Effect of chloride transients on corrosion of low-alloyed steel under oxygenated high-temperature water conditions

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Abstract Stress corrosion cracking (SCC) in low alloyed steels (LAS) has been extensively investigated during the last two decades. One finding from recent investigations with standard 1” CT specimen geometry is that even very small amounts (2…5 ppb) of chlorides increase tremendously the cracking susceptibility of LAS. However, no LAS cracking incidents in real plants have ever been attributed to a chloride transient. In the present work, the corrosion potential at the bottom of the crack tip of a 1”CT LAS specimen was calculated using a mixed-potential model for the corrosion reaction of low-alloyed steel at the metal/water interface allowing for active dissolution (mainly of iron), active-to-passive transition and dissolution in the passive state. The model was coupled to equations describing dilute solution transport for all the ionic and neutral species in the crevice associated with the crack tip. The chemical and electrochemical conditions at the bottom of the crevice, as well as an estimate of the enrichment factor of chloride in it, were obtained from the calculations. In the experimental part, the corrosion behavior of LAS in a crevice environment forming during a 50-ppb bulk water chloride transient was studied by in-situ electrochemical impedance spectroscopy (EIS) and mixed potential measurements, coupled to ex-situ characterization of the oxides by microscopic and surface analytical techniques as well as corrosion rate estimation from exposure coupons. The material studied was 20MnMoNi55 from the reactor coolant line of a German NPP. The general corrosion rate was found to increase several times when LAS was exposed to chloride from the start of the experiment, the effect vanishing after about 150 h. The EIS data revealed that the effect of chloride transients on an existing oxide film is moderate, concerns mostly the processes at the inner oxide layer/water interface and is to a major extent reversible. The SSRT experiments showed that LAS is susceptible to SCC in the crevice environment above a threshold potential of about -0.35 V (SHE). The model calculations revealed that the corrosion potential at the crack tip of a 1”CT specimen is about -0.24 V (SHE), almost irrespective of the crevice geometry. However, the chloride enrichment was found to depend strongly on the crevice geometry, increasing as the crevice width or depth increases. Thus, any limit concentration for chloride concentration based on 1”CT specimen laboratory SCC crack growth rate test results should be considered carefully and bearing in mind the possible differences in crevice width and depth between the 1”CT specimen and those of a realistic LAS flaw. Based on all the results obtained, it can be concluded that chloride transients up to 50 ppb in high temperature water do not result in any serious consequences for the corrosion of low alloyed steel with stainless steel cladding.

Keywords: low-alloyed steel, pressure vessel, stress corrosion cracking, chloride impurity
**Introduction**

Localized corrosion modes of low alloy steel (LAS) have been extensively investigated in several laboratories during the last decades. Very small amounts of chlorides have been shown to increase the susceptibility of LAS to such corrosion modes [1-19]. However, there are no reported cases of strain induced corrosion cracking (SICC) or stress corrosion cracking (SCC) in boiling water reactor (BWR) plants that can be attributed to a combination of a penetrating cladding flaw and chloride in-leakage. Initiation of SICC/SCC in LAS involves changes in the oxide film at the bottom of a stainless-steel cladding flaw or in the oxide on the surface of LAS. Thus, investigating the oxide film properties in different simulated environments was deemed an appropriate approach [20-23]. Modelling results indicate that chloride enrichment in a realistic cladding flaw [21] is more than two magnitudes smaller and potential at the crevice bottom much lower than that in a 1″CT specimen [24] typically used in laboratory experiments. These findings effectively explain the discrepancy between the plant experience and the laboratory SCC test results for cladded low alloyed steel. However, there are parts in some BWR plants where LAS is in contact with the coolant without the cladding protection, and these areas could be under threat by chloride.

In that context, the aim of the present work is twofold: first, to simulate the electrochemical conditions inside the crack of a LAS CT specimen with variable width and depth. This is performed by using a model for the corrosion reaction of low alloyed steel allowing for active dissolution of iron, active-to-passive transition and dissolution in the passive state. Experimentally determined oxygen reduction and iron dissolution rates on LAS are used in the calculations. The model is coupled to dilute solution transport for all species in the crevice associated with the CT specimen. The conditions obtained from such calculations are compared in view of the effect of geometry on their degree of aggressiveness. Further, the present paper explores the possibility that the rates of both general and localized corrosion processes within the crack are controlled by potential. For that purpose, the effect of potential on general corrosion and SCC susceptibility of LAS is studied using in-situ and ex-situ methods. Finally, a viable explanation of the apparent effect of chloride on the susceptibility of LAS to stress corrosion modes is offered.

**Theoretical background**

**Specimen geometry**

Based on yield stress and Young’s modulus values for LAS at 288 °C, the crack tip and crack mouth opening displacements for stress intensity ($K_i$) values of 30 and 50 MPa m$^{1/2}$ are 0.01 and 0.06 mm and 0.025 and 0.1 mm, respectively. The crack depth in a CT specimen may vary from about 5 mm to over 20 mm (depending on the length of the pre-crack, type of starter notch etc.) while the width of a 1″CT specimen is fixed at 25 mm, that of $\frac{1}{2}$″CT specimen to 12.5 mm and so forth. Thus, calculations were performed with a geometry corresponding to a CT specimen with a crevice opening of 0.01 mm and different width (5-25 mm) and depth (0.1-25 mm), represented by a rectangular domain shown in Figure 1. The crack in the CT specimen is modeled as a crevice with parallel walls. Even if 3D simulations were performed throughout the present work, the results are represented as 2D y-z contour plots since the x-dimension (the opening of the crevice) is much smaller than the other two dimensions (width, or y-dimension and depth, or z-dimension).
Chemical species

Considering the appropriate set of chemical species is a prerequisite for any successful calculation of the sort attempted in the present study. Following the approach described previously [21,22], the set of species that define the chemical environment are

\[
\{ \text{H}^+, \text{OH}^-, \text{Cl}^-, \text{H}_2, \text{O}_2, \text{Fe}^{2+}, \text{Fe(OH)}^-, \text{FeCl}^-, \text{Fe(OH)}_2 \} \tag{1}
\]

The chemical reactions are assumed to be fast and considered to elementary, i.e. the ratio of the forward and reverse rate constants is presumed equal to the thermodynamic equilibrium constant at the temperature of calculation. A model of 10 species (including water) seems to be representative for the crevice corrosion of low-alloyed steel. In fact, to simulate the effect of Cr in the solution phase, also the hydroxide and chloride complexes of the chromium cation need to be added. However, at the present state of the research, this was judged premature due to the lack of data on the equilibrium and stability constants of chromium-containing species, especially at high temperature. At the crevice mouth, bulk solution concentrations are imposed in such a manner to fulfill equilibrium conditions for chemical reactions, with very low concentrations for metal cations, so that the corresponding electrostatic potential is negligible.

Homogeneous chemical reactions

The species considered are linked by the following homogeneous reactions.
The equilibrium constants have been adopted from reference 24. In fact, since the aqueous dissolved Fe(OH)$_2$ is a neutral species and thus does not enter the charge balance for ionic species in the crevice solution, we have chosen to treat the third and the fourth reaction of (2) as a single step for the sake of simplicity.

Heterogeneous electrochemical reactions

The cathodic reactions considered at the LAS/crevice solution interface are

\[
2\text{H}^+ + 2e^- \xrightarrow{k_{1}} \text{H}_2, \quad i_H = -a_{H^+} c_{H^+} e^{-\frac{2F}{RT} E}
\]

\[
2\text{H}_2\text{O} + 2e^- \xrightarrow{k_{10}} \text{H}_2 + 2\text{OH}^-, \quad i_{H,O} = -a_{H,O} c_{H,O} e^{-\frac{2F}{RT} E}
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \xrightarrow{k_{1}} 4\text{OH}^-, \quad i_O = -a_{O^2} c_{O^2} e^{-\frac{4F}{RT} E}
\]

Since there were no data available for oxygen reduction rate on LAS, it was determined experimentally. The rate of the charge transfer reaction of oxygen reduction on LAS can be expressed by the equation

\[
i_{\text{O}_2} = i_0 \cdot \text{O}_2^{0.5} \exp \left( -\frac{(1-\alpha)4F}{RT} (E_{eq} - E) \right)
\]

The model calculations below are performed using this equation for the oxygen reduction. Both the exchange current density and the transfer coefficient of oxygen reduction on LAS are smaller than the corresponding values for stainless steel, i.e. oxygen reduction on LAS in BWR conditions is ca. three times slower than on stainless steel [22].

The anodic reaction involving an active-to-passive transition for the steel are adopted from references 24-26 as

\[
\begin{align*}
M \xrightarrow{k_{a}} M^{2+} + 2e^- \\
i_M = \theta i_M^{active} + (1 - \theta) i_M^{passive} \\
\theta = \begin{cases} 
1 & E < E_{pass} \\
e^{-\frac{E - E_{pass}}{E_0}} & E > E_{pass}
\end{cases}
\end{align*}
\]

\[
i_M^{active} = i_{0, M}^{active} e^{\frac{2F}{RT} E}, \quad i_M^{passive} = i_{0, M}^{passive} e^{\frac{2F}{RT} E}
\]
i.e. a Weibull transition between the active and passive state is implemented. The kinetic parameters used in the subsequent simulations are listed in Table 1. Since no experimental data for the current vs. potential curves of iron, carbon and low-alloyed steels in neutral high-temperature water were found in the open literature, fitting of our own data for LAS to the model described by equation (7) was used. The average values of the current densities in the active and in the passive state at 0 V\textsubscript{SHE} as well as the respective average transfer coefficients are given in Table 1.

The second anodic reaction that needs to be considered is the oxidation of hydrogen that is generated during corrosion. This reaction is the reverse reaction of (3) and the corresponding current density is written as

$$H_2 \rightarrow 2H^+ + 2e^-, \quad i_{H_2} = a_{H_2}c_{H_2}e^{-\frac{2F}{RT}E} \quad (8)$$

The third anodic reaction that is considered is the deposition of magnetite by oxidation of Fe(OH)$_2$, i.e. the Schikorr reaction

$$3Fe(OH)_2 \longrightarrow Fe_3O_4 + H_2O + H_2 \quad (9)$$

This reaction is treated as a combination of two coupled electrochemical reactions – reaction (3) and the anodic process

$$3Fe(OH)_2 \longrightarrow Fe_3O_4 + H_2O + 2H^+ + 2e^-, \quad i_{Fe(OH)_2} = a_{Fe(OH)_2}c_{Fe(OH)_2}e^{-\frac{2F}{RT}E} \quad (10)$$

Table 1: Kinetic parameters of the electrochemical reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Pre-exponential factor</th>
<th>Transfer coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen reduction</td>
<td>$a_O = 0.054$ A m\textsuperscript{-2} (m\textsuperscript{3} mol\textsuperscript{-1})$^{a,0.59}$</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>$n_O = 0.59$</td>
<td></td>
</tr>
<tr>
<td>Proton reduction</td>
<td>$a_H = 3.2 \times 10^{-5}$ A m mol\textsuperscript{-1}</td>
<td>0.57</td>
</tr>
<tr>
<td>Water reduction</td>
<td>$a_{H_2O} = 7.5 \times 10^{-8}$ A m\textsuperscript{-2}</td>
<td>0.57</td>
</tr>
<tr>
<td>Hydrogen oxidation</td>
<td>$a_{H_2} = 2.8$ A m\textsuperscript{-1}</td>
<td>0.20</td>
</tr>
<tr>
<td>Active dissolution</td>
<td>$a_{0,Fe}^{\text{active}}(0 \text{ V}_{\text{SHE}}) = 10.2$ A m\textsuperscript{-2}</td>
<td>0.18</td>
</tr>
<tr>
<td>Passive dissolution</td>
<td>$a_{0,Fe}^{\text{passive}}(0 \text{ V}_{\text{SHE}}) = 1.71$ A m\textsuperscript{-2}</td>
<td>0.09</td>
</tr>
<tr>
<td>Schikorr reaction</td>
<td>$a_{0,Fe(OH)<em>2}(0 \text{ V}</em>{\text{SHE}}) = 0.025$ A m mol\textsuperscript{-1}</td>
<td>0.20</td>
</tr>
</tbody>
</table>

The behavior of each species in solution is governed by the respective Nernst-Planck equation

$$\frac{\partial c_i}{\partial t} = D_i \left[ \nabla^2 c_i + \frac{z_iFE}{RT} \nabla (c_i \nabla \varphi) \right] + R_i \quad (11)$$

where $D_i$ and $c_i$ are the diffusion coefficient and the concentration of species $i$, and $\varphi$ is the electrostatic potential. The term $R_i$ for production/depletion depends on the homogeneous...
chemical reactions considered in the crevice solution, and on the electrochemical reactions occurring on the walls of the crevice, as described above. The diffusion coefficients implemented in the simulations are adopted from references 24 and 27. To estimate the chloride enrichment in the crevice formed by the cladding flaw/CT specimen crack and the electrostatic potential drop in it, an additional equation is needed, the electro-neutral condition (or Laplace equation)

\[ \nabla^2 \phi = 0, \text{ or } \sum_i z_i c_i = 0 \]  

(12)

To obtain the corrosion potential and the steady-state profiles of the main constituents of the crevice solution in the cladding flaw/CT specimen crack considered in the present study, a finite-element method is employed in a 3-D geometry version. Nernst-Planck equations without a convective term were used for all species considered, i.e. a quiescent solution was assumed. Isotropic diffusion in both length and width directions was implemented for all species. The conditions in the bulk solution were assumed to be identical to a nominal BWR coolant, except for the introduction of chloride impurity as HCl.

**Modeling results**

The 2-D contour plots of the steady-state concentrations of H⁺, Cl⁻, Fe²⁺ and O₂, as well as the corrosion potential E_{corr}, are depicted in Figure 2 - Figure 5 as depending on crevice depth ranging from 0.1 to 15 mm at a constant crevice width of 25 mm (corresponding to the 1″ CT specimen). Analogous calculations were performed with crevice widths of 5, 10, 15 and 20 mm.

![Figure 2](image-url)  

*Figure 2* Contour plots of the concentrations of hydrogen ion (above, left), chloride (above, middle), divalent iron (above, right), oxygen (below, left) and corrosion potential (below, right) for a 0.1 mm deep crevice (opening 0.01 mm, width 25 mm).
Figure 3 Contour plots of the concentrations of hydrogen ion (above, left), chloride (above, middle), divalent iron (above, right), oxygen (below, left) and corrosion potential (below, right) for a 1 mm deep crevice (opening 0.01 mm, width 25 mm).

Figure 4 Contour plots of the concentrations of hydrogen ion (above, left), chloride (above, middle), divalent iron (above, right), oxygen (below, left) and corrosion potential (below, right) for a 4-mm deep crevice (opening 0.01 mm, width 25 mm). Steady-state result.
A summary of the above results is attempted in Figure 6, in which the steady-state concentrations of the main ionic species, oxygen and corrosion potential at the bottom of the crevice are plotted vs. the crevice depth for different widths of the crevice. It can be concluded that the acidification of the crevice (increase in concentration of hydrogen ions above their concentration in the bulk solution), as well as enrichment of chloride and divalent iron in it proceed smoothly, i.e. the deeper the crevice is, the more aggressive the conditions in it are. However, as the crevice deepens, there is a certain tendency of levelling off the concentrations of the main ionic species, i.e. they will reach constant values for a deep enough crevice. On the other hand, the oxygen in the crevice is practically consumed for depths larger than 6 mm, and accordingly the corrosion potential decreases and reaches constant values (at about -0.24 V SHE) for crevices deeper than 10 mm (since it is influenced not only by availability of oxygen, but also by the pH of the crevice). This potential level is much higher than that for a realistic cladding flaw bottom, i.e. -0.47 V SHE [21]. Focusing on the chloride concentration and comparing to the level predicted for a crack depth of 25 mm (i.e. 60 mol m⁻³), the concentration is predicted to be half of that for a crack depth of 10 mm and one tenth of that for a crack depth of 4 mm. The crevice width has also an important influence on the main parameters characterizing the aggressiveness of the medium. Namely, the smaller the crevice width, the lower the acidification and the enrichment of chloride in the crevice are (e.g. for a crevice of 5 mm width, the chloride enrichment is 20 times smaller than for a crevice of 25 mm width and the concentration of hydronium ions is 5 times smaller).
Figure 6 Concentrations of main ionic species and corrosion potential at the bottom of the crevice at steady-state as depending on the crevice depth (0.1 to 25 mm). From top to bottom: crevice widths 5, 10, 15 and 25 mm.
Experimental

A 20MnMoNi55 low-alloyed steel (composition in wt.%: 0.12%C, 1.33%Mn, 0.33%Si, 0.01%P, 0.003%S, 0.15%Cr, 0.64%Ni, 0.48%Mo, 0.17%Cu, 0.02%Al, balance Fe) was used as a test material. The experiments were performed in a de-aerated solution containing 42 µmol dm\(^{-3}\) (1.5 wppm) of chloride and 10 µmol dm\(^{-3}\) (0.560 wppm) Fe\(^{2+}\) as a mixture of HCl and FeCl\(_2\) ×6H\(_2\)O. Per electrochemical calculations presented in previous works [21-23], these concentrations correspond to bulk chloride content of 1.41 µmol kg\(^{-1}\) (50 ppb), i.e. to action level 3 of the VGB-guideline 401J. All measurements were performed at 288 °C in a recirculation water loop with hot parts made of Ti. A LAS cylinder placed symmetrically around the working electrode was used as a counter electrode to perform electrochemical measurements in controlled potential conditions. The potential was measured vs. an external pressure balanced AgCl/Ag electrode filled with 0.001 M KCl and re-calculated to the standard hydrogen electrode (SHE) scale.

After stabilization of the system at open circuit for 150 h, electrochemical impedance spectra were measured at different potentials with a Autolab PGSTAT302F/FRA32M system in the frequency range 0.02 mHz – 10 kHz at a signal amplitude of 30 mV (rms). The validity of the impedance spectra was ensured by checking the linearity condition, i.e. measuring spectra at signal amplitudes between 5 and 50 mV (rms), and by checking the causality using a Kramers-Kronig transform test included in the measurement software. The reproducibility of the impedance spectra was ±3% by magnitude and ±4º by phase angle. The steady-state was ensured by measuring spectra by varying the potential first in the positive direction from the open-circuit potential and then the negative direction from the highest potential reached. The values of the potentials were corrected for the IR-drop by using the high-frequency intercept of the impedance spectra. The best-fit calculations with respect to the appropriate transfer function were performed with Originlab software.

Separate LAS samples polarized to different potentials for 150 h using a multi-channel potentiostat were subsequently characterized using weight gain/loss measurements, SEM and GDOES. The values of potential were IR-drop corrected using a current interrupt method. In-depth composition profiles were obtained by GDOES on three separate areas of about 5 mm\(^2\), using a GDA 750 instrument with a polychromator of 750 mm focal length and a grating of 2400 grooves/mm. The operational parameters were: primary voltage 800 V / 80 mA and regulation pressure 3 hPa. Quantitative interpretation of the data was based on approximation of matrix-independent emission yields. The repeatability of the measurements was better than ±2% both by concentration and sputtering depth at which the concentration reached 50% of the surface value for the O signal. The position of the oxide/alloy interface was estimated by averaging the results from sigmoidal fits of the depth profiles of Fe and O, whereas the position of the interface between the in-grown and deposited layer was estimated from sigmoidal fits of the Cr and Mo depth profiles. SSRT – experiments were performed with a constant stain rate of 10\(^{-6}\) s\(^{-1}\) at different potentials, their values being once again corrected for the IR drop using current interrupt method. The fracture morphologies were subsequently characterized by SEM.

Results and Discussion

Effect of potential on general corrosion

The GDOES profiles of the atomic concentrations of constituents in oxide films formed at different potentials are depicted in Figure 7. They indicate the gradual development of a thicker deposited layer (estimated to be 0.67 µm at -0.32 V, 0.8 µm at -0.26 V and ca. 1.4-1.5 µm at -0.21 and -0.12 V). On the other hand, the inner layer thickness increases only slightly.
with potential, remaining within the range 0.30-0.40 μm. An increase of the maximum concentration of Cr and Mo in the inner layer with potential is observed, whereas the concentration of Ni is the highest in the outer layer. All these observations can be interpreted by an accelerating effect of potential on Fe and Ni dissolution through the inner layer, followed by deposition of an outer layer.

Figure 7 GDOES depth profile of the atomic concentrations of constituent elements of the oxide formed on LAS for 168 h at -0.32 V (above, left), -0.26 V (above, right), -0.21 V (below, left) and -0.12 V (below, right) in a simulated cladding flaw environment. Positions of the inner layer/alloy interface and inner layer/outer layer interface marked with vertical lines.

The electrochemical impedance spectra of LAS as depending on potential are illustrated in Figure 8. To gain the largest possible amount of information from these measurements, the low-frequency end of the measurements was extended down to 2 μHz, i.e. the measurement of a single spectrum took ca. 24 h. Thus, we felt it necessary to check for a possible evolution of the system during the measurement and adopted the following procedure. After a 96 h exposure at open circuit, first the spectra were measured from -0.55 V in the positive direction, and then the direction was reversed so that the final potential coincided with the initial one. The spectra measured at the same potential regardless of the direction are identical within the measurement error, indicating that the system was at steady-state during the experiments.
Figure 8 Electrochemical impedance spectra measured in the positive and negative direction at several potentials in a simulated cladding flaw environment. Left – impedance magnitude vs. frequency, right – phase angle vs. frequency. Points – experimental data, lines – best-fit calculation per the proposed model.

The impedance magnitude at low frequencies (|Z|f→0), which is tentatively identified with the inverse of the steady state corrosion/oxidation rate, decreases quasi-exponentially with increasing potential, indicating its significant effect on general corrosion and oxidation of LAS in simulated cladding flaw solution in the presence of chloride. This is most probably due to the increase of the rate of the anodic reactions (oxidation/film growth and dissolution of iron through the oxide) with increasing potential. On the other hand, in analogy to previous studies [21-23], three time constants were identified by deconvolution of the spectra after subtraction of the uncompensated solution resistance. The higher frequency time constant (detected at ca.100-500 Hz) can be associated with the electronic properties of the inner, compact sub-layer of oxide, the intermediate frequency time constant (0.1-10 Hz) – with the processes at the interface of this sub-layer with the high-temperature water, and the transport process at still lower frequencies would correspond to ionic conduction in the inner compact layer.

To interpret quantitatively the impedance results, the Mixed-Conduction Model for oxide films was employed, in analogy to previous calculations for corrosion of LAS in simulated cladding flaw solution at the open-circuit potential [21-23]. An improved version of the model that can discriminate between inner layer growth and metal dissolution through it resulting in the formation of an outer layer was used. It is worth noticing that in our previous paper [23], this version could account for the corrosion rates as depending on the type of impurity (chloride or sulfate) and exposure time. If the composition of the inner layer is close to magnetite, it can be stated that at the steel / inner layer interface, the following oxidation reactions proceed (a Kroger-Vink notation is used)

\[
\begin{align*}
Fe_m & \xrightarrow{k_m} Fe^{2+} + 2e^- \quad (13) \\
3Fe_m & \xrightarrow{k_m} 3Fe^{2+} + 4V_0^{2+} + 8e^- \quad (14)
\end{align*}
\]

where \(Fe_m\) is an iron atom in the alloy, \(Fe^{2+}\) is a divalent iron cation in an interstitial position, \(Fe^{2+}\) is an iron cation in a lattice position, and \(V_0^{2+}\) an oxygen vacancy.

The transport of matter and charge through the inner compact layer formed in the high-temperature electrolyte is assumed to be governed by solid-state transport of point defects.
(oxygen vacancies and interstitial iron cations) in the inner layer of oxide. This transport proceeds mainly by diffusion due to the relatively low values of the field strength in oxides formed in high-temperature water [21-23]. At the inner layer / water interface, the following lattice-conservative reactions proceed resulting in inner layer growth via filling of oxygen vacancies and dissolution of Fe via ejection of interstitial cations:

\[
\text{Fe}^{2+}_{\text{aq}} \xrightarrow{k_{2M}} \text{Fe}^{y+}_{\text{aq}} + (y-2)e^-
\]

\[
4\text{H}_2\text{O} + 4\text{V}^0 \xrightarrow{k_{2O}} 4\text{O}_2 + 8\text{H}^+
\]

Another anodic reaction that needs to be considered is the deposition of magnetite from excess divalent iron (the coupled oxidation half-reaction of the Schikorr reaction, see above)

\[
3\text{Fe}^{2+}_{\text{aq}} + 6\text{OH}^- \xrightarrow{ } 3\text{Fe(OH)}_2 \xrightarrow{k_s} \text{Fe}_3\text{O}_4 + 2\text{H}^+ + 2e^- + 2\text{H}_2\text{O}
\]

Assuming for the sake of simplicity that this reaction is a single-step reaction, the impedance at the film/solution interface is represented by a parallel combination of a charge-transfer resistance \( R_{F/S} \) and an interfacial capacitance \( C_{F/S} \) (generalized in the form of a constant phase element, CPE, to account for the energetic and/or geometric heterogeneity of the interface)

\[
Z_{F/S} = \frac{1}{j\omega C_{F/S} + R_{F/S}^{-1}}
\]

The impedance of the inner oxide, on the other hand, is represented as a parallel combination of an impedance characterizing the electronic properties of the semiconductor phase in that oxide and an impedance of the transport of point defects through it

\[
Z_f = \left( Z_e^{-1} + Z_{\text{ion,O}}^{-1} + Z_{\text{ion,Fe}}^{-1} \right)^{-1}
\]

where, per the MCM

\[
Z_e \approx \frac{RT}{2j\omega F \bar{E}L C_{sc}} \ln \left[ 1 + j\omega \rho_d e \bar{e}_0 \exp \left( 2kL \right) \right], \quad K = \frac{F}{RT} \bar{E}, \quad \rho_d = \frac{RT}{F^2 D_e} k_0 + k_M,
\]

\[
k_M = k_0^M \exp \left( \frac{2\alpha_M F}{RT} \left( 1 - \alpha \right) E - \bar{E}L \right), \quad k_0 = k_0^0 \exp \left( \frac{2\alpha_0 F}{RT} \left( 1 - \alpha \right) E - \bar{E}L \right),
\]

\[
k_{2M} = k_2^M \exp \left( \frac{2\alpha_2 F}{RT} \alpha E \right), \quad k_{2M} = k_2^0 \exp \left( \frac{2\alpha_2 F}{RT} \alpha E \right),
\]

\[
Z_{\text{ion,O}} \approx \frac{RT}{4F^2 k_0 (1 - \alpha) \left( 1 + \frac{4j\omega}{D_0 K^2} \right)}, \quad Z_{\text{ion,M}} \approx \frac{RT}{4F^2 k_M (1 - \alpha) \left( 1 + \frac{4j\omega}{D_M K^2} \right)}
\]

The overall impedance is in turn given by

\[
Z = R_d + Z_f + Z_{F/S}
\]

The results from the fitting of the impedance spectra to the transfer function described by equations (18)-(21) are shown in Figure 8 with solid lines and demonstrate the ability of the model to reproduce in a satisfactory fashion both the magnitude and the frequency distribution of the experimental impedances for all potentials. The kinetic and transport parameters estimated by the fitting procedure for all the experimental runs are collected in Figure 9 (for the parameters that exhibit a pronounced dependence on potential) and Table 2 (for the remaining parameters that do not show any meaningful dependence on potential). Following previous experience [28-31], the part of the potential consumed at the film/solution interface, \( \alpha \), was assumed a value of 0.8, whereas mean values of 12 and \( 5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} \) were adopted for the dielectric constant of the inner oxide and the diffusion coefficient of electronic charge carriers through it.
Table 2: Kinetic parameters that do not show an appreciable dependence on potential.

<table>
<thead>
<tr>
<th>E (V vs. SHE)</th>
<th>R_t (Ω cm²)</th>
<th>10^16 D_O (cm² s⁻¹)</th>
<th>10^16 D_M (cm² s⁻¹)</th>
<th>E / kV cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.53</td>
<td>33</td>
<td>1.3</td>
<td>1.0</td>
<td>12</td>
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<tr>
<td>-0.4</td>
<td>64</td>
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<td>1.0</td>
<td>11</td>
</tr>
<tr>
<td>-0.25</td>
<td>45</td>
<td>1.3</td>
<td>1.0</td>
<td>10</td>
</tr>
<tr>
<td>-0.19</td>
<td>23</td>
<td>1.3</td>
<td>1.0</td>
<td>12</td>
</tr>
</tbody>
</table>

The results collected in Figure 9 and Table 2 allow for the following main conclusions to be drawn:

1) In accordance to the model predictions, the rate constants of the electrochemical reactions at both interfaces depend quasi-exponentially on the applied potential, indicating that the rates of oxidation and corrosion increase significantly for potentials above -0.4 V. The respective transfer coefficients of the reactions at the alloy/inner oxide interface are of the order of 0.3, whereas those at the oxide/electrolyte interface ca. 0.7, which are typical values for electrochemical reactions.

2) The inner layer thickness increases with potential, but the overall increase is rather small which reflects the low field strength in the oxide. It is worth mentioning that the values of the inner layer thickness obtained from the impedance measurements (ca. 0.3-0.4 μm) are in good agreement with those estimated from GDOES depth profiling despite the approximate nature of the latter procedure.

3) The capacitance of the space charge layer in the inner oxide, C_sc, decreases with increasing potential, indicating the n-type semiconducting properties of the inner oxide phase. The C_sc⁻² vs. E dependence (not shown) was found to be non-linear, i.e. the donor density (usually identified with the concentration of predominant point
defects acting as electron donors) depends on potential and/or position within the oxide.

4) The diffusion coefficients of point defects and the field strength in the inner layer, on the other hand, are practically independent on potential, indicating that the structure and electrical properties of the inner layer of oxide remain essentially the same. This is in line with the fact that the transformation of magnetite to a higher-valence iron oxide (maghemite, Fe₂O₃, as expected from potential – pH diagrams) in the outer part of the inner layer preserves the spinel structure of that layer [28].

5) The reciprocal value of the charge transfer resistance at the inner oxide/electrolyte interface increases with potential in an exponential fashion. This is in accordance to the assumption that it is inversely proportional to the rate of reaction (17) responsible for the formation of the outer layer as a result of metal dissolution through the inner oxide.

An attempt to quantify the effect of potential on general corrosion of LAS using data obtained from all the methods used in the present paper is presented in Figure 10. In that figure, the overall corrosion rate estimated from weight loss/gain and the total oxidation rate derived from oxide thickness measurements are compared to the rate constants of reactions (13) and (14) that are believed to be the rate limiting steps for cation release and oxidation rates, respectively. A good correspondence is obtained, once again demonstrating the profound effect of applied potential on the general corrosion and oxidation rates of LAS.

![Graph of corrosion rate vs. potential](image)

*Figure 10 Corrosion rate (estimated from weight gain/loss) and total oxidation rate (derived from oxide thickness) compared to cation release rate (estimated from the rate constant kₘ) and oxidation rate (estimated from the rate constant kₒ) vs. potential.*

**Effect of potential on stress corrosion cracking susceptibility**

The correlation between increasing corrosion potential and increasing crack growth rate of stainless steels in BWR water at temperatures around 300 °C has been shown in several investigations [32,33]. It is usually assumed that the potential which influences the repassivation kinetics, i.e. the formation and growth of the passive film on the freshly exposed surface at the crack tip, is the main rate determining factor of the crack growth rate [32]. Slow strain rate tests were conducted in the cladding flaw bottom crevice chemistry to explore the effect of potential on LAS stress corrosion cracking susceptibility. The stress-strain curves shown in Figure 11(left) reveal that the fracture strain decreases markedly as the potential
increases from the open circuit potential of -0.49 V. A loss of ductility (LOD) parameter was calculated as

\[ \text{LOD} = \frac{\varepsilon_f(E_{oc}) - \varepsilon_f(E)}{\varepsilon_f(E_{oc})} \times 100\% \]  

where \( \varepsilon_f(E_{oc}) \) is the fracture strain at the open circuit corrosion potential and \( \varepsilon_f(E) \) the fracture strain at a given potential \( E \). This parameter is shown as a function of potential in Figure 11 (right). The estimated corrosion potentials for the case of 5 to 10 mm cladding flaw bottom and that of LAS 1"CT crack tip are also indicated. The cladding flaw bottom potential is in the range of potentials where LOD = 0, whereas the potential of the LAS 1"CT crack tip is in the potential range where LOD = 70%.

To conclude, SSRT specimens tested at potentials higher than ca. -0.3 V showed susceptibility to SCC, the tendency increasing with potential. SSRT specimens tested at lower potentials did not show any signs of SCC. Based on these results, the realistic cladding penetrating flaw bottom with a potential of -0.4 V_{SHE} should not be susceptible to SCC, while a LAS 1"CT specimen with a crack tip potential of -0.2 V_{SHE} should be strongly susceptible to SCC. Crack growth rate measurements with specimens that are more closely representative to the realistic cladding flaw case are currently underway and the results will be communicated soon.

![Stress-strain curves](image1)

**Figure 11 (left)** Stress-strain curves of LAS measured at different potentials in the simulated cladding flaw bottom chemistry. A temperature excursion due to heater failure marked with an arrow; (right) Loss of ductility as a function of potential. The potentials calculated to prevail at the bottom of a cladding flaw and at the crack tip of a 1"CT LAS specimen marked in the figure.

**Conclusions**

In the modeling part of this work, steady-state calculations concerning the chemical and electrochemical conditions in a CT specimen made of LAS and with a 0.01 mm wide crevice opening under a bulk chloride transient of 50 ppb are reported as a function of the width (5 to 25 mm) and depth (0.1 to 25 mm) of the crevice. The following conclusions can be drawn from the obtained parameter values for a chloride concentration of 1.4 mmol m⁻³, or 50 wppb in the bulk water:

- The maximum chloride concentration at the crevice bottom increases as a function of both crevice depth and width.
For crevice width less than about 15 mm, the chloride concentration seems to reach a saturation level as the crevice depth increases, while for a width of 25 mm (i.e. 1” CT specimen case) the maximum chloride concentration continues to increase as the crevice depth increases, at least up to 25 mm depth.

The corrosion potential at the bottom of the crevice is almost independent of the crevice geometry (at about -0.24 V_{SHE}) for crevice depth more than ca.10 mm.

In the experimental part of this investigation, the effect of potential on oxidation and general corrosion, as well as stress corrosion susceptibility of LAS exposed to simulated cladding flaw solution in the presence of chloride impurity was studied using in-situ impedance spectroscopy, ex-situ characterization of in-depth composition of oxide films and slow strain rate tests (SSRT). As a conclusion, it can be stated that general corrosion rates increase significantly for potentials 0.3-0.4 V more positive than the corrosion potential. Both the processes of metal oxidation, corrosion release and outer layer deposition are significantly accelerated for potentials higher than -0.3 V. In addition, SSRT specimens showed susceptibility to SCC in the simulated crevice chemistry with 1500 ppb chloride at potentials higher than ca. -0.3 V, the tendency increasing with potential. Based on both the experimental and modelling results the following can be concluded:

- due to the predicted high potential of about -0.24 V_{SHE} prevailing within the crack of CT LAS specimens (and in cracks in real components of similar geometry in absence of cladding) SCC is to be expected provided that chloride enrichment is high enough (this is the opposite to the case of a realistic cladding flaw where the predicted potential is much lower, i.e. -0.47 V_{SHE}).
- The crevice geometry has a strong effect on the chloride enrichment tendency, thus, any limit concentration for chloride concentration based on 1”CT specimen laboratory SCC crack growth rate test results should be considered carefully and bearing in mind the difference in crevice width and depth between the 1”CT specimen and those of a realistic LAS flaw.

References