------------|---------------------------------|
|                                      | $\alpha$ | $n_\eta$ | $D_{\text{eff}/358} (10^{-5} \text{ cm}^2 \text{s}^{-1})$ | $\alpha$ | $n_\eta$ | $D_{\text{eff}/358} (10^{-5} \text{ cm}^2 \text{s}^{-1})$ |
| 2.01                                 | 0.1     | 0.96    | 2.51                          | 2.62 | 0.96    | 2.53                          | 2.6 |
| 0.3                                  | 0.91    | 2.56    | 2.49                          | 0.91 | 2.61    | 2.43                           |
| 1                                    | 0.78    | 2.7     | 2.13                          | 0.77 | 2.87    | 2                             |
| 3                                    | 0.54    | 3.09    | 1.52                          | 0.54 | 3.24    | 1.44                           |

1D pit at RT: 1 M NaCl ([$\text{Na}^+]_b = 1 \text{ M}$), [$\text{Na}^+]_b = 0; X_{\text{pit}} = 0 and $n_{\text{eff}} = 2.14$. The average viscosity of pit solution can be determined more simply by taking the pit concentration at half depth as inputs for the OLI software. This gave 1.91 cp for the average viscosity at RT. $\eta_\text{ave}$ is then 2.15, calculated by dividing 1.91 cp by $\eta_\text{ave}$ (0.89 cp). Assuming the contribution of migration is relatively independent of temperature, $\alpha_{\text{ave}} = 0.79$, calculated for 85°C (Table IV), can be used for the pit dissolution at RT as well. Applying $\alpha_{\text{ave}} = 0.79$ and $n_\eta = 2.15$, the calculated $D_{\text{eff}}$ for S13Cr pit dissolution in the considered condition is $8.8 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$, which is comparable to $8.24 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ reported for SS 304 pit dissolution in 1 M NaCl bulk solution.

Comparison of Experimental and Modeled $D_{\text{M}+} \cdot C_{\text{sat}}$

The modeled $D_{\text{M}+} \cdot C_{\text{sat}}$ values of S13Cr at 85°C can now be obtained by the product of $C_{\text{sat}}/X_{\text{Fe}}$ ($C_{\text{sat}}$ values in Table II and $X_{\text{Fe}} = 0.81$) and $D_{\text{eff}/358}$ (in Tables IV and V) as written in Eq. 37.

$$D_{\text{M}+} \cdot C_{\text{sat}} \text{ (modeled)} = \frac{D_{\text{eff}/358} \cdot C_{\text{sat}}}{X_{\text{Fe}}} = 1.23D_{\text{eff}/358} \cdot C_{\text{sat}} \quad [37]$$

Recall that the experimental $D_{\text{M}+} \cdot C_{\text{sat}}$ can be determined from the measured $I_{\text{tot}}$ and $Q_\text{th}$ using Eq. 7. The comparison of experimental and modeled $D_{\text{M}+} \cdot C_{\text{sat}}$ for different [$\text{Na}^+]_b$ and $X_{\text{pit}}$ conditions is shown in Figs. 5a and 5b for [NaCl] = 0.1 to 3 M. For the $X_{\text{pit}} = 0$ condition, the modeled $D_{\text{M}+} \cdot C_{\text{sat}}$ values for both zero and max. [$\text{Na}^+]_b$ are fairly close to the experimental value in [NaCl] = 0.1 M, but the modeled values with max. [$\text{Na}^+]_b$ deviate from the experimental values for [NaCl] = 0.3 to 3 M (Fig. 5a). This supports the idea that Na$^+$ ions are depleted at the dissolving pit bottom. Then assuming [$\text{Na}^+]_b = 0$, the experimental $D_{\text{M}+} \cdot C_{\text{sat}}$ values lie between the modeled values with $X_{\text{pit}} = 0$ and 0.1 (Fig. 5b), implying that the degree of complexation of metal with Cl$^-$ ions in pits is lower than 10%.

In the modeling of $D_{\text{M}+} \cdot C_{\text{sat}}$ presented here, the decrease in $D_{\text{M}+}$ (shown in Tables IV and V) is much more pronounced than $C_{\text{sat}}$ (in Table II) with increasing [NaCl]. This approach is clearly distinguished from other modeling of $D_{\text{M}+} \cdot C_{\text{sat}}$, which emphasized the effect of bulk Cl$^-$ concentration on decreasing $C_{\text{sat}}$ and considered $D_{\text{M}+}$ to be invariant. Laycock et al. assumed that $C_{\text{sat}}$ could further decrease by increasing the fraction of Cl$^-$ complexed non-ferrous metal ions which would allow more ingress of Cl$^-$ into the saturated pit solution. To fit the [NaCl]-dependent decline of experimental $D_{\text{M}+}$, they chose a high extent of complexation, where 56% of the non-ferrous metal ions were assumed to be complexed. The C$_{\text{sat}}$ in a 1D pit of Fe-18Cr-13Ni alloy in a constant bulk Cl$^-$ concentration was measured using in situ X-ray microprobe, but evidence of decreasing $C_{\text{sat}}$ with increasing bulk Cl$^-$ concentration is hard to find. Tester and Isaacs predicted that a decrease in $C_{\text{sat}}$ would be probable for bulk Cl$^-$ concentration higher than 5 M but would not be pronounced for bulk Cl$^-$ concentration.
less than 3 M. Considering that [NaCl], in this modeling was 3 M or lower, C_{sat} of $\text{S}_{13}\text{Cr}$ may not notably decrease with an increase in bulk Cl$^{-}$ concentration. It is then reasonable to assume that the decrease in $D_{M\text{tot}}$ with increasing [NaCl], would dominate the decrease in $D_{M\text{tot}} \cdot C_{sat}$ as discussed here.

Conclusions

An alternative approach to model $D_{M\text{tot}} \cdot C_{sat}$ for diffusion-limited dissolution of $\text{S}_{13}\text{Cr}$ in 1D pit electrode was discussed and applied to fit previously-measured experimental dissolution of S13Cr in 1D pit electrode was discussed and applied to metal ions (X$^+$). The formation of complexed metal ions determines the effective charge of metal ionic species ($\eta_{eff}$) associated with electromigration. The fitting results also suggest that the degree of complexation of metal and Cl$^{-}$ ions is low (less than 10%). A good fit found between experimental and modeled $D_{M\text{tot}} \cdot C_{sat}$ supports the validity of modeling method discussed in this paper.

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