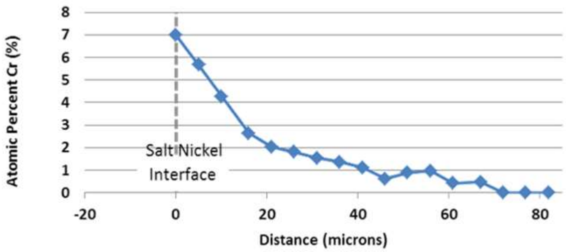
Introduction: Corrosion Mechanism in $MgCl_2$-KCl (Previous SRNL SunShot Project)



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

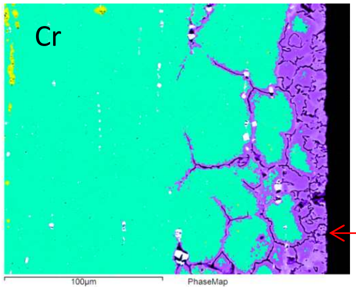
Disproportionation (Crucible)	
Ox :	$2CrCl_2 + 2Cl^- \rightarrow 2CrCl_3 + 2e^-$
Red :	$Ni + CrCl_2 + 2e^- \rightarrow NiCr + 2Cl^-$
Total :	$Ni + 3CrCl_2 \rightarrow NiCr + 2CrCl_3$

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

Overal Reaction : $Ni + CrCl_3 \leftrightarrow NiCr$

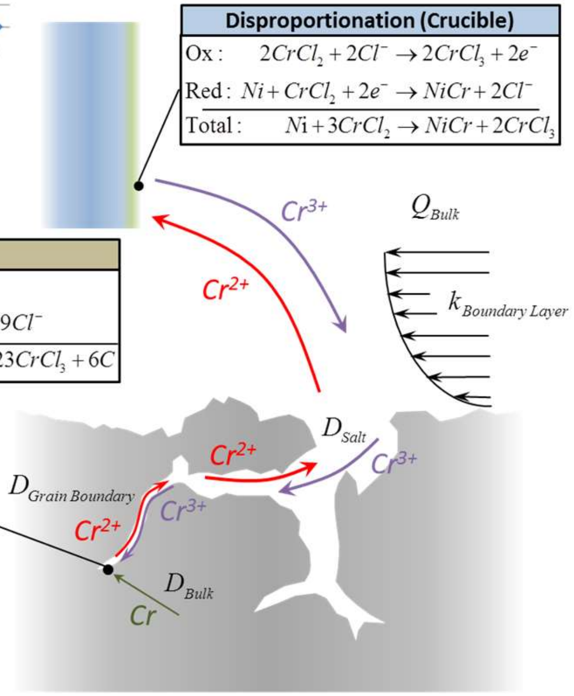
Initiation	
Ox :	$Cr_{23}C_6 + 69Cl^- \leftrightarrow 23CrCl_3 + 6C + 69e^-$
Red :	$34.5MgCl_2 + 34.5H_2O + 69e^- \leftrightarrow 34.5H_{2(g)} + 34.5MgO + 69Cl^-$
Total :	$34.5MgCl_2 + 34.5H_2O + Cr_{23}C_6 \leftrightarrow 34.5H_{2(g)} + 34.5MgO + 23CrCl_3 + 6C$

EDS X-ray map of Cr from Haynes 230 cross-section

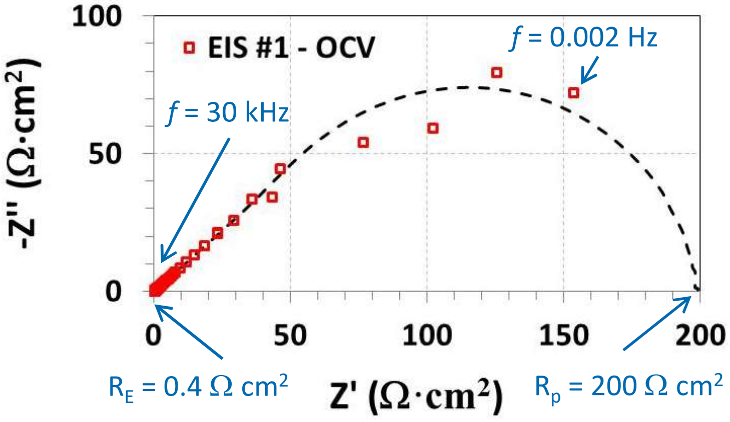


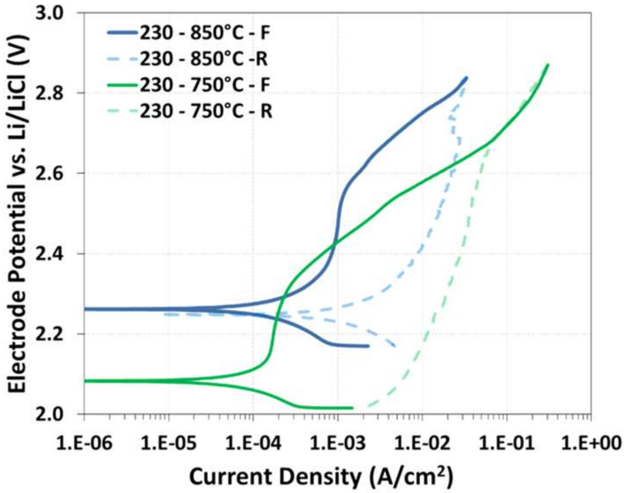
Alloy Surface

Propagation (Alloy)	
Ox :	$Cr + 2Cl^- \rightarrow CrCl_2 + 2e^-$
Red :	$2CrCl_3 + 2e^- \rightarrow 2CrCl_2 + 2Cl^-$
Total :	$Cr + 2CrCl_3 \rightarrow 3CrCl_2$



Accelerated Corrosion Results – Electrochemical Analysis (Haynes 230 in $MgCl_2$-KCl at 750 & 850°C)



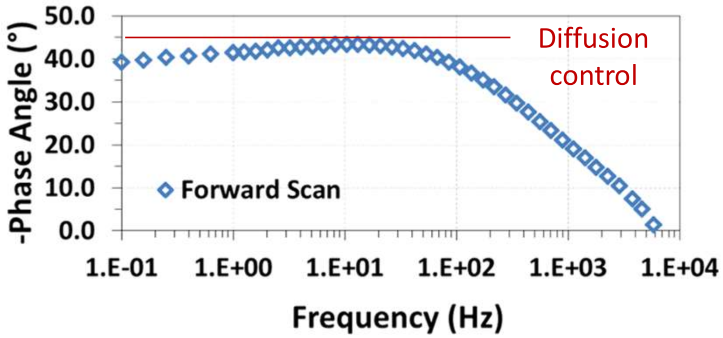


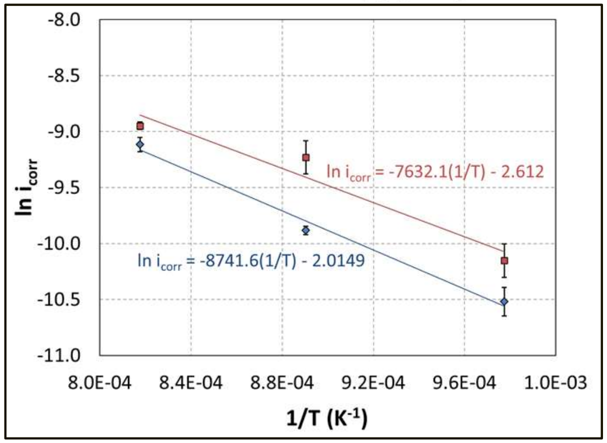
For Diffusion Limited Reaction:

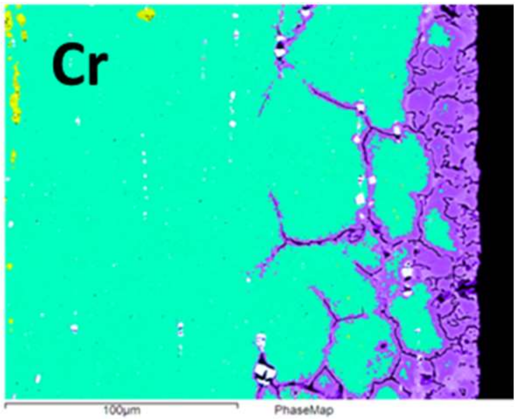
$$\frac{D_1}{D_2} \propto \frac{T_1^{3/2}}{T_2^{3/2}}$$

Anticipated Ratio of D = **0.84**

Ratio of i_{corr} from LPR Scans = **0.87**

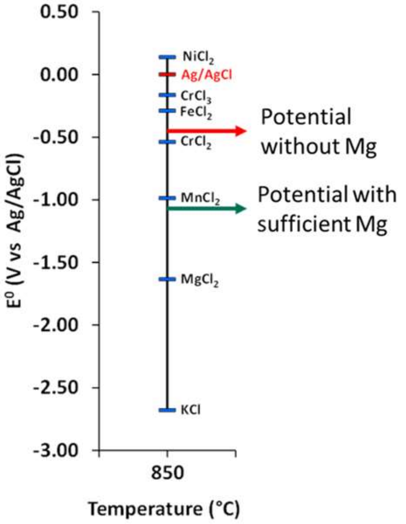


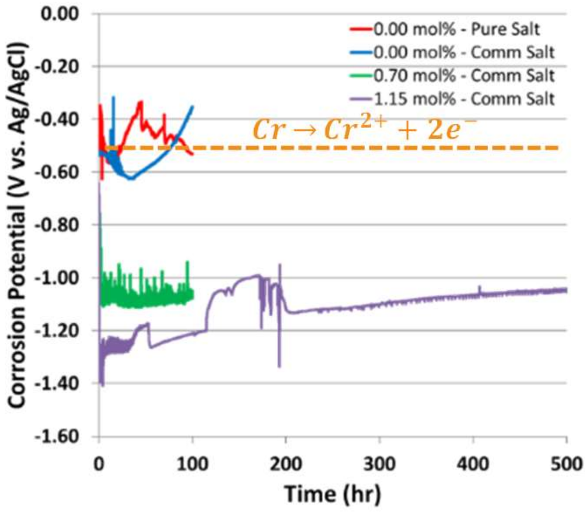


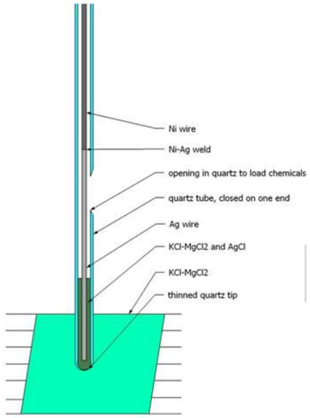


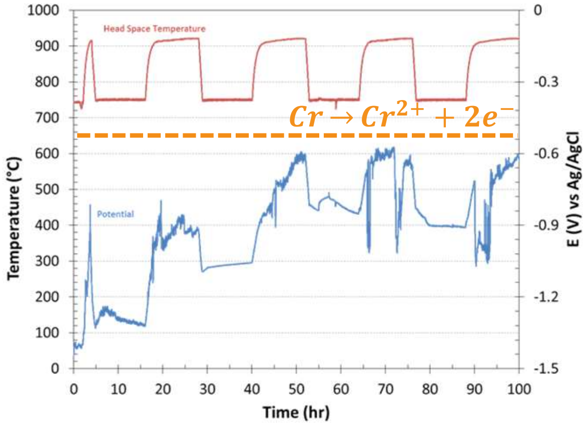
Potential Monitoring for Corrosion Mechanism in $MgCl_2$-KCl using Mg

- 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

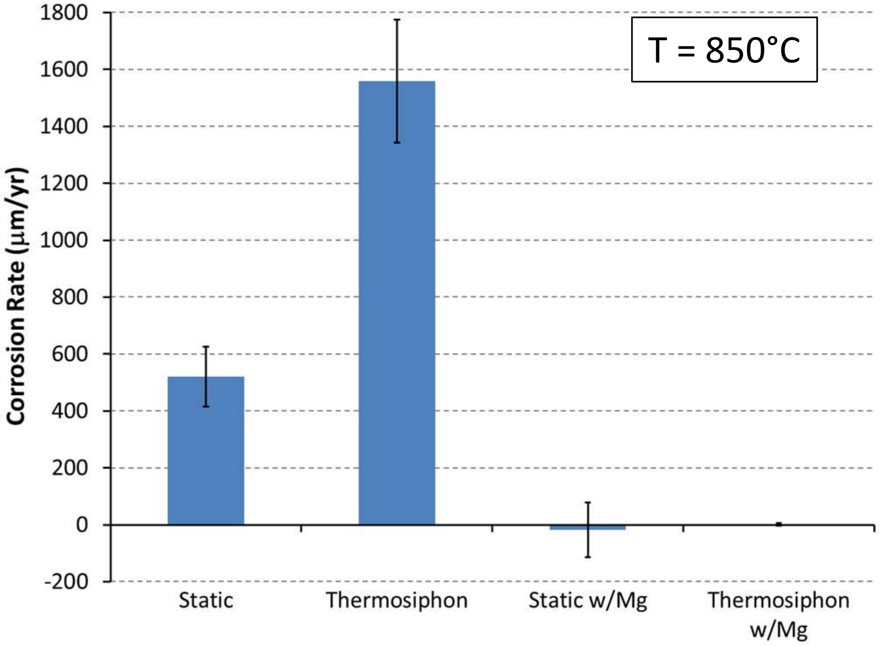




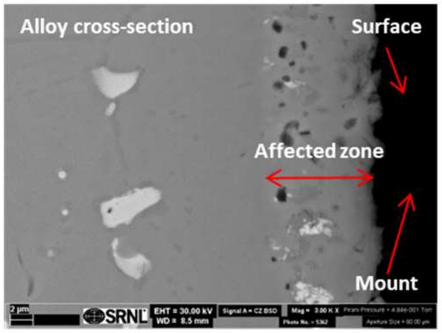




Assessment of Cathodic Protection Effectiveness



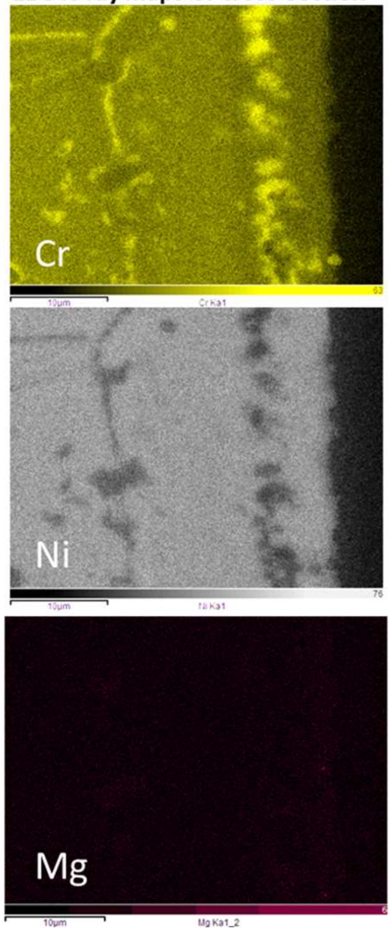
- Isothermal corrosion for Haynes 230 in $MgCl_2$-KCl is 35 times higher than the 15 microns per year target
- Non-isothermal corrosion for Haynes 230 with only free convection is over 100 times higher than the target



SEM of Cross-section

- 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

EDS X-ray maps of cross-section



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