U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

SOLAR ENERGY TECHNOLOGIES OFFICE

SETO CSP Program Summit 2019

Corrosion Mitigation for Gen 3 CSP Systems

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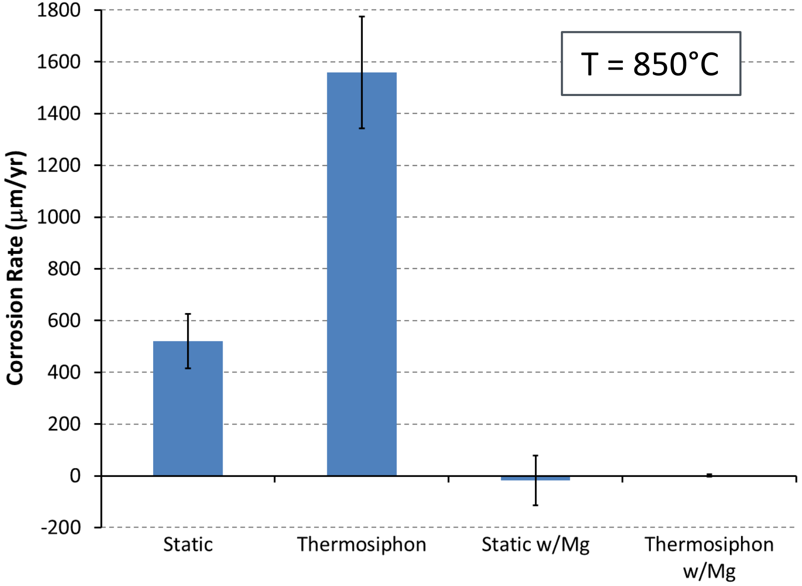
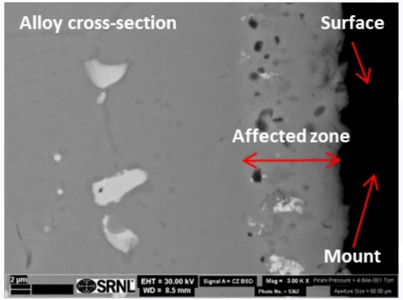
3/18/2019

Assessment of Cathodic Protection Effectiveness

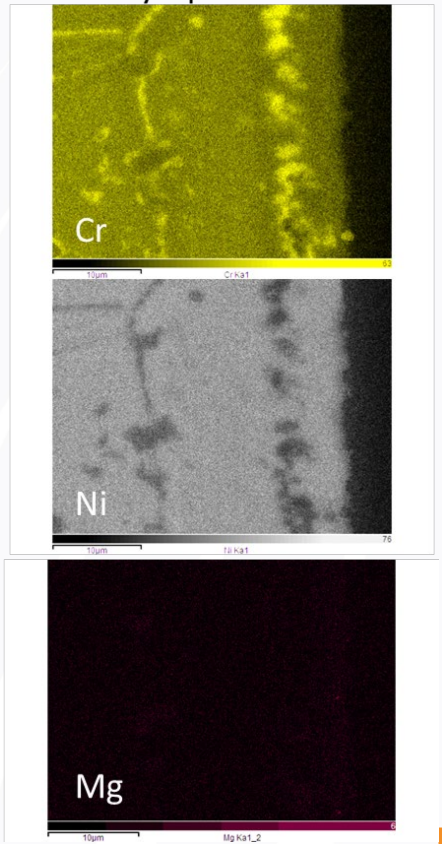


- Isothermal corrosion for Haynes 230 in $MgCl_2$-KCl is 35 times higher than the 15 microns per year target
- Non-isothermal corrosion for Haynes 230 with only free convection is over 100 times higher than the target



SEM of Cross-section

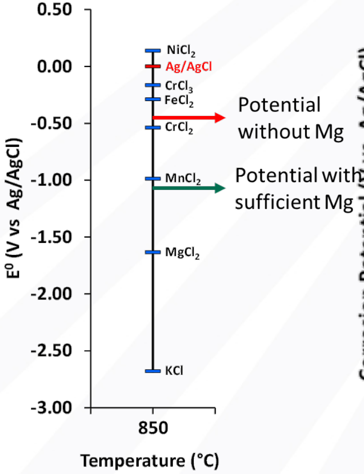
EDS X-ray maps of cross-section

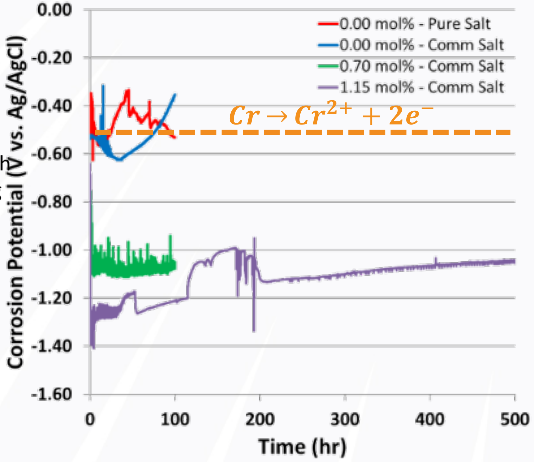


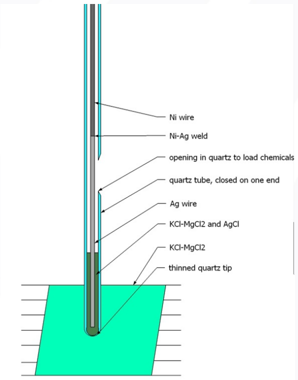
- Tests with Mg as a corrosion inhibitor species eliminated weight loss in the samples for static test
- An improved understanding of the long term behavior of systems with Mg corrosion inhibition is needed along with a method to reliably control the amount of Mg present in a system

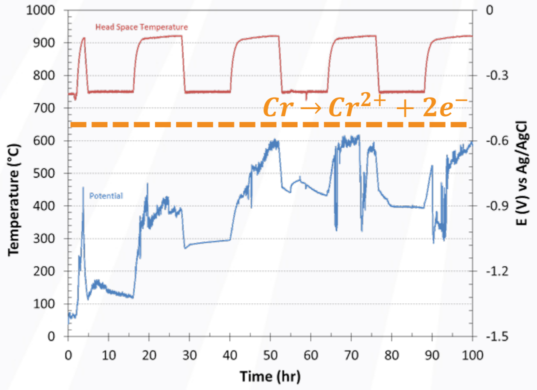
Potential Monitoring for Corrosion Mechanism in $MgCl_2$-KCl using Mg

- 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



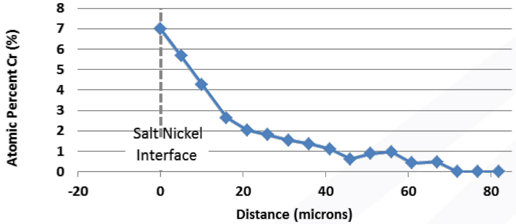






Introduction: Corrosion Mechanism in $MgCl_2$-KCl (Previous SRNL SunShot Project)

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: $2CrCl_2 + 2Cl^- \rightarrow 2CrCl_3 + 2e^-$

Red: $Ni + CrCl_2 + 2e^- \rightarrow NiCr + 2Cl^-$

Total: $Ni + 3CrCl_2 \rightarrow NiCr + 2CrCl_3$

Overal Reaction: $Ni + CrCl_3 \leftrightarrow NiCr$

Initiation

Ox: $Cr_{23}C_6 + 69Cl^- \leftrightarrow 23CrCl_3 + 6C + 69e^-$

Red: $34.5MgCl_2 + 34.5H_2O + 69e^- \leftrightarrow 34.5H_{2(g)} + 34.5MgO + 69Cl^-$

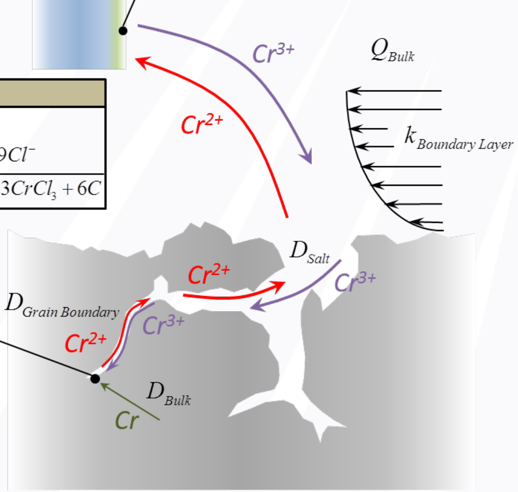
Total: $34.5MgCl_2 + 34.5H_2O + Cr_{23}C_6 \leftrightarrow 34.5H_{2(g)} + 34.5MgO + 23CrCl_3 + 6C$

Propagation (Alloy)

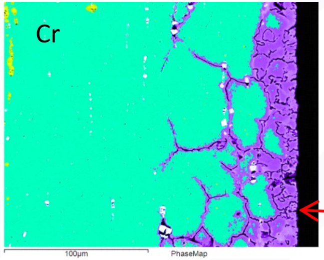
Ox: $Cr + 2Cl^- \rightarrow CrCl_2 + 2e^-$

Red: $2CrCl_3 + 2e^- \rightarrow 2CrCl_2 + 2Cl^-$

Total: $Cr + 2CrCl_3 \rightarrow 3CrCl_2$



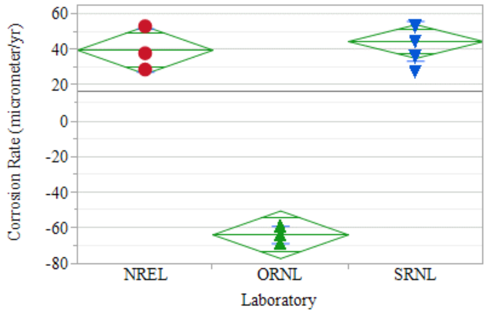
EDS X-ray map of Cr from Haynes 230 cross-section



Alloy Surface

Task 1.0: Exchange of Samples and Data with Project Cohorts – Comparison Between National Labs

NREL vs ORNL vs SRNL



- The test of the null hypothesis of equal variances cannot be rejected at the 5% significance level; thus, there is no indication of a difference in variances across the three labs.

Oneway Anova
Summary of Fit

Rsquare	0.964734
Adj Rsquare	0.956898
Root Mean Square Error	10.20109
Mean of Response	16.39167
Observations (or Sum Wgts)	12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Laboratory	2	25620.709	12810.4	123.1028	<.0001*
Error	9	936.560	104.1		
C. Total	11	26557.269			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
NREL	3	39.800	5.8896	26.48	53.12
ORNL	3	-63.567	5.8896	-76.89	-50.24
SRNL	6	44.667	4.1646	35.25	54.09

Std Error uses a pooled estimate of error variance

Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
NREL	3	12.06275	8.600000	7.966667
ORNL	3	4.65224	3.155556	3.100000
SRNL	6	10.97500	8.677778	8.666667

Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	0.7174	2	9	0.5139
Brown-Forsythe	0.7593	2	9	0.4958
Levene	1.3131	2	9	0.3160
Bartlett	0.7359	2	.	0.4791

Warning: Small sample sizes. Use Caution.

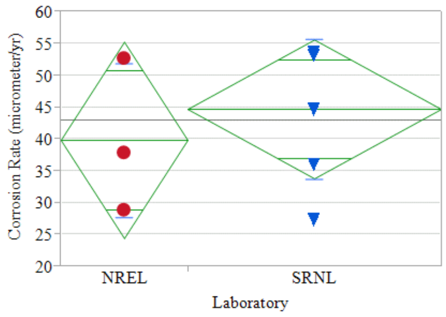
Means Comparisons
Comparisons for all pairs using Tukey-Kramer HSD
Connecting Letters Report

Level			Mean
SRNL	A		44.66667
NREL	A		39.80000
ORNL		B	-63.56667

Levels not connected by same letter are significantly different.

NREL vs SRNL

- The test of the null hypothesis of equal means is rejected at the 5% significance level; with the additional test results indicating that SRNL and NREL show no difference in their mean corrosion rates, while both labs are different from ORNL.



Oneway Anova
Summary of Fit

Rsquare	0.050358
Adj Rsquare	-0.08531
Root Mean Square Error	11.29648
Mean of Response	43.04444
Observations (or Sum Wgts)	9

t Test
SRNL-NREL

Assuming equal variances

Difference	4.867	t Ratio	0.609261
Std Err Dif	7.988	DF	7
Upper CL Dif	23.755	Prob > |t|	0.5616
Lower CL Dif	-14.022	Prob > t	0.2808
Confidence	0.95	Prob < t	0.7192

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Laboratory	1	47.36889	47.369	0.3712	0.5616
Error	7	893.27333	127.610		
C. Total	8	940.64222			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
NREL	3	39.8000	6.5220	24.378	55.222
SRNL	6	44.6667	4.6118	33.762	55.572

Std Error uses a pooled estimate of error variance

Tests that the Variances are Equal

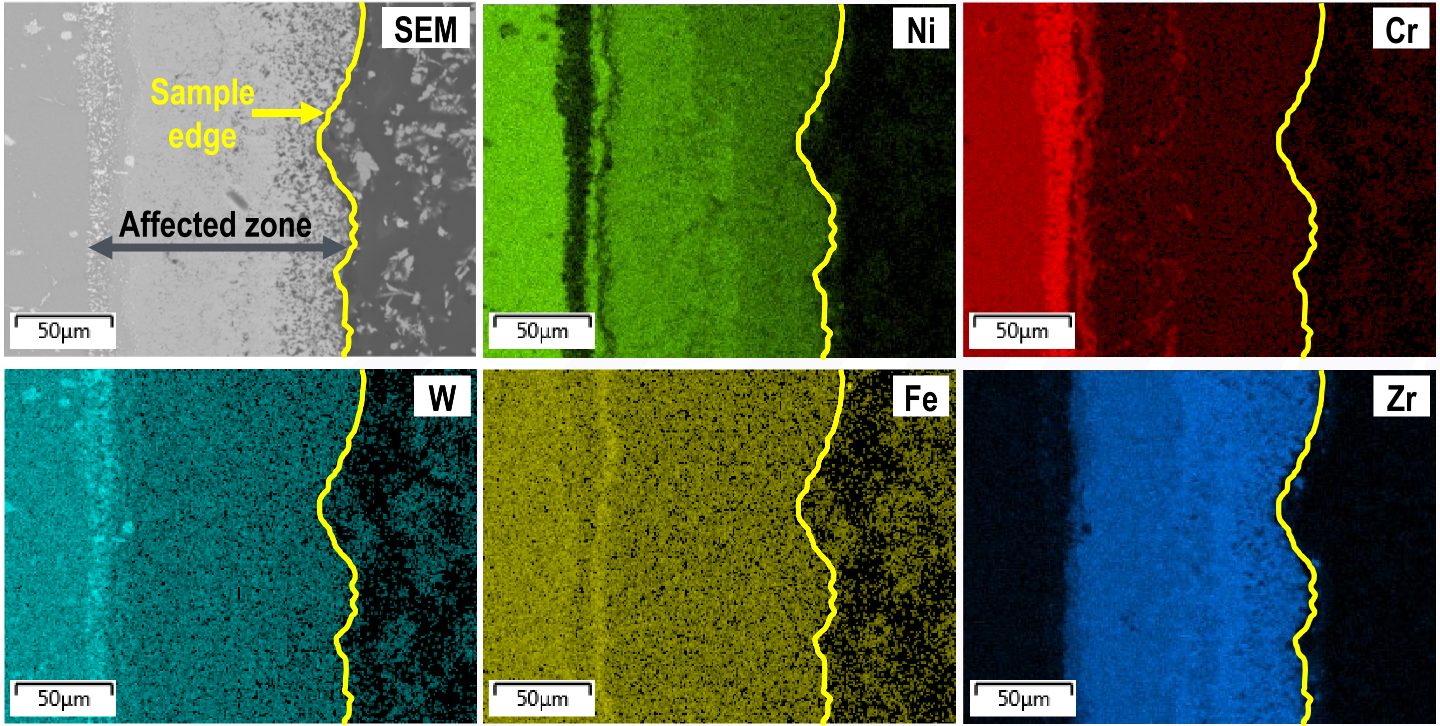
Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
NREL	3	12.06275	8.600000	7.966667
SRNL	6	10.97500	8.677778	8.666667

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.0522	1	7	0.8258
Brown-Forsythe	0.0185	1	7	0.8956
Levene	0.0004	1	7	0.9849
Bartlett	0.0221	1	.	0.8819
F Test 2-sided	1.2080	2	5	0.7465

Warning: Small sample sizes. Use Caution.

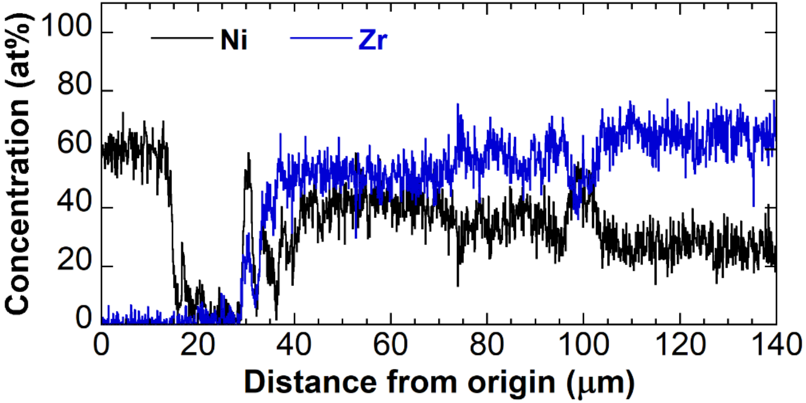
Subtask 2.1.2: Self-Healing Coatings as Corrosion Inhibitors – Elemental Mapping of H230-G3-SRC-Zr4

- EDX mapping of cross-section confirms formation of Zr coating on Haynes 230
- Affected zone composed of Cr/W-rich region near bulk and Ni/Zr-rich regions closer to edge



Subtask 2.1.2: Self-Healing Coatings as Corrosion Inhibitors – H230-G3-SRC-Zr4 Ni/Zr-rich Region

EDX analysis indicates presence of NiZr and $NiZr_2$ phases



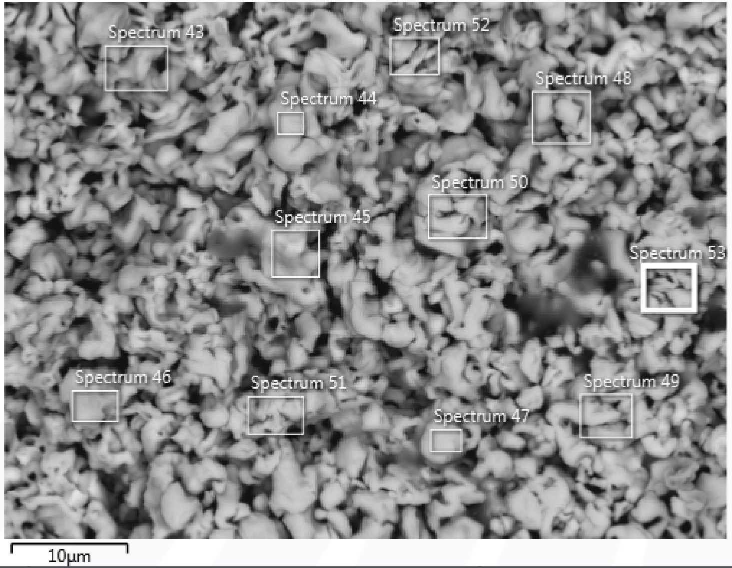
Between ~70 – 90 µm from edge

Parameter	Value
Average Zr Atomic Fraction	0.53 ± <0.1
NiZr Atomic Fraction	0.5

Within 30 µm of edge

Parameter	Value
Average Zr Atomic Fraction	0.67 ± <0.1 g
$NiZr_2$ Atomic Fraction	0.67

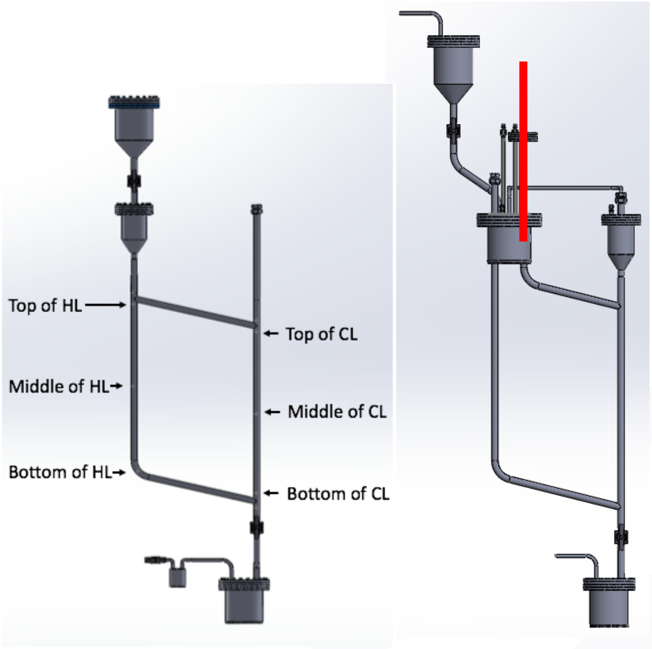
Point scans of surface near edge of Ni/Zr-rich region



Element	Mean Concentration (at%)	Standard Deviation (at%)
Ni	31.2	2.6
Cr	0.4	0.1
W	0.3	0.1
Zr	67.2	3.1

Zr atomic fraction within 2% of ideal $NiZr_2$ value

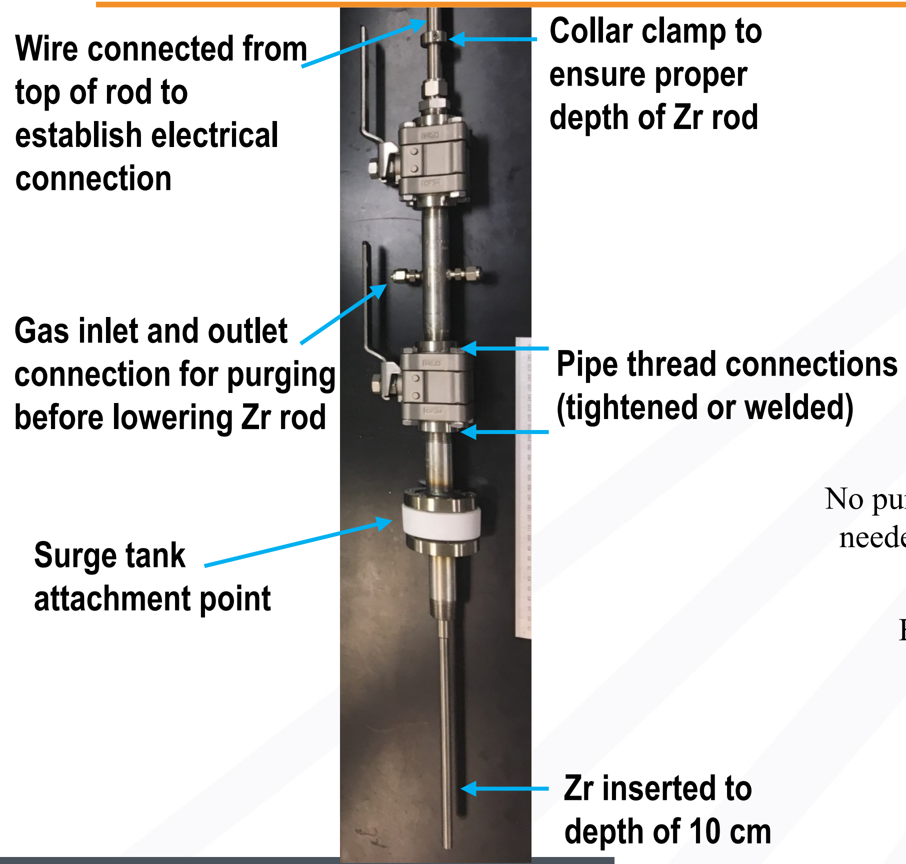
Subtask 2.1.3: Design and Test a Getter Bed for a Thermosiphon Reactor in Collaboration with ORNL



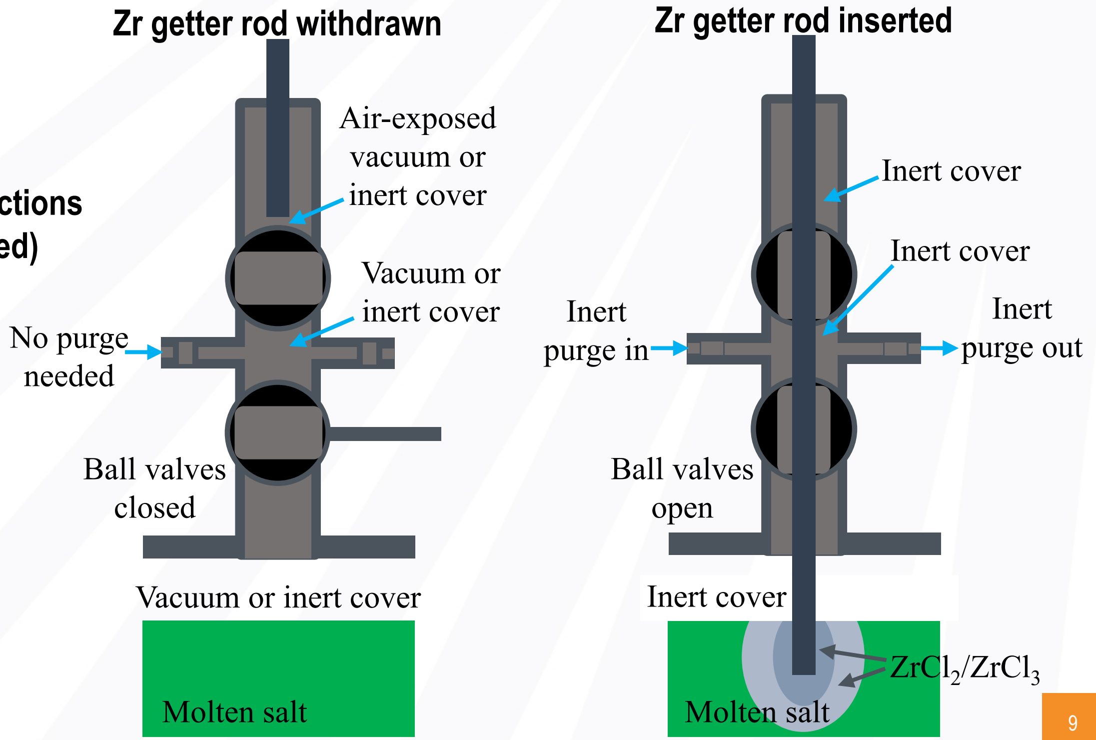
ORNL provided drawing of old and new natural convection flow loop designs

- SRNL provided a corrosion control solution in redesigned ORNL loop
  - Potential install location in red
- New flow loop design should be comparable to old design → compare old data with corrosion inhibited
- Two options have been designed
  - Zr getter rod
  - Electrolysis rod apparatus
- Zr rod will reduce corrosion by
  - 1) Galvanic protection
    - Zr rod more anodic than piping → corrode first if in electrical contact with loop
    - Zr in salt may coat pipe→ galvanic buffer if rod withdrawn
  - 2) Redox control
    - $Zr^0 \rightarrow ZrCl_2 \rightarrow ZrCl_3 \rightarrow ZrCl_4$ occur prior to Cr oxidation → buffer against $Cr^0 \rightarrow Cr^{2,3+}$
- Mg Electrolysis (in situ)
  - 1) Galvanic protection
    - Galvanic protection capability, can coat some walls if below melting point
    - Mg^0 is soluble (small) in the salt → buffer. May also present some galvanic protection
  - 2) Redox control
    - $Mg^0 \rightarrow Mg^{2+}$ will prevent $Cr^0 \rightarrow Cr^{2,3+}$
    - Mg^0 is soluble (small) in the salt, and this solubility will act as a buffer.
  - 3) Oxide sink: MgO → most stable oxide in system

Subtask 2.1.3: Design and Test a Getter Bed for a Thermosiphon Reactor in Collaboration with ORNL



Schematic of Zr gettering assembly with rod when inserted and withdrawn



Subtask 2.1.3: Design and Test a Getter Bed for a Thermosiphon Reactor in Collaboration with ORNL

Enlarged view of electrode assembly