Introduction: Corrosion Mechanism in MgCl$_2$-KCl (Previous SRNL SunShot Project)

Corrosion initiation step can be caused by impurities such as moisture or oxygen that add a finite concentration of chromium chloride to the salt.

EDS line scan from a cross-section of a Ni crucible containing a single Incoloy-800H coupon.

**Disproportionation (Crucible)**

- Ox: $2 \text{CrCl}_2 + 2\text{Cl}^- \rightarrow 2\text{CrCl}_3 + 2\text{e}^-$
- Red: $\text{Ni} + \text{CrCl}_3 + 2\text{e}^- \rightarrow \text{NiCr} + 2\text{Cl}^-$
- Total: $\text{Ni} + 3\text{CrCl}_2 \rightarrow \text{NiCr} + 2\text{CrCl}_3$

**Overall Reaction**: $\text{Ni} + \text{CrCl}_3 \leftrightarrow \text{NiCr}$

**Initiation**

- Ox: $\text{Cr}_2\text{O}_3 + 69\text{Cl}^- \leftrightarrow 23\text{CrCl}_3 + 6\text{Cr} + 69\text{e}^-$
- Red: $34.5\text{MgCl}_2 + 34.5\text{H}_2\text{O} + 69\text{e}^- \leftrightarrow 34.5\text{H}_2\text{O} + 34.5\text{MgO} + 69\text{Cl}^-$
- Total: $34.5\text{MgCl}_2 + 34.5\text{H}_2\text{O} + \text{Cr}_2\text{O}_3 \leftrightarrow 34.5\text{H}_2\text{O} + 34.5\text{MgO} + 23\text{CrCl}_3 + 6\text{Cr}$

**Propagation (Alloy)**

- Ox: $\text{Cr} + 2\text{Cl}^- \rightarrow \text{CrCl}_2 + 2\text{e}^-$
- Red: $2\text{CrCl}_3 + 2\text{e}^- \rightarrow 2\text{CrCl}_4 + 2\text{Cl}^-$
- Total: $\text{Cr} + 2\text{CrCl}_3 \rightarrow 2\text{CrCl}_4$

EDS X-ray map of Cr from Haynes 230 cross-section.
Accelerated Corrosion Results – Electrochemical Analysis (Haynes 230 in MgCl$_2$-KCl at 750 & 850°C)

For Diffusion Limited Reaction:

\[
\frac{D_1}{D_2} \propto \frac{T_1^{3/2}}{T_2^{3/2}}
\]

Anticipated Ratio of D = 0.84

Ratio of $i_{\text{corr}}$ from LPR Scans = 0.87
Potential Monitoring for Corrosion Mechanism in MgCl₂-KCl using Mg

- Corrosion mitigation is thermodynamic and can be monitored looking at sample potential versus a reference electrode
- SRNL used thermodynamic modeling to determine the equilibrium potentials for elements in the system
- The equilibrium potential for Cr oxidation/reduction is near -0.5 V vs. Ag/AgCl in molten chlorides at 850 °C
- Mg has an equilibrium potential of -1.5 V vs. Ag/AgCl and can prevent oxidation of Cr
- Haynes 230 samples in salt with no Mg had potentials that were above -0.5 V for extended periods of time and these samples showed typical corrosion levels
- Haynes 230 samples in salt with Mg had potentials well below -0.5 V for the entire experimental period and these samples showed no statistically significant weight change
- System electrochemical potential increased with operating temperature, which demonstrates that high temperature conditions have the ability to cause more corrosion
- Using reference electrodes can be used for control of redox agents
Assessment of Cathodic Protection Effectiveness

- Tests with Mg as a corrosion inhibitor species eliminated weight loss in the samples for static test
- An improved understanding of the long-term behavior of systems with Mg corrosion inhibition is needed along with a method to reliably control the amount of Mg present in a system

- Isothermal corrosion for Haynes 230 in MgCl₂-KCl is 35 times higher than the 15 microns per year target
- Non-isothermal corrosion for Haynes 230 with only free convection is over 100 times higher than the target

![Graph showing corrosion rates under different conditions with T = 850°C](image)
Corrosion Mechanism in MgCl$_2$-KCl using Zr

- SRNL also tested Zr as an alternative to Mg for corrosion mitigation
- Zr and the ZrCl$_2$/ZrCl$_3$ couple have been used for impurity gettering and corrosion mitigation in molten salt nuclear reactors
- Both Zr and ZrCl$_2$/ZrCl$_3$ readily react with oxygen and moisture to protect other system components such as the process tubing
- Zr formed an intermetallic surface layer with Ni from the Haynes 230 alloy
- Zr forms close packed carbides that are significantly more stable than chromium carbides like Cr$_{23}$C$_6$
- Reaction of Zr with chromium carbides can help to stabilize them and prevent them from corroding.
- Zr can be used as a surrogate for similar elements such as Ti, Hf, V, Nb, and Ta
- Adjustments to using Zr could be made by moving to other elements or forming mixtures with other elements