Cathodic protection is one way to mitigate corrosion of metal surfaces of concentrated solar power (CSP) systems, by shifting the potential of the alloy below its open circuit potential (OCP). The behavior of molten salt CSP systems under cathodic protection can be obtained by developing a three-dimensional (3-D) computational corrosion model. A corrosion model was designed for and benchmarked against a thermosiphon reactor. For the cathodic protection case, magnesium (Mg) was added to the salt as a sacrificial anodic species, which reduces the corrosion rate by cathodic polarization of a corroding metal surface. The model then calculated the new corrosion rate at the surface of the coupons. Results were in good agreement with experimental values for the cases with and without the cathodic protection and at isothermal and non-isothermal conditions. The results showed that by adding even small amounts of Mg into the molten salt (KCl-MgCl₂) can rapidly reduce the corrosion rate at the surface of the coupons for both isothermal and non-isothermal conditions. The predicted results also showed that the corrosion rate of Haynes-230 in KCl-MgCl₂ containing 1.15 mol% Mg was 35 times lower than baseline tests with no cathodic protection and met the DOE SunShot targets.

For most superalloys, the principal corrosion mechanism in high-temperature molten salt systems is the selective oxidation of Cr that occurs preferentially at the surface of the alloys along the grain boundaries. Adding a sacrificial anodic species, such as Mg, to the system can hold the redox potential of the salt at a point where Cr dissolution from superalloys into the molten salt is suppressed. Additionally, Mg metal has a significant solubility in KCl-MgCl₂ potentially allowing for a buffering effect on the salt redox chemistry.

Previous studies of high temperature molten salt systems showed that the corrosion rate at the alloy surface is a function of the corrosion environment, ionic diffusivity in the salt, and the reaction kinetics at the metal-salt interfaces. In addition, the effect of environmental conditions, including the temperature gradient and fluid flow, on these processes, should be taken into account. Adding Mg as a sacrificial anodic species to the system also makes this study of the system more complicated. A modeling approach can help to identify the relationship between these processes and the performance of cathodic protection in molten salt systems. Numerical techniques that incorporate the nonlinear boundary conditions can describe the reaction kinetics and provide a reliable estimate of the corrosion rate at the surface of the alloys under cathodic protection. In our previous work, a high temperature corrosion model was developed that accounts for the impact of thermal gradients and fluid flow on the corrosion rate for the selective oxidation of chromium. In this study, the corrosion model has been extended to include the effect of cathodic protection of superalloys Haynes-230, Haynes-163, and Inconel-800 H under expected conditions of advanced future CSP plants. The model is baselined with experimental coupon studies that were conducted between 700–1000 °C within KCl-MgCl₂ molten salt in a thermosiphon reactor designed to allow exposure of the coupons to the isothermal and non-isothermal conditions. Coupled with computational fluid dynamics (CFD), the corrosion rates associated with cathodic protection can be predicted in systems with temperature gradients, fluid flow and heat transfer. The Mg cathodic protection of superalloys in KCl-MgCl₂ salt was considered because of interest in their proposed use in CSP plants. The KCl-MgCl₂ salt used in this work is composed of 32 mol% KCl and 68 mol% MgCl₂. The compositions of the alloys are shown in Table I. It is expected from the thermodynamic equilibrium potentials of the metals that the corrosion potential of the samples in contact with Mg will have a lower corrosion potential (more cathodic) than samples that have no contact with Mg. Mg should decrease the corrosion potential of the sample and, as a result, also its corrosion current density. The polarization method was used to determine the
corrosion potential and the corrosion current density. The rate of Mg consumption, the corrosion potential, and the corrosion current density are dependent on several studied variables such as temperature, fluid flow, Mg concentration, and the alloy grain boundaries, which are all examined extensively in this work.

Experimental

The experimental procedure for the non-cathodic protection conditions has been reported in our previous publications\(^\text{12}\) and will only be briefly discussed here. A thermosiphon was designed to test the exposure of alloy coupons to both the isothermal and the non-isothermal conditions with and without cathodic protection. In the isothermal case in which the temperature was kept constant in the system at 850\(^\circ\)C, due to the constant temperature, there was no fluid flow in the system. In the non-isothermal condition, there were temperature gradients inside the thermosiphon (i.e., temperature difference of 800–850\(^\circ\)C around the coupons has been shown by experimental data\(^\text{13}\)). In this condition, the fluid flow circulated by natural convection due to changes in the molten salt properties between the top and bottom of the thermosiphon. Figure 1a shows a sketch of the Ni thermosiphon used for corrosion measurements for the non-isothermal conditions, with coupons placed in both the bottom hot zone and the top cold zone. Hot and cold zones were attained by inserting the bottom of the thermosiphon into a furnace, with the top either in an insulated region or partially out of the furnace; additionally, the top of the thermosiphon was inset in a water-cooled shell. For the case without cathodic protection, after the entire salt media was added to the thermosiphon, it was brought to the final temperature and the experiment began. The thermosiphon tests with cathodic protection differ in the salt filling step. The proper amount of Mg discs (i.e., from 0 to 1.15 mol%), cut from a Mg rod (99.8%, Alfa Aesar) about 1 mm thick and 33 mm diameter, was placed at the top of the inner annular flow tube.

Salt chunks were then placed in the thermosiphon above the Mg discs, but below the top (cold zone) coupons. The salt contacted the Mg and the Mg became molten prior to attaining the ultimate test temperatures. Salt was initially melted at 600\(^\circ\)C, Mg melts at 650\(^\circ\)C, and KCl-MgCl\(_2\) melts at 850\(^\circ\)C. When all the salt was melted, the vessel was then fully assembled and brought to operating temperature where the Mg would melt.

The salt mostly had to pass through the Mg discs after melting, which introduced a minute amount of Mg into the KCl-MgCl\(_2\) to act as an early reducing redox buffer. According to Peng et al.\(^\text{14}\) when Mg is added into the MgCl\(_2\), it can be present in the salt as MgCl\(_2\) and as Mg (0 oxidation state). In addition, metals will have higher solubility in fully reduced state in their own chlorides. Figure 1b shows the initial salt melt and Mg disc placement.

At the end of the exposure periods, the reactor heating was turned off and the contents were allowed to cool to room temperature. Afterwards, the samples were broken out of the condensed salt media and cleaned for analysis. A sample of the salt was saved as well for analysis by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) to examine trace elemental impurities.

The primary post-experimental measurements were the mass loss and change in physical dimensions. These measurements were made using an analytical balance and caliper measurements, respectively.\(^\text{12}\)

Model Development

Model geometry.—Figure 2a shows the computational domain of the thermosiphon reactor that was designed according to the experimental setup (refer to the Experimental Procedures). The computational domain of the thermosiphon is composed of: Ni crucible, Ni crucible insert, superalloy coupons (which are located at the top and bottom of the thermosiphon), and eutectic KCl-MgCl\(_2\) salt. The temperature boundary conditions were put into the model according to the temperature gradients, which were attained by inserting the thermosiphon into a furnace, as described before.\(^\text{12,13}\) The geometry mesh that represents the experimental system of the thermosiphon was created by using CATIA and HyperMesh software. Since the model geometry and computational mesh has been reported in detail in our previous publications,\(^\text{12,13}\) they will only be briefly discussed here. The cross section of the coupon is shown in Figure 2b. Figure 2c shows

---

**Table I. The compositions of the superalloys used in this study; numbers are rounded and may not total 100\%.**

| Alloy (wt\%) | Cr | Mo | W | Al | Ti | Fe | C | Co | Ni | Mn | V | Si |
|-------------|----|----|---|----|----|----|---|---|----|----|----|----|
| Haynes-230  | 22.1 | 1.23 | 14.2 | 0.37 | 0.01 | 1.02 | 0.10 | 0.21 | 59.9 | 0.52 | -- | 0.3 |
| Incoloy-800H | 20.8 | -- | -- | 0.54 | 0.52 | 46.3 | 0.07 | 0.04 | 30.7 | 0.49 | -- | 0.3 |
| Haynes-163  | 27.7 | 0.27 | -- | 0.17 | 1.33 | 21.2 | 0.09 | 40.7 | 8.1 | 0.22 | 0.05 | 0.2 |

---

Figure 1. (a) Thermosiphon reactor for non-isothermal corrosion experiments. Internal corrosion vessel is shown with sample locations in upper cold zone and lower hot zone.\(^\text{12,13}\) (b) The initial salt melt and Mg disc placement.
the thin layer at the surface of the coupon where the electrochemical reactions happen. The cylindrical geometry and symmetry in the thermosiphon design allows for simplification of the computational domain when performing CFD. Symmetric boundary conditions were applied to a 90° section of the model for the CFD study. The total grid size of this model geometry is composed of 208,033 hybrid grid cells made up of structured and unstructured grids. For the cathodic protection case, different amounts of Mg from 0 to 1.15 mol% were considered in KCl-MgCl₂ as described in the experimental procedure section. Table II shows the KCl-MgCl₂ properties that were used in the model prediction. The temperature boundary conditions at the surface of the thermosiphon were applied to match the formerly-used experimental measurements for non-isothermal condition. Equation 1 calculates the temperature boundary conditions at the surface of the thermosiphon as a function of the thermosiphon height (z). Applying these temperature boundary conditions at the surface of the thermosiphon will cause the temperature difference of 800–950 °C in the salt around the coupons which is comparable to the experimental data.¹²,¹³

\[
1000 (1 - z) \leq z \leq 0.05 m \\
T = 976 - 521 z \quad 0.05 < z \leq 0.242 m \quad [1] \\
2997 - 8871 z \quad 0.242 < z
\]

** Governing equations and electrochemical kinetics.**—Our previous study¹⁵ showed that immersing Haynes-230 in KCl-MgCl₂ salt for 100 hours at 850°C caused Cr depletion at the surface and along the grain boundaries. Figure 3 shows the SEM/EDS images of Haynes-230 in contact with KCl-MgCl₂ salt. EDS results show that the Cr depletion at the surface and along the grain boundaries is the most important corrosion phenomenon.¹³ The electronegative metals (i.e., Cr) dissolve into the salt with a low oxidation state (i.e., CrCl₂). The electrochemical oxidation and reduction reactions for Haynes-230, Haynes-163, and Incoloy-800 H in the KCl-MgCl₂ salt are assumed to be a chromium oxidation reaction and CrCl₃ reduction reaction.

**Reduction reaction :** 2CrCl₂ + 2e⁻ → 2CrCl₃ + 2Cl⁻ [3]

where CrCl₃ results from a disproportionation reaction of CrCl₂ at the Ni crucible as explained in detail in our previous studies.¹²,¹³,¹⁵

**Oxidation reaction :** 2CrCl₂ + 2Cl⁻ → 2CrCl₃ + 2e⁻ [4]

**Reduction reaction :** Ni + CrCl₃ + 2e⁻ → NiCr + 2Cl⁻ [5]

At high temperatures, there is a galvanic coupling between the superalloys and the Ni crucible. As a result, the disproportionation product, Cr³⁺, can facilitate the oxidation of the structural alloy.⁷ The presence of Cr²⁺ and Cr³⁺ in molten salt are considered as an effect of Reactions 2 through 5 at the Ni crucible and coupon surfaces. By introducing the magnesium (Mg (0 oxidation state)) species in the salt solution in this work, oxidation of chromium (i.e. Reaction 2) is replaced by oxidation of Mg (i.e. Reaction 6). All other metals that are more noble than Mg (higher reduction potential than Mg) will tend to stay in the metallic state until all Mg is oxidized. The new oxidation reaction which is introduced to the system in addition to Reactions 2 through 5 at the Ni crucible and coupon surfaces is:

**Oxidation reaction :** Mg + 2Cl⁻ → MgCl₂ + 2e⁻ [6]

### Table II. Equations for KCl-MgCl₂ salt properties as inputs to the model:¹³ \( T \) [K].

| Property                      | Unit            | Equation                                                      | Temperature   |
|-------------------------------|-----------------|---------------------------------------------------------------|---------------|
| Density                       | [kg m⁻¹]        | \( \rho = 2000.7 - 0.4571 T \)                               | 1030-1140 K   |
| Dynamic viscosity             | [kg m⁻¹ s⁻¹]    | \( \mu = 1.46 \times 10^{-6} \exp(\frac{46}{T}) \)            | 873-1073 K    |
| Thermal conductivity¹⁴        | [W m⁻¹ K⁻¹]     | \( \kappa = 0.775 Y_{\text{Mg}} + 0.43 \)                    | 987 K         |
| Specific heat capacity        | [J kg⁻¹ K⁻¹]    |                                                               | No correlation|
| Vapor pressure                | [mmHg]          |                                                               | 1173 K        |
| Melting point                 | [°C]            |                                                               |               |
| Boiling point                 | [°C]            |                                                               |               |

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Samples in contact with Mg will have more cathodic corrosion potential than the samples that have no contact with Mg based on thermodynamics. This will also decrease the corrosion current. Cathodic polarization of the structure controls the kinetics of the surface processes occurring at the alloy-electrolyte interface. An Evans diagram (Figure 4) was constructed for Haynes-230 in KCl-MgCl$_2$ without and with Mg as an example by using such parameters as Tafel slopes, exchange current densities, and equilibrium potentials to describe the electrochemical corrosion system graphically. The parameters that were used are shown in Table III. The construction of the Evans diagram allows for predictions and explanations of the effects that were observed experimentally. Figure 4 shows that for a Cr oxidation reaction and CrCl$_3$ reduction reaction of Haynes-230 in KCl-MgCl$_2$ (i.e., without Mg), the corrosion current, $i_{\text{corr}}$, and the corrosion potential, $E_{\text{corr}}$, occur at the point of intersection of the oxidation and reduction curve (dotted line).

Adding Mg to the system also caused the cathodic polarization of the structure to control the kinetics of the reactions occurring on the metal-electrolyte interface. As shown in Figure 4, polarization of the oxidation reaction in a negative direction from the corrosion potential decreases the corrosion rate of Cr from the alloy. Polarizing the system from $E_{\text{corr}}$ from Reactions 2 and 3 to the sacrificial potential of $E_{\text{corr}}$ from Reactions 3 and 6 causes the corrosion current density to decrease from $i_{\text{corr}}$ from Reactions 2 and 3 to a new smaller value of current density, $i_{\text{corr}}$.

Introducing Mg to the system caused the Mg to oxidize to Mg$^{2+}$ by reducing CrCl$_3$ to CrCl$_2$, and CrCl$_2$ to Cr$^0$ (i.e., Reactions 3, and 6) according to the experimental data. Reactions 3 and 6 can be rewritten as a simplified format of Equations 7 and 8:

Reduction reaction : $2\text{CrCl}_3 + 2\text{e}^- \rightarrow \text{CrCl}_2 + \text{Cr}^0 + 3\text{Cl}^- \quad [7]$

Oxidation reaction : $\text{Mg} + 2\text{Cl}^- \rightarrow \text{MgCl}_2 + \text{e}^- \quad [8]$

According to Butler-Volmer kinetics, in the present model, for the oxidation and reduction reactions (i.e., Reactions 7 and 8), the kinetics for cathodic and anodic reactions are described respectively:

$$
\eta_c = -i_0 \frac{C_{\text{CrCl}_3}^{\text{eq}}}{C_{\text{CrCl}_3}^{\text{eq}}} \exp \left[ \frac{-\alpha_{\text{c}} n_F}{R T} (\eta_c) \right] \quad [9]
$$

$$
\eta_a = k_0 \frac{C_{\text{Mg}}^{\text{eq}}}{C_{\text{Mg}}^{\text{eq}}} \exp \left[ \frac{(1 - \alpha_{\text{a}}) n_F}{R T} (\eta_a) \right] \quad [10]
$$

$$
\eta = E - E^{\text{eq}} \quad [11]
$$

Here, subscripts $c$ and $a$ refer to Reactions 7 and 8 respectively, $i$ is the current density, $\eta$ is overpotential, $E$ is surface potential, $E^{\text{eq}}$ is equilibrium potential, and $i_0$ is the exchange current density. $C_i^{\text{eq}}$ is the concentration of species $i$ adjacent to the surface and $C_i^{\text{eq}}$ is the
reference concentration of species i which is assumed equal to 1.0 mol m$^{-3}$. The concentration reaction expressions have been assumed to be first order, as the experimental results showed a linear increase in the corrosion rate with chromium species in the salt. The equilibrium potentials of oxidation and reduction reactions are determined by the Nernst equation:

$$E^\circ_i = E^\circ_a + \frac{RT}{n_a F} \ln\left(\frac{C_i}{C_{a^\circ}}\right)$$  \[12\]

$$E^\circ_c = E^\circ_d + \frac{RT}{n_d F} \ln\left(\frac{C_i^c}{C_{d^\circ}}\right)$$  \[13\]

where $C_i$ is the concentration of species $i$ in the bulk, and $E^\circ_a$ and $E^\circ_d$ are the oxidation and reduction standard potentials calculated from the standard Gibbs energy of each corrosion product. The calculated $E^\circ$ values versus Li/LiCl reaction (LiCl + $e^-$ = Li + Cl$^-$), which are functions of temperature for oxidation and reduction reactions, are shown in Table IV, respectively. The details of calculation have been described in our previous studies.2,13

The corrosion potential is calculated by applying the mixed-potential theory to explain Mg dissolution. The convention that anodic current densities are positive and cathodic current densities are negative has been applied.18

$$-i_a = i_c = i$$  \[14\]

where $i_a$ is the reaction current (see Figure 3). Once the corrosion potential, $E_{corr}$ for Mg reaction is obtained by solving Equations 9 through 14, the corrosion current density is also computed.

This reaction potential, $E_{corr}$, can be applied for a Cr depletion reaction (i.e. Reaction 2) at the surface of the alloy and allows us to be able to predict the corrosion rate, $i_{corr}$, for the alloy in contact with molten salt. By writing Reaction 2 in the simplified format of Equations 15:

**Oxidation reaction**: $Cr \rightarrow Cr^{2+} + 2e^-$  \[15\]

The corrosion rate can be calculated by:

$$i_{corr} = i_{o,c} \frac{C_{Cr^{2+}}^c}{C_{Cr^{2+}}^a} \exp\left[\frac{(1 - \alpha_v) n_a F}{RT} (E_{corr} - E^\circ_{a})\right]$$  \[16\]

where subscripts $a$ refer to the chromium depletion reaction (i.e. Reaction 15) at the surface and along the grain boundaries. The reaction potential, $E_{corr}$ is much lower than the corrosion potential that was calculated from Reactions 7 and 8 (i.e., $E^\circ_{a}$) which causes the lower corrosion rate for the case with Mg.

**Transport of ionic species under cathodic protection.**—The experimental results from scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) mapping without cathodic protection,13 showed the selective depletion of Cr in the alloy that formed a void structure near the surface, which is open to the salt or, if not open, presents faster diffusion pathways orders of magnitude higher than bulk diffusion. This can be concluded from the X-ray maps of the cross-section of the corroded alloy, which indicates a selective depletion of Cr in the alloy, showing that metal diffuses out from this layer. Figure 3 shows the SEM/EDS images of development of the void structure at the surface of the super-alloy by Cr depletion (in this case Haynes 230). The Cr depletion at this layer mostly occurred at the grain boundaries of the alloy.13 The grain boundaries layer at the surface of the alloy is assumed to be of a constant thickness of $\delta$ and acts as a porous layer with constant porosity of $\epsilon$, and diffusion of the ionic species takes place in this region.2,12,13

The complete mass and momentum equations (Navier-Stokes flow) and heat equations were solved with the inclusion of the gravity effect. As a result, the concentrations of species (i.e., Cr$^{3+}$, Cr$^{2+}$, Mg, and Mg$^{2+}$) inside the salt are attained. The details have been described in our previous publications.2,13

For the case of cathodic protection, Mg and Mg$^{2+}$ ions in addition to Cr$^{3+}$ and Cr$^{2+}$ can diffuse and diffuse back through the porous layer and can react with Cr$^{3+}$ ions at the surface. The flux of each dissolved species, through the electrolyte in the pores of the porous layer is given by:

$$N_i = -D^{eff}_{i} \frac{\partial C_i}{\partial x}\bigg|_{x=0}$$  \[17\]

$D^{eff}_{i}$ is the effective diffusion coefficient of species $i$ that can be expressed as:19

$$D^{eff}_{i} = \frac{i D_i}{\tau}$$  \[18\]

$D_i$ is the diffusion coefficient of species $i$ in the salt, and the values of pre-exponential factor for $D_i$ are listed in Table IV. In this paper the $\epsilon$ (porosity) is defined as the volume fraction of grain boundaries, which is a function of grain boundary size.25 $\tau$ is the tortuosity and in the absence of information of the value of $\tau$, it is taken to be inversely proportional to the square root of porosity, in an analogy with the theory of porous electrodes.25

$$\tau = \epsilon^{-0.5}$$  \[19\]

A single reaction can be written in symbolic form as:24

$$n_i e^- \leftrightarrow \sum_{j=1}^{r} x_{i,j} S^j$$  \[20\]

where $x_{i,j}$ is the stoichiometric coefficient, $S$ is the $p^{th}$ species with a charge $z_i$, and the sum is over all the species for a given reaction at one electrode. For any species, the influx at the surface can be determined from:

$$N_i = -\sum_{j=1}^{r} x_{i,j} S^j$$  \[21\]

The flux of ionic species at the surface of the alloy can be determined by:

$$N_{Mg^{2+}} = \frac{1}{n_{a,F}}$$  \[22\]

$$N_{Mg} = \frac{-i_{a}}{n_{a,F}}$$  \[23\]
Table V. Temperature variation of exchange current density for Haynes-230.

| Electrochemical reactions                                      | i_0 [A m^{-2}] |
|----------------------------------------------------------------|----------------|
| CrCl\textsubscript{2} + 2e\textsuperscript{-} = Cr + 2Cl\textsuperscript{-} | i_0,\textsubscript{a} = 77.3 \times 10^4 \exp\left(-\frac{27000}{T}\right) |
| CrCl\textsubscript{2} + Cl\textsuperscript{-} = CrCl\textsubscript{3} + e\textsuperscript{-} | i_0,\textsubscript{c} = 0.502 \exp\left(-\frac{12464}{T}\right) |
| MgCl\textsubscript{2} + 2e\textsuperscript{-} = Mg + 2Cl\textsuperscript{-}  | i_0,\textsubscript{Mg} = 1.74 \exp\left(-\frac{13166}{T}\right) |

where subscripts c and a refer to Reactions 7 and 8 and subscripts a' refers to Reaction 15 respectively.

For calculation of kinetic parameters, the values of the polarization data have been fitted to the experimental results at the isothermal conditions (i.e., 750 °C, 850 °C, and 950 °C) by using a small value of \( \frac{1}{T} \) (i.e., ~0.08 m\textsuperscript{-1}) that caused the mass transfer effect at the surface of the coupons to be negligible where the kinetic effects are dominant and mass transfer effects can be neglected.\(^{12}\) The parameters then can be used for non-isothermal conditions where both kinetic and mass transfer effects are important. Kinetic parameters that were put into the model for isothermal and non-isothermal conditions are listed in Tables III and V respectively.

Numerical model.—The numerical model is three-dimensional, steady state, and non-isothermal. The conservation of mass and energy along with the Navier-Stokes equations were all solved in the three-dimensional commercial CFD software, STAR-CD 4.18. The process of corrosion is generally a time-dependent event; however, since the time scale of the corrosion process is substantially larger than most other transport processes, a quasi-steady state can be assumed.\(^{24}\) The CFD code is modified to include the electrochemical corrosion reactions under cathodic protection. The additional models are incorporated via the user-defined function modules linked to the CFD code. This numerical model predicts the three-dimensional effect of heat transfer and fluid flow on the corrosion rates at the surface of the coupons under cathodic protection. The equations are solved by using the Semi-Implicit Method for Pressure Linked Equations (SIMPLE) algorithm and the calculations are carried out with double-precision accuracy. The convergence criteria for the species transport were set for all residuals less than 1 \times 10^{-12}. The detailed equations and boundary conditions have been described in our previous publications\(^{12,13}\) and will not be repeated here in detail. The temperature boundary conditions at the surface of the thermosiphon were applied to match the formerly-used experimental measurements for isothermal and non-isothermal conditions as mentioned earlier. For the non-isothermal case (T~800–950 °C) there is a temperature gradient inside the thermosiphon, which causes the temperature gradient around the coupons at the bottom to be different from the temperature around the coupons at the top. For convenience, we called the upper and lower side of the thermosiphon the cold and hot zones, respectively, as are shown in Figure 2a. By solving the Equations 7 through 19, the corrosion rate and the corrosion potential have been calculated for each computational cell at the surface of the coupons. The equations to make the Evans diagram were applied to all of the computational cells at the surface of the coupons (i.e., Figure 2b) for calculating the new corrosion rate and the corrosion potential. Then the average of the corrosion rate (\( \bar{i}_{\text{avg}} \)) has been calculated for the coupons at both cold zones and hot zones.

Results and Discussion

As explained earlier, for the experimental studies, there are isothermal and non-isothermal cases, which are explained in detail in our previous studies.\(^{12,13}\) For the isothermal condition the temperature keeps constant in the system at 850 °C. Due to the constant temperature, there is no fluid flow in the system. There is also a non-isothermal condition where there are temperature gradients inside the thermosiphon (i.e., non-isothermal conditions with temperature gradient of 800–950 °C around the coupons) which the fluid flow circulates by natural convection. The calculations for the cases with and without Mg were carried out at these different isothermal and non-isothermal conditions and the results are discussed as below.

Isothermal conditions.—For the study of the effect of Mg on the corrosion rate, results were modeled for the local corrosion rates of Haynes-230, Haynes-163, and Incoloy-800 H coupons in KCl-MgCl\textsubscript{2} for 100 hours in isothermal condition of 850 °C with and without Mg and at different concentrations. The model results show that Haynes-230 has the lowest corrosion rate without cathodic protection and can be the best candidate for high-temperature KCl-MgCl\textsubscript{2} molten salt systems if corrosion minimization is the sole motivation. This could be due to the fact that the kinetic parameters that related to Haynes-230 are lower than the two other alloys (i.e., Table III). Figures 5a, 5b, and 5c compare the corrosion rates at the surface of the alloy with varying Mg content in the salt for Haynes-230, Haynes-163, and Incoloy-800 H, respectively. These results show that even by adding a small amount of Mg to the salt, the corrosion rate fell rapidly to a small value and then changed slowly as a function of Mg concentration. Adding small amount of Mg to the system causes the cathodic polarization of the alloy that controls the kinetics of the surface processes occurring on the metal-electrolyte interface. As a result, the corrosion rate decreases rapidly after adding even a small amount of Mg. Increasing the amount of Mg then affects the mass transfer at the surface of the coupons (i.e., Equation 17) so it has a decreasing effect. The experimental corrosion test results for the coupons in the salt were also obtained by a number of investigations, and the results are also shown in Figures 5a to 5c. The results proved that the model’s calculated corrosion rates are in good agreement with the experimental values as are shown in Figures 5a to 5c. Figure 6 shows the corrosion rate predictions by the model at different temperatures for the isothermal case without Mg and with 1.15 mol\% Mg (\( Y_{\text{Mg}} \)) for Haynes-230. The temperature of thermosiphon was varied between 650 °C and 1050 °C in the model, while keeping all other parameters constant. The results show that increasing the salt temperature increases the corrosion rate for both cases — with and without Mg. These results also show that adding the Mg to the salt caused significant reductions in the corrosion rates (i.e., more than 95%) for all of the temperatures.

As discussed in our previous studies,\(^{12,13,15}\) in our model, the creation of Cr\textsuperscript{3+} from the oxidation of Cr\textsuperscript{2+} at the surface of the Ni crucible creates an oxidizing agent that can diffuse to the alloy surface of the coupon and accelerate the Cr dissolution. Figure 7 shows the effect of different mol\% of Cr\textsuperscript{3+} (\( Y_{\text{Cr}^{3+}} \)) in the salt on the corrosion rate of the coupons for Haynes-230, Haynes-163, and Incoloy-800 H at an isothermal condition of 850 °C. The linear relationships are shown in Figure 7 between the amount of Cr\textsuperscript{3+} and the corrosion rate for all cases. In early stages of oxidation, the concentration is sufficiently low to allow linear oxidation kinetics. It is evident that decreasing the amount of Cr\textsuperscript{3+} is imperative to decrease the corrosion rate of materials in molten chloride salts. Although Cr\textsuperscript{3+} can diffuse through the porous layer when there is Mg in the salt, the Cr\textsuperscript{3+} first...
and then the rest of Cr$^{3+}$ consumed by the Cr in the alloy (i.e., Reactions 3 and 6) and the rest of Cr$^{3+}$ consumed by the Cr in the alloy (i.e., Reactions 2 and 3). The results also show that increasing the Cr$^{3+}$ concentration causes a more rapid increase in the corrosion rate of Incoloy-800 H when compared to Haynes-230 and Haynes-163. This is also shown by experimental data and can be due to the different kinetic parameters for these different alloys.

**Non-isothermal condition.**—For the non-isothermal condition, the model’s temperature distributions at the surface of the coupons and around the coupons for Haynes-230 has been calculated for both cases without and with 1.15 mol% Mg respectively. The validation of the model temperature profiles with experimental data have been shown in our previous study. The temperature gradient is slightly higher than the case without Mg. The average temperature around the coupons for the hot and cold zones, respectively, are 905.5$^\text{o}$C and 929.6$^\text{o}$C for the case without Mg and are 911.5$^\text{o}$C and 926.5$^\text{o}$C for the case with Mg. From the experimental results, the changes in density and viscosity of salt mixture was negligible, but a significant increase in thermal conductivity of the salt mixture was observed with the addition of just 1% Mg (i.e., Table II). The data showed that the thermal conductivity of KCl-MgCl$_2$ salt increased linearly with an increasing amount of Mg. This increase is mainly because of the thermal conductivity of Mg, which is much greater than that of KCl-MgCl$_2$ salt. The addition of Mg to the salt promotes the thermal conductivity, and as a result the average temperature at the surface of the coupons.

Figure 8 shows the corrosion current density distribution at the coupon surfaces without and with 1.15 mol% Mg introduced into the salt for the non-isothermal condition. The average corrosion rate and corrosion potential are also shown in Figure 8. The overall results show that, after introducing Mg into the salt solution, the corrosion current and corrosion potential were reduced around 99% and 20% respectively. The local distribution of corrosion current looks fairly uniform, and as expected, the corrosion rate is higher in the hot zone of the reactor for both cases.

The results in Figure 9 show that for non-isothermal corrosion of Haynes-230, like the isothermal case (i.e. Figure 4), adding even small amounts of Mg reduces the corrosion rate to near negligible values. This reduction is seen at both the cold and hot zones. In this case there is a convective flow inside the thermosiphon that brings Mg to the metal surface faster. The rate of Mg reactions is increased as a result, (i.e. Reactions 3 and 6), which further reduces corrosion compared to the isothermal case.

For the non-isothermal condition, the comparison of corrosion rate for different porosity for the cases without Mg and with 1.15% Mg for Haynes-230 for different porous layer porosity are shown in Figure 10a and 10b, respectively. The results show that there is almost a uniform distribution of corrosion rates at the surface for all cases. The corrosion rate appeared marginally affected by porosity for the cathodic protection case, as increasing the porosity from 0.1% to 0.5% only increased the corrosion rate by 2.0% and 5.0% at the cold and hot zones, respectively. Increasing the porosity from 0.1% to 0.5% for the case without Mg, however, changes the corrosion rate by 70.0%.
Figure 8. The corrosion current density distribution at the coupons without Mg (a) and with Mg (b) introduced into the salt solution at the control temperature of 800–950 °C, with the amount of Mg being 1.15 mol%.

Figure 9. The predicted corrosion rates at the surface of the alloy with varying Mg content in the salt for both the cold zone and the hot zone at non-isothermal case (800–950 °C).

Figure 10. The effect of porous layer porosity on the corrosion rate at both cold and hot zones for the cases (a) without Mg and (b) with 1.15% Mg at non-isothermal case (800–950 °C).

Figure 11. The effect of porous layer thickness on the corrosion rate at both cold and hot zones for the cases (a) without Mg and (b) with 1.15% Mg at non-isothermal case (800–950 °C).
and 30.0% at the cold and hot zones, respectively. This can be due to the mass transfer parameters having more effect on the corrosion rate for the case without Mg, as the kinetic effect was dominant relative to the mass transfer effect when Mg was added to the system.

SEM results of Haynes-230 samples exposed to KCl-MgCl₂ at 850°C for 100 hours showed that corrosion occurs in a layer of finite thickness at the surface of the coupons (i.e., the thickness can be changed from 8 μm to 70 μm for different alloys in contact with the molten salts). This layer was considered to be a porous microstructure open to the salt. The effect of porous layer thickness on the corrosion rate at cold and hot temperatures for the cases without Mg and with 1.15% Mg, shown in Figures 1a and 1b, respectively. The results show the porous layer thickness has an effect on the corrosion rate at both the cold and hot zones. The corrosion rate is decreased by increasing the thickness of the porous layer, as increasing the thickness by 20 times reduces the corrosion rate around 9.0% at the cold and hot zones for the cases both with Mg and without Mg. That is caused by the fact that a thicker layer has a higher corrosion resistance, as the species such as Cr³⁺ should diffuse a longer distance through this porous layer to react with Cr at the surface and the species such as Cr²⁺ should diffuse back a longer distance to the salt (i.e., Equation 14).

Summary

A 3-D corrosion model has been developed that accounts for the corrosion mechanisms of superalloys in KCl-MgCl₂ molten halide salts under cathodic protection. The electrochemical kinetics were incorporated into the CFD model, and both isothermal and non-isothermal conditions were considered. The results from the model were in good agreement with experimental data, showing less than a 3% difference. The effect of Mg concentrations were considered in the model and the results showed that adding even small amounts of Mg into the salt can rapidly reduce the corrosion rate at the surface of the coupons for both isothermal and non-isothermal conditions. The predicted results also showed that the thermal driven fluid flowing in the non-isothermal condition could accelerate the corrosion rate’s reduction due to the more rapid movement of Mg to the metal surface. The results of cathodic protection showed that the corrosion rate of Haynes-230 in KCl-MgCl₂ containing 1.15 mol% Mg showed 35 times lower corrosion than baseline tests with no cathodic protection and met the DOE SunShot targets (corrosion rates below 15 microns /yr).³

Acknowledgments

The authors gratefully acknowledge the financial support for this work by the DOE EERE SunShot Initiative (grant #: Garcia-Diaz_A) under a subcontract from SRNL to the University of South Carolina. The authors would also like to thank the University of South Carolina-Center for Fuel Cells and CD-adapco group for their support. The authors also thank Cody Wilkins for his comments.

List of Symbols

| Symbol | Description |
|--------|-------------|
| Cᵢₑ | concentration of species i in the bulk, [mol m⁻³] |
| Cᵢₛ | concentration of species i at the surface, [mol m⁻³] |
| Cᵢₑᵣ | reference concentration of species i, 1.0 mol m⁻³ |
| Dᵢₑff | effective diffusion coefficients of reactant salts in grain boundary pores [m² s⁻¹] |

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