SRNL

SAVANNAH RIVER NATIONAL LABORATORY

Corrosion in Very High-Temperature Molten Salt for Next Generation CSP Systems

Brenda Garcia Diaz (PI), Josh Gray (Co-PI),
Luke Olson, Michael Martinez-Rodriguez, Roderick Fuentes (SRNL)
Ramana Reddy, John Van Zee (University of Alabama)

Project Identifier: Garcia-Diaz_A

Project Start: Q1 - FY2013

April 1st , 2013

Outline

- Motivation
  - Innovation
  - Goals and Objectives
- Background
  - Molten Salt and Material Selection
  - Molten Salt Corrosion Review
- Current status
  - Corrosion measurements/Inhibitor studies
  - Thermodynamic modeling
  - Electrochemical Kinetics and CFD Corrosion Modeling
- Future plans

Motivation: Enable efficient, long-term high temperature heat transfer using molten salts

- SunShot program seeks major price reductions
- Higher temperature energy conversion allows for better thermodynamic efficiencies
- Temp. Range for Study: 800 – 1000 °C
- Limited number of options for very high temperature heat transfer
  - Steam or other gases
    - **Large pipe diameters needed**
    - **Large pumping power required**
  - Molten Glass
    - **Viscous**
    - **Low thermal conductivities**
  - Liquid metals
    - **Limited operating temperature range**
    - **Alloying with piping materials**
    - **Vapor pressures**
  - Molten Salts
    - **Heat transfer behavior at 700 °C similar to water at 20 °C**

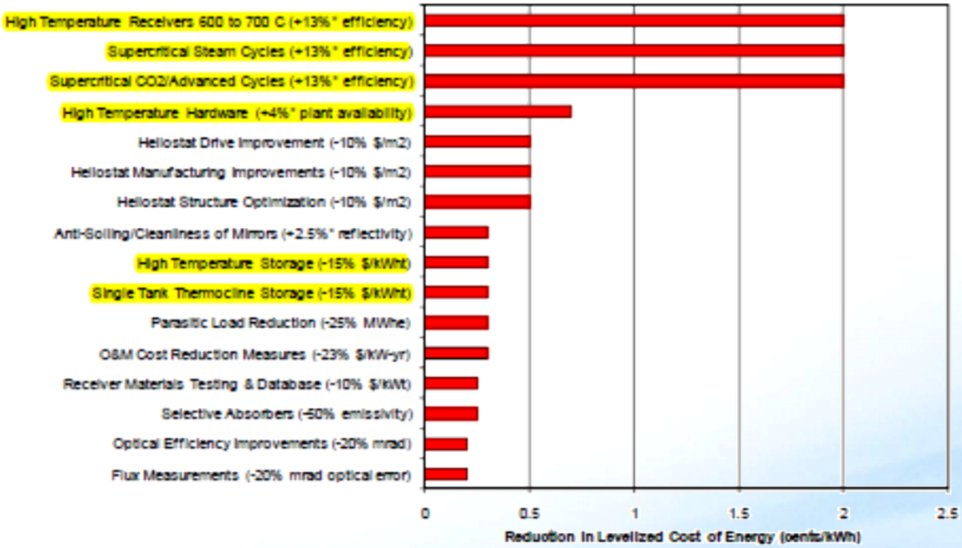


Image Source: NREL, available: http://earthobservatory.nasa.gov/Features/RenewableEnergy/Images/solar_two.jpg
Table Source: SAND2011-2419

Goals and Objectives

- **Goal #1 – Identify molten salt / material combinations that have long service life and meet performance needs**
- **Goal #2 – Characterize corrosion rates, corrosion mechanisms, and methods to reduce corrosion**
- Objective #1 – Perform experiments that quantify corrosion rates and provide information to determine corrosion mechanisms under isothermal and non-isothermal operation
- Objective #2 – Determine corrosion products and predict corrosion potentials through thermodynamic modeling
- Objective #3 – Determine corrosion reaction kinetics and modeling corrosion reactions in realistic systems using CFD

Salt Selection

- DOE has invested considerable effort in determining ideal salt candidates for heat transfer candidates for nuclear applications (no exposure to radiation)
- Corrosion inhibitors that could not be used for nuclear application may have solar applications
- Need High Boiling Point and Low Vapor Pressure

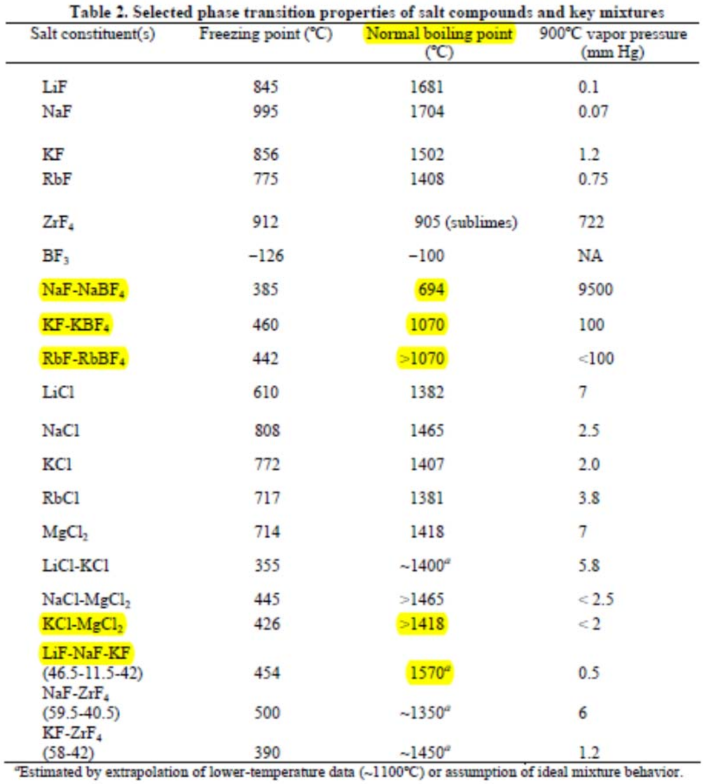


Table 2. Selected phase transition properties of salt compounds and key mixtures

Salt constituent(s)	Freezing point (°C)	Normal boiling point (°C)	900°C vapor pressure (mm Hg)
LiF	845	1681	0.1
NaF	995	1704	0.07
KF	856	1502	1.2
RbF	775	1408	0.75
ZrF_4	912	905 (sublimes)	722
BF_3	−126	−100	NA
$NaF-NaBF_4$	385	694	9500
$KF-KBF_4$	460	1070	100
$RbF-RbBF_4$	442	>1070	<100
LiCl	610	1382	7
NaCl	808	1465	2.5
KCl	772	1407	2.0
RbCl	717	1381	3.8
$MgCl_2$	714	1418	7
LiCl-KCl	355	~1400[a]	5.8
$NaCl-MgCl_2$	445	>1465	< 2.5
$KCl-MgCl_2$	426	>1418	< 2
LiF-NaF-KF (46.5-11.5-42)	454	1570[a]	0.5
$NaF-ZrF_4$ (59.5-40.5)	500	~1350[a]	6
$KF-ZrF_4$ (58-42)	390	~1450[a]	1.2

[a] Estimated by extrapolation of lower-temperature data (~1100°C) or assumption of ideal mixture behavior.

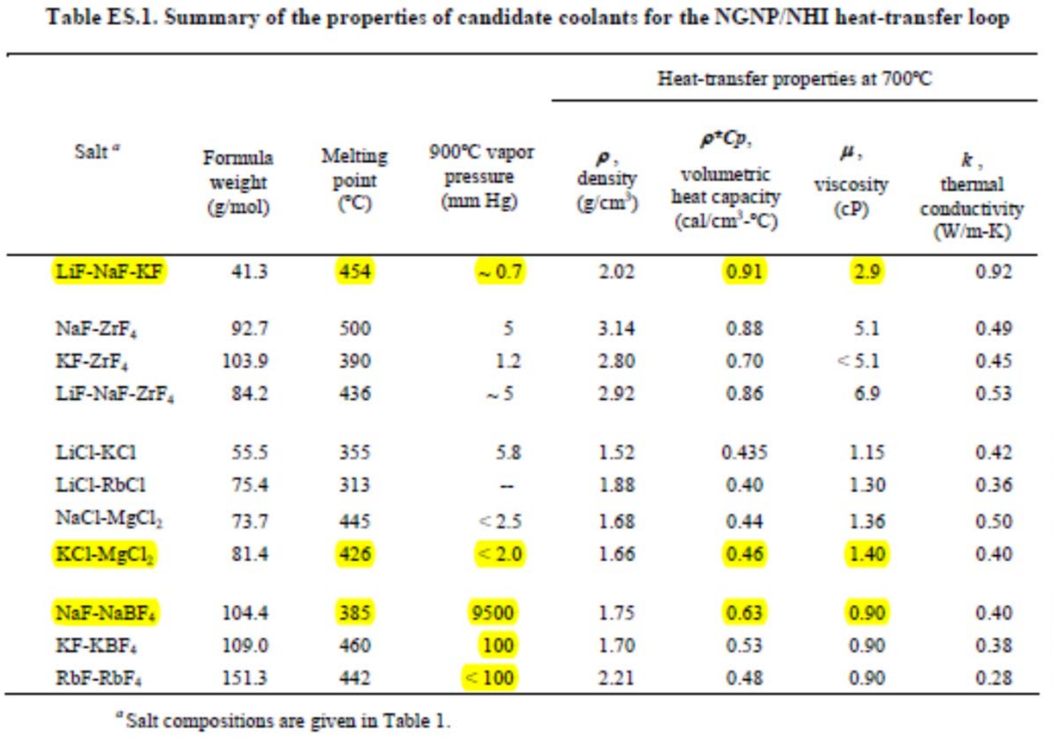


Table ES.1. Summary of the properties of candidate coolants for the NGNP/NHI heat-transfer loop

				Heat-transfer properties at 700°C			
Salt [a]	Formula weight (g/mol)	Melting point (°C)	900°C vapor pressure (mm Hg)	ρ, density (g/cm^3)	ρ*Cp, volumetric heat capacity (cal/cm^3-°C)	μ, viscosity (cP)	k, thermal conductivity (W/m-K)
LiF-NaF-KF	41.3	454	~ 0.7	2.02	0.91	2.9	0.92
$NaF-ZrF_4$	92.7	500	5	3.14	0.88	5.1	0.49
$KF-ZrF_4$	103.9	390	1.2	2.80	0.70	< 5.1	0.45
$LiF-NaF-ZrF_4$	84.2	436	~ 5	2.92	0.86	6.9	0.53
LiCl-KCl	55.5	355	5.8	1.52	0.435	1.15	0.42
LiCl-RbCl	75.4	313	--	1.88	0.40	1.30	0.36
$NaCl-MgCl_2$	73.7	445	< 2.5	1.68	0.44	1.36	0.50
$KCl-MgCl_2$	81.4	426	< 2.0	1.66	0.46	1.40	0.40
$NaF-NaBF_4$	104.4	385	9500	1.75	0.63	0.90	0.40
$KF-KBF_4$	109.0	460	100	1.70	0.53	0.90	0.38
$RbF-RbF_4$	151.3	442	< 100	2.21	0.48	0.90	0.28

[a] Salt compositions are given in Table 1.

[1]: Williams, D., Assessment of Candidate Molten Salt Coolants for the NGNP/NHI Heat-Transfer Loop, ORNL/TM-2006/69.

Salt Selection:

- Figure of merits are below for salts (Lower is better)
- FLiNaK has best heat transfer characteristics
- KCl-$MgCl_2$ is cheapest salt
- KCl-$MgCl_2$ is 60% of the cost of common eutectic nitrate salts used in lower temperature heat transfer
- FLiNaK is much higher in price (Significant contribution is from the cost of the Li)

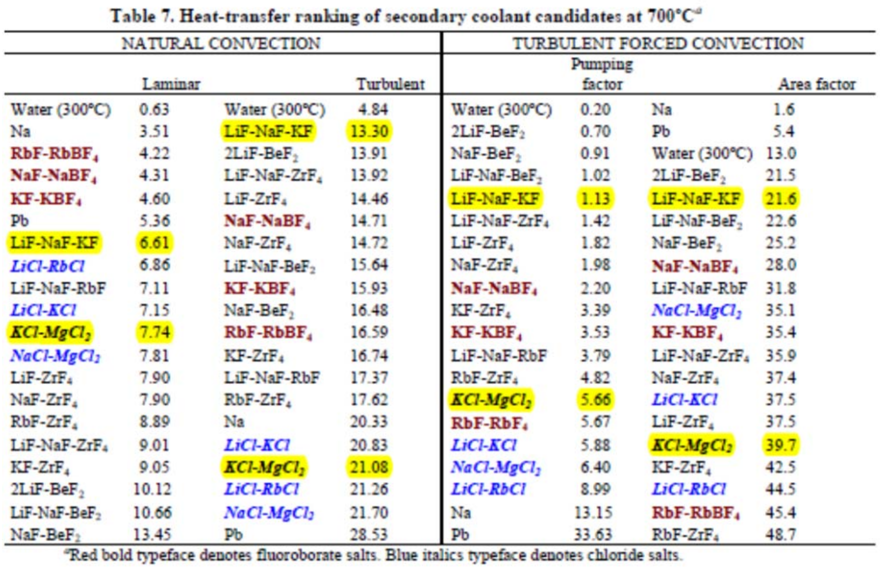


Table 7. Heat-transfer ranking of secondary coolant candidates at 700°C[a]

NATURAL CONVECTION				TURBULENT FORCED CONVECTION			
	Laminar		Turbulent		Pumping factor		Area factor
Water (300°C)	0.63	Water (300°C)	4.84	Water (300°C)	0.20	Na	1.6
Na	3.51	LiF-NaF-KF	13.30	2LiF-BeF_2	0.70	Pb	5.4
RbF-$RbBF_4$	4.22	2LiF-BeF_2	13.91	NaF-BeF_2	0.91	Water (300°C)	13.0
NaF-$NaBF_4$	4.31	LiF-NaF-ZrF_4	13.92	LiF-NaF-BeF_2	1.02	2LiF-BeF_2	21.5
KF-KBF_4	4.60	LiF-ZrF_4	14.46	LiF-NaF-KF	1.13	LiF-NaF-KF	21.6
Pb	5.36	**NaF-$NaBF_4$**	14.71	LiF-NaF-ZrF_4	1.42	LiF-NaF-BeF_2	22.6
LiF-NaF-KF	6.61	NaF-ZrF_4	14.72	LiF-ZrF_4	1.82	NaF-BeF_2	25.2
LiCl-RbCl	6.86	LiF-NaF-BeF_2	15.64	NaF-ZrF_4	1.98	**NaF-$NaBF_4$**	28.0
LiF-NaF-RbF	7.11	**KF-KBF_4**	15.93	**NaF-$NaBF_4$**	2.20	LiF-NaF-RbF	31.8
LiCl-KCl	7.15	NaF-BeF_2	16.48	KF-ZrF_4	3.39	*NaCl-$MgCl_2$*	35.1
KCl-$MgCl_2$	7.74	**RbF-$RbBF_4$**	16.59	**KF-KBF_4**	3.53	**KF-KBF_4**	35.4
NaCl-$MgCl_2$	7.81	KF-ZrF_4	16.74	LiF-NaF-RbF	3.79	LiF-NaF-ZrF_4	35.9
LiF-ZrF_4	7.90	LiF-NaF-RbF	17.37	RbF-ZrF_4	4.82	NaF-ZrF_4	37.4
NaF-ZrF_4	7.90	RbF-ZrF_4	17.62	*KCl-$MgCl_2$*	5.66	*LiCl-KCl*	37.5
RbF-ZrF_4	8.89	Na	20.33	**RbF-RbF_4**	5.67	LiF-ZrF_4	37.5
LiF-NaF-ZrF_4	9.01	*LiCl-KCl*	20.83	*LiCl-KCl*	5.88	*KCl-$MgCl_2$*	39.7
KF-ZrF_4	9.05	*KCl-$MgCl_2$*	21.08	*NaCl-$MgCl_2$*	6.40	KF-ZrF_4	42.5
2LiF-BeF_2	10.12	*LiCl-RbCl*	21.26	*LiCl-RbCl*	8.99	*LiCl-RbCl*	44.5
LiF-NaF-BeF_2	10.66	*NaCl-$MgCl_2$*	21.70	Na	13.15	**RbF-$RbBF_4$**	45.4
NaF-BeF_2	13.45	Pb	28.53	Pb	33.63	RbF-ZrF_4	48.7

[a] Red bold typeface denotes fluoroborate salts. Blue italics typeface denotes chloride salts.

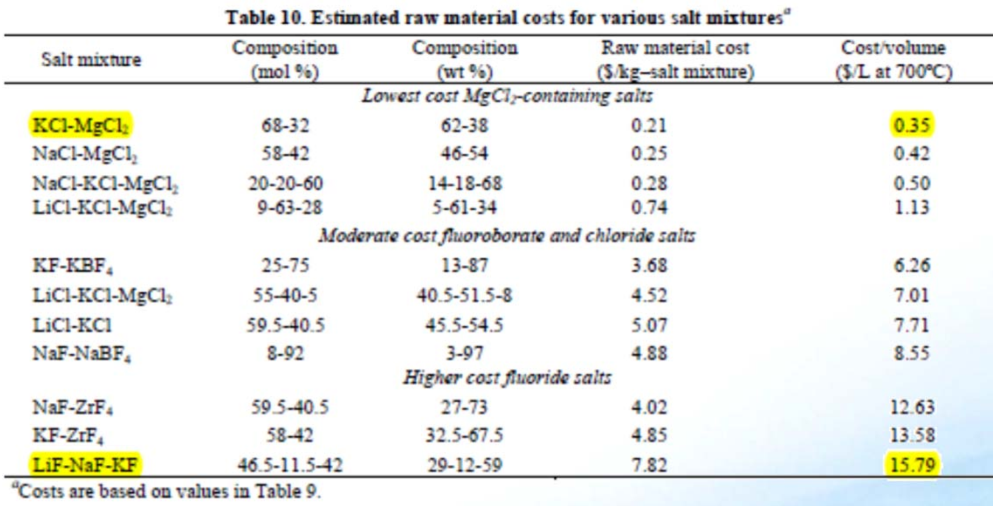


Table 10. Estimated raw material costs for various salt mixtures[a]

Salt mixture	Composition (mol %)	Composition (wt %)	Raw material cost ($/kg–salt mixture)	Cost/volume ($/L at 700°C)
		Lowest cost $MgCl_2$-containing salts		
KCl-$MgCl_2$	68-32	62-38	0.21	0.35
NaCl-$MgCl_2$	58-42	46-54	0.25	0.42
NaCl-KCl-$MgCl_2$	20-20-60	14-18-68	0.28	0.50
LiCl-KCl-$MgCl_2$	9-63-28	5-61-34	0.74	1.13
		Moderate cost fluoroborate and chloride salts		
KF-KBF_4	25-75	13-87	3.68	6.26
LiCl-KCl-$MgCl_2$	55-40-5	40.5-51.5-8	4.52	7.01
LiCl-KCl	59.5-40.5	45.5-54.5	5.07	7.71
NaF-$NaBF_4$	8-92	3-97	4.88	8.55
		Higher cost fluoride salts		
NaF-ZrF_4	59.5-40.5	27-73	4.02	12.63
KF-ZrF_4	58-42	32.5-67.5	4.85	13.58
LiF-NaF-KF	46.5-11.5-42	29-12-59	7.82	15.79

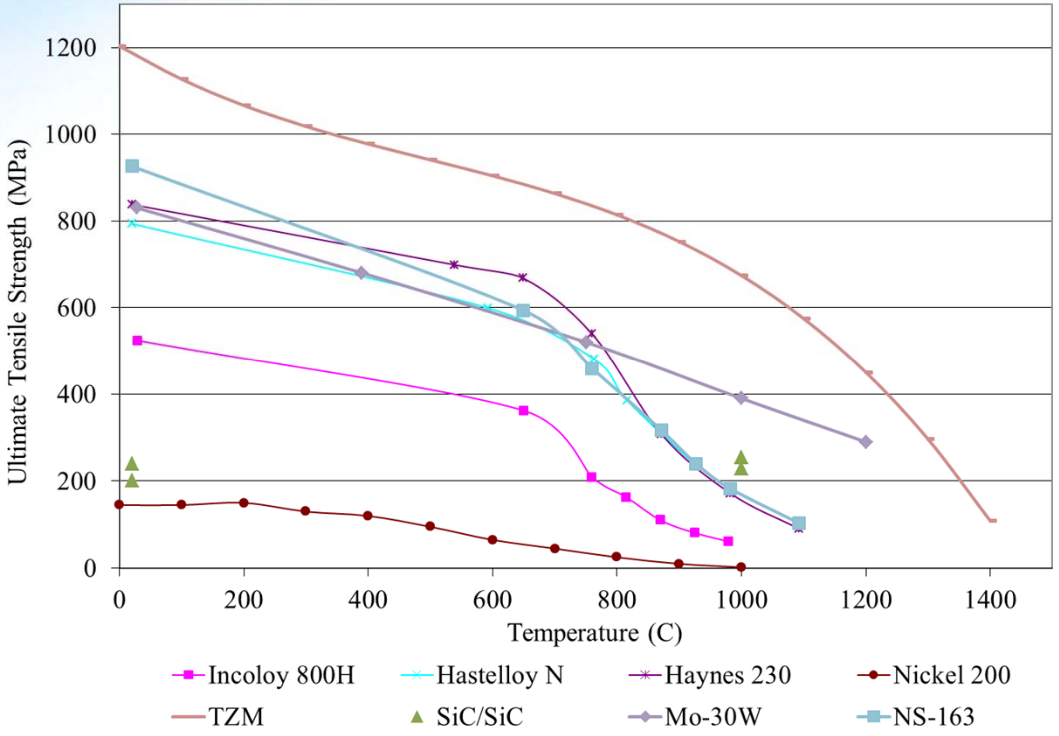
[a] Costs are based on values in Table 9.

[1]: Williams, D., Assessment of Candidate Molten Salt Coolants for the NGNP/NHI Heat-Transfer Loop, ORNL/TM-2006/69.

Materials Selection

- **Goal is to look at a wide range of materials and alloy systems for the most widespread characterization of corrosion inhibitors possible**
- Alloys
  - Capable of being formed into piping
  - Reasonable strength between 800-1000 C
  - Compatibility with salt
  - Single alloys must be oxidation resistant on outside, salt compatible on inside, or:
    - Plating or bilayer piping for salt compatibility, oxidation resistant coatings
- Ceramics and Composites
  - Less affected by heat
  - SiC has proven fluoride/chloride compatibility
  - SiC/SiC composites can be tailored to a range of physical properties such as thermal expansion and tensile strength

Material Selection:
Physical Property Considerations



	Hours to Rupture		
	760˚C/103 MPa	**871˚C/31 MPa**	**982˚C/14 MPa**
Haynes-230	**8 200**	**6 500**	**5 000**
Incoloy-800H	**130**	**1 200**	**920**
304 Stainless Steel	**10**	**100**	**72**

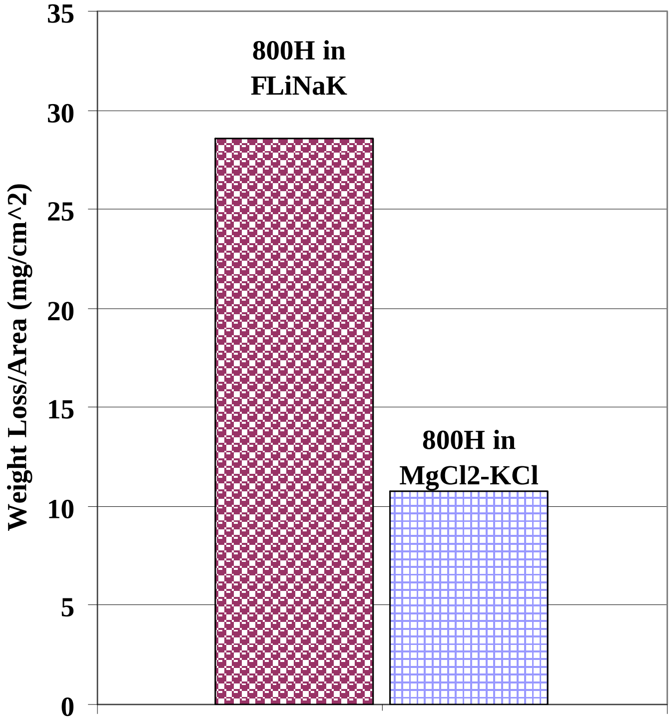
- **High temperature strength:**
  all except Ni
- **Dissolution resistance:**
  Ni-201, SiC/SiC composite, TZM, Mo-30W
- **High creep rupture resistance:**
  Haynes-230, Haynes-NS-163
- **Past molten halide salt experience:**
  Hastelloy-N
- **Expense and utility use:**
  Incoloy-800H
- **High temperature refractory alloy:**
  TZM, Mo-30W

Experimental Setup: High Purity Requirements, Multiplicity of Engineering Solutions Required

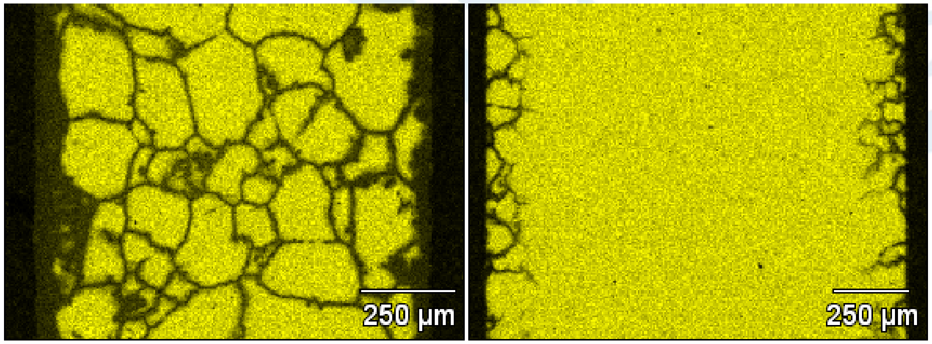
- **Several aspects of this research were extremely challenging for a variety of reasons**

  - **Toxicity and safety**
    - Fluorine major constituent
    - High temperature liquids and surfaces
  - **Little active research in recent years on fluorides/chlorides, most data from 50s-70s**
    - Extreme amount of literature survey required
  - **Extreme purity requirements of salt exposure experiments**
    - Purity requirements not easy/cheap
    - Ar atmosphere: Glovebox/Glovebags
    - Heaters, sealed corrosion vessels, pressure, atmosphere control
  - **Long amounts of time required for static cell data acquisition: for a single data point up to 1000h (~1.5 months)**
  - **Custom fabrication of apparatus ("Off the Shelf" systems unavailable)**

Corrosion Attack far More Severe in Molten Fluoride Salts than Molten Chloride Salts



Graphite capsules, 500 h, 850˚C

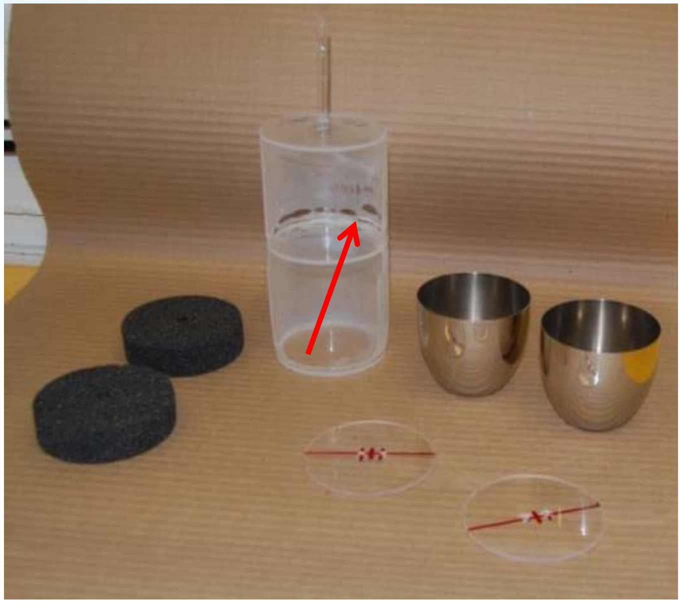


FLiNaK exposed sample cross-section Cr EDS x-ray map

$MgCl_2$-KCl exposed sample cross section Cr EDS x-ray map

- Grain boundary attack was less severe in $MgCl_2$-KCl contacted 800H in that the depth of voiding is less than compared to FLiNaK exposed samples
- Further investigation is needed to determine whether the lower weight-loss of the 800H in the $MgCl_2$-KCl was from a lower chemical potential, lower chromium solubility, or its lack of supporting a Cr-C reaction

Task 1.1:Measure Corrosion Properties in Static and Isothermal Systems

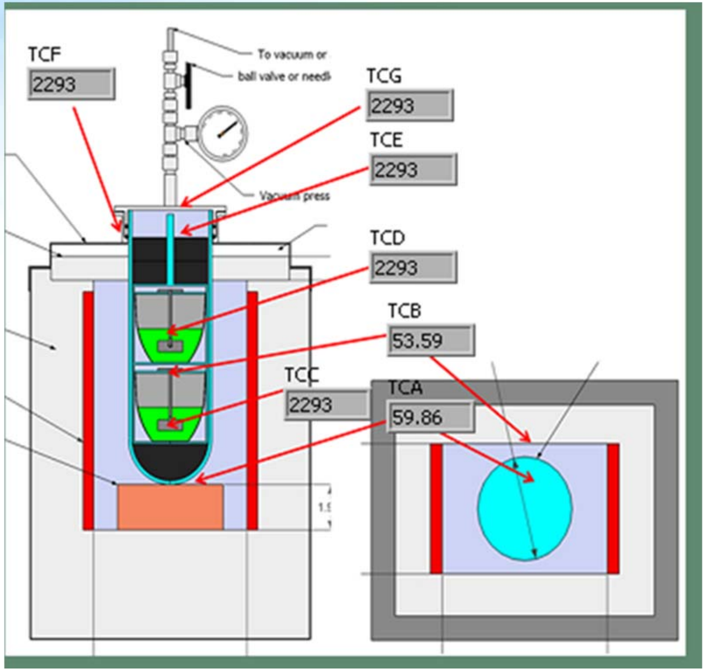


Corrosion samples will hang from quartz lids with Ni wire

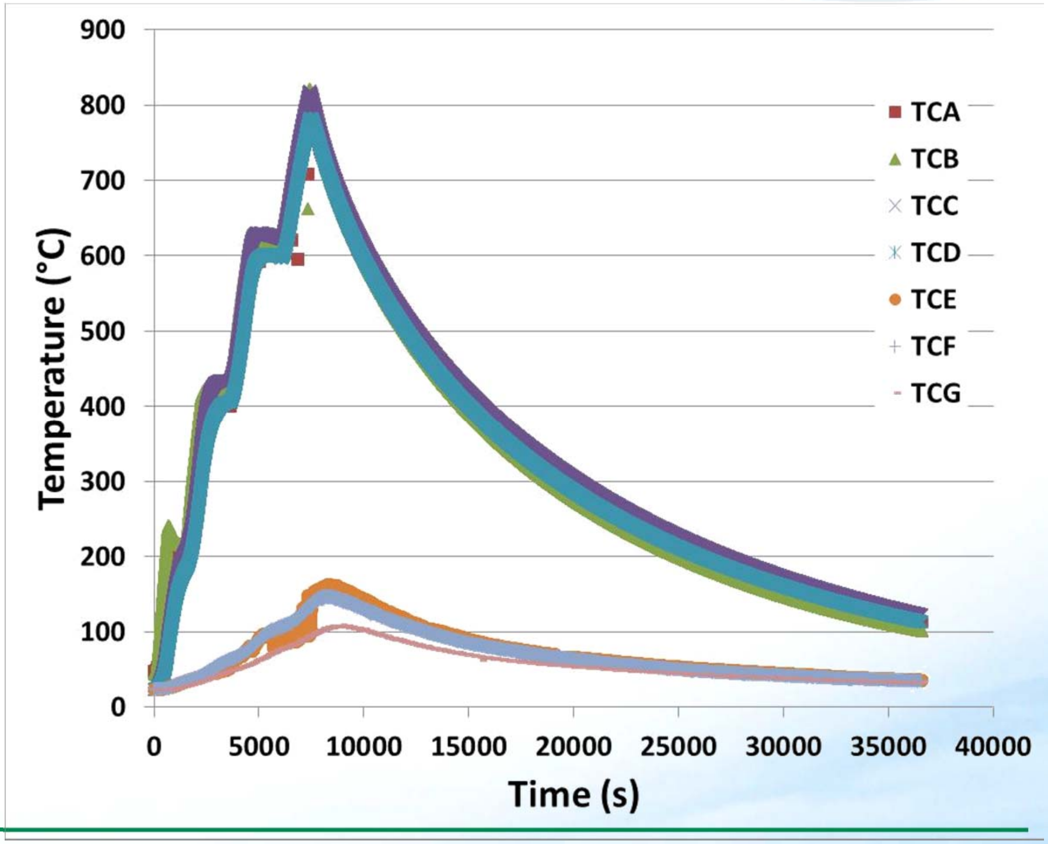
Corrosion test #1

Corrosion test #2

Reactor Thermal Profiling



- Reactor has uniform temperature inside
- Reactor is cool on the outside
- Radiation shielding may be necessary to achieve optimal temperature uniformity between cells



- Thermal profiling ensures uniform heating and adequate temperature control

Thermodynamic Modeling

Calculations were performed based on the method of Gibbs energy minimization under the condition of mass balance:

$$G = \sum_{gas} n_i (g_i^o + RT\ln P_i) + \sum_{\substack{pure\\ condensed\\ phase}} n_i g_i^o + \sum_{solution-1} n_i (g_i^o + RT\ln X_i + RT\ln\gamma_i)$$

$$+ \sum_{solution-2} n_i (g_i^o + RT\ln X_i + RT\ln\gamma_i) + \ldots$$

Where G - total Gibbs energy of the system; g_i^o - standard molar Gibbs energy of species i at T and P; n_i - number of mole of species i; P_i - partial pressure of species i=$(n_i/n_t)P_{total}$; X_i - mole fraction of species i; and ,γ_ι - activity coefficient of species i. We will find n_i which minimize G subject to mass balance constraints.

N.A. Gokcen and R.G. Reddy, Thermodynamics, Plenum Press, 1996

Predicting stable corrosion products

Molten Salt System: Incoloy-800H in the LiF-NaF-KF molten salt with air

- The most stable corrosion product phases were calculated based on the change of Gibbs Energy of various possible reactions in the corrosion process
- All the possible corrosion products have been considered in the thermodynamic calculations

As shown in Fig.1, when in contact with air, the Cr_2O_3 and Cr_2FeO_4 will be the most stable corrosion product with small amount of $LiCrO_2$, $KCrO_2$, K_3AlF_6 and FeO. Other oxides such as $LiAlO_2$, $LiFeO_2$ and Fe_3O_4 are negligible.

Phases	Corrosion Products (mol%)				Corrosion Products (moles)			
	700	800	900	1000	700	800	900	1000
Cr2O3	65.61	63.50	58.98	53.64	8.53E-02	8.31E-02	7.84E-02	7.27E-02
Cr2FeO4	16.52	17.12	18.83	20.86	2.15E-02	2.22E-02	2.45E-02	2.71E-02
KCrO2	5.24	6.30	8.45	11.20	6.80E-03	8.18E-03	1.10E-02	1.45E-02
K3AlF6	8.46	8.45	8.40	7.98	1.10E-02	1.10E-02	1.09E-02	1.04E-02
LiCrO2	4.08	4.65	5.79	7.28	5.29E-03	6.04E-03	7.51E-03	9.45E-03
FeO	0.14	0.28	0.55	1.04	1.84E-04	3.63E-04	7.15E-04	1.35E-03

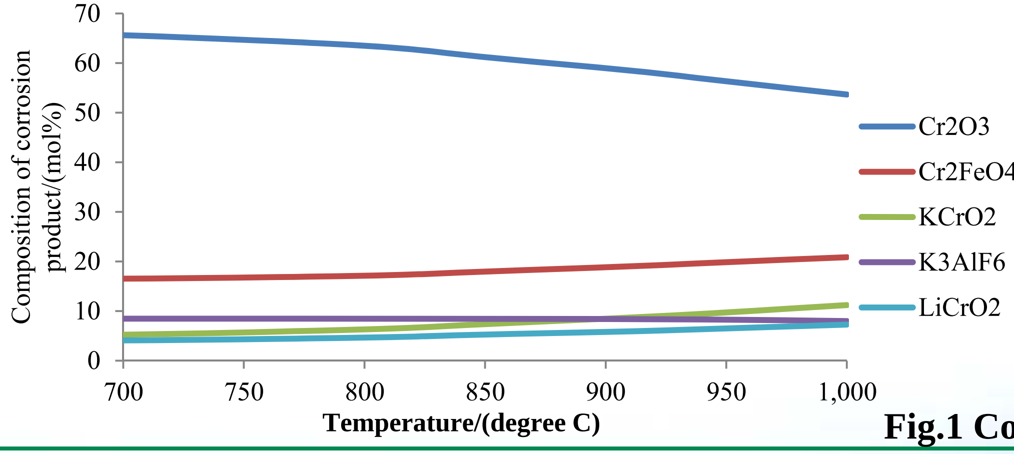


Fig.1 Corrosion Products formed with air

Predicting stable corrosion products

Model system: Incoloy-800H in the LiF-NaF-KF molten salt with N2 or Ar

- The most stable corrosion product phases were calculated based on the change of Gibbs Energy of various possible reactions in the corrosion process
- All the possible corrosion products have been considered in the thermodynamic calculations

As shown in Fig.2, when in contact with N_2 or Ar gas, the corrosion effect will be minimized. K_3AlF_6 will be most stable corrosion product.

Phases	Corrosion Products (moles)				Corrosion Products (mol%)			
	700	800	900	1000	700	800	900	1000
K3AlF6(N2)	5.91E-05	2.71E-04	9.28E-04	2.27E-03	100%	100%	100%	100%
K3AlF7(Ar)	1.16E-03	2.86E-03	5.39E-03	7.31E-03	100%	100%	100%	100%

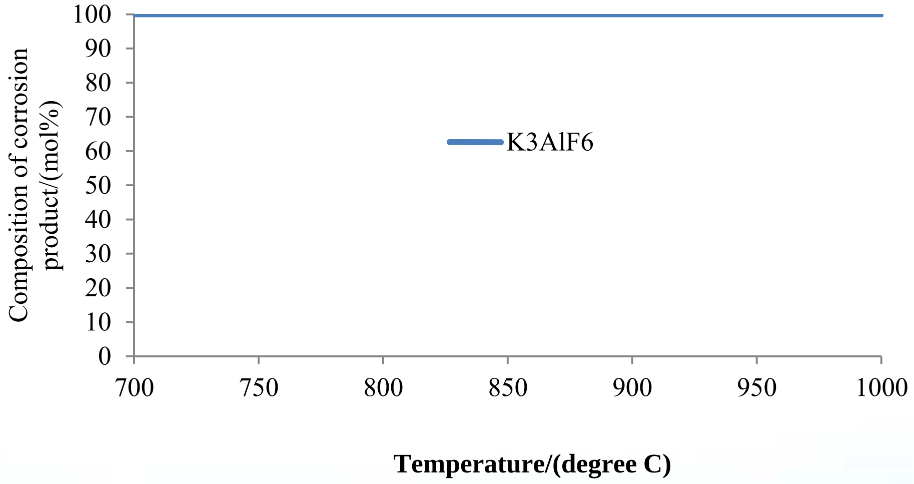
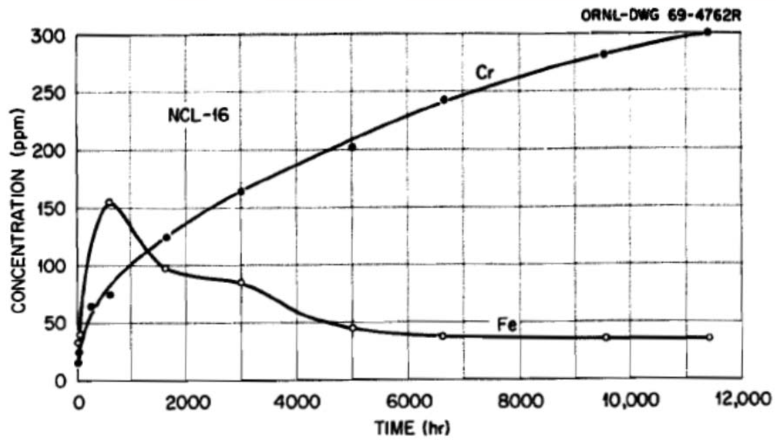


Fig.2 Corrosion Products formed with N2 or Ar gas

Corrosion Models (0-D and 1-D foundations of CFD)

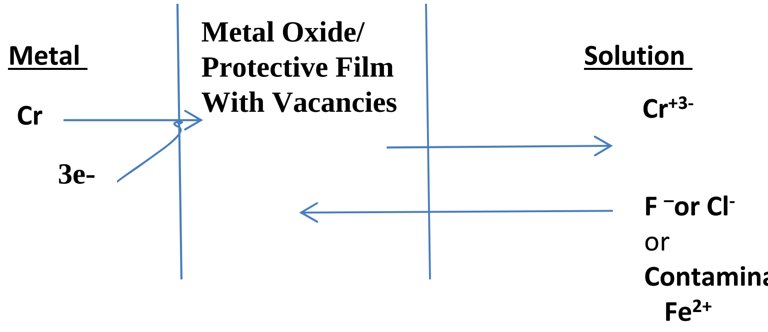
The driving force for corrosion is due to

- Impurities
    - $FeF_2 + Cr \rightarrow CrF_2 + Fe$
- Activity Gradient
    - Activity of all parts in contact with salt must be equal (on microscale as well)
    - Boundary layer governs solution
    - Stability predictions from Thermodynamics models



Reduction of FeF_2 impurities causes Cr to be move from metal to salt. (ORNL-TM-4188)

Applying Point-Defect &Growth/Thinning Oxide Layer Models



Metal

Cr

3e-

Metal Oxide/ Protective Film With Vacancies

Solution

Cr^{+3-}

F^- or Cl^-
or
Contaminants:
Fe^{2+}

Solubility/Complexes

$Cr^{+3} + 3\ Cl^- = CrCl_3$
or
$Cr^{+3} + 3\ F^- = CrF_3$

Important Activity ratios

Cr(II)/C(III)
Fe(II)/Fe(III)
Cr_3C/Fe_3C
Cr(II)/Ni(II)

Kinetics & Mass Transfer Corrosion Models (model interaction of Fluid/Structure/Corrosion with CFD)

- The Boundary Layers, δ, Influence
  - Local Concentrations and Corrosion Chemistry

    Driving forces for impurity, activity & thermal corrosion

    Driving forces for inhibitor concentration
  - Diffusion and Thermal Gradients in
    - Solution and in Metals

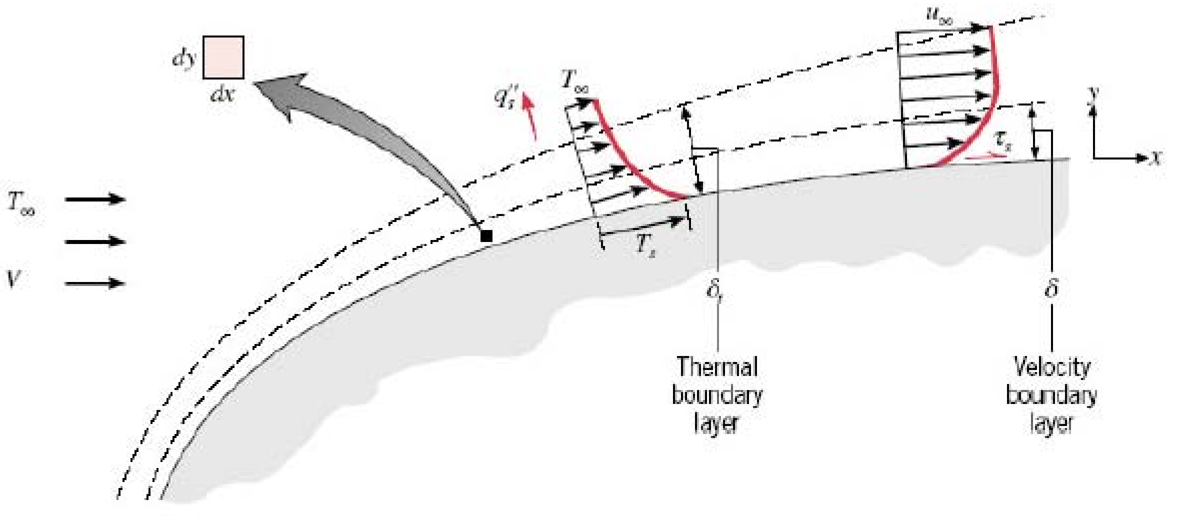
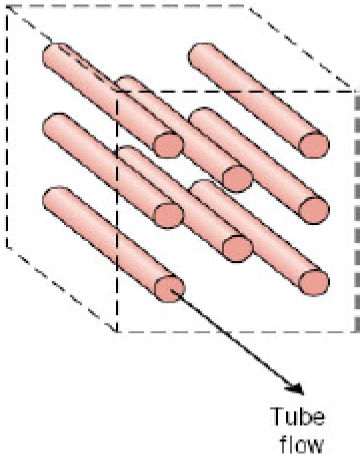


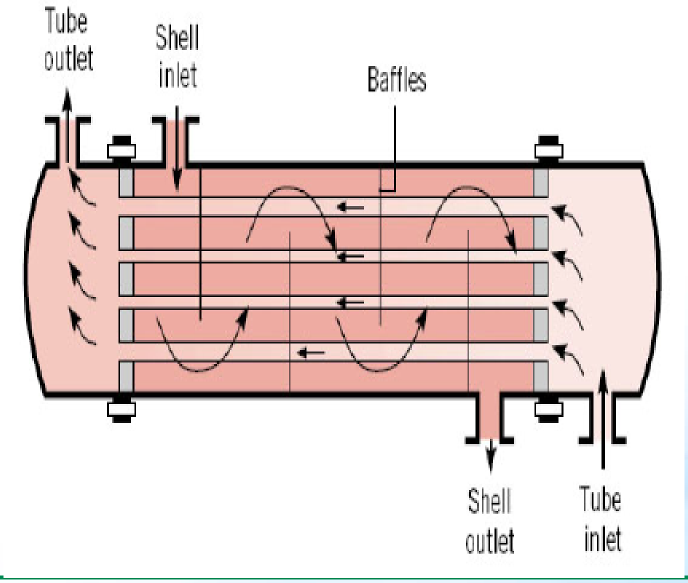
Fig. from Incropera et al., 5th Ed. John Wiley & Sons, Inc., NJ, Chapter 8, 2007.

Kinetics & Mass Transfer Corrosion Models
(the interaction of Fluid/Structure with Corrosion)

Geometry affects δ

- CSP Designs use Tanks (TES) and Tubes (HX)
- Tubes have well defined velocities and hence δ
- Tanks have both <u>Stagnant</u> and <u>Growing</u> δ
- model studies will consider multiple geometries



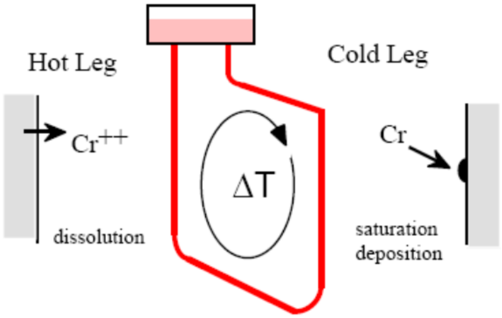


Figures from Incropera et al., 5th Ed. John Wiley & Sons, Inc., NJ, Chapter 11, 2007.

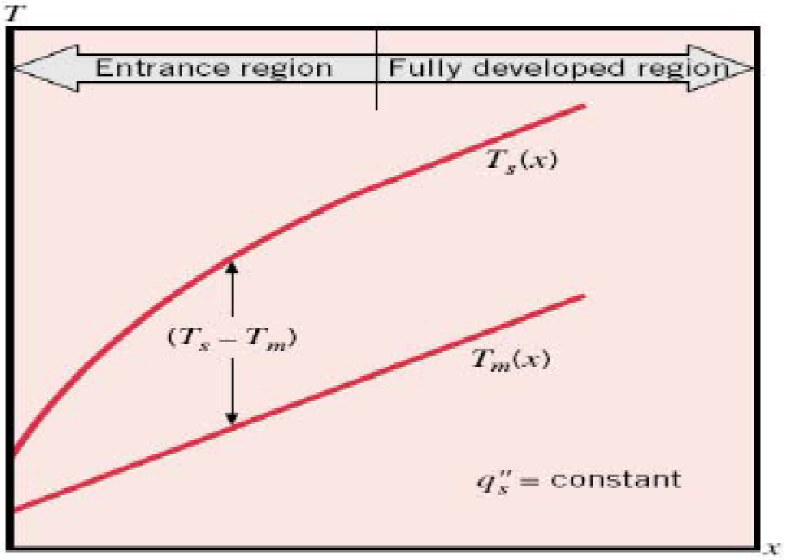
Corrosion Mechanisms/Models: Temperature Gradients

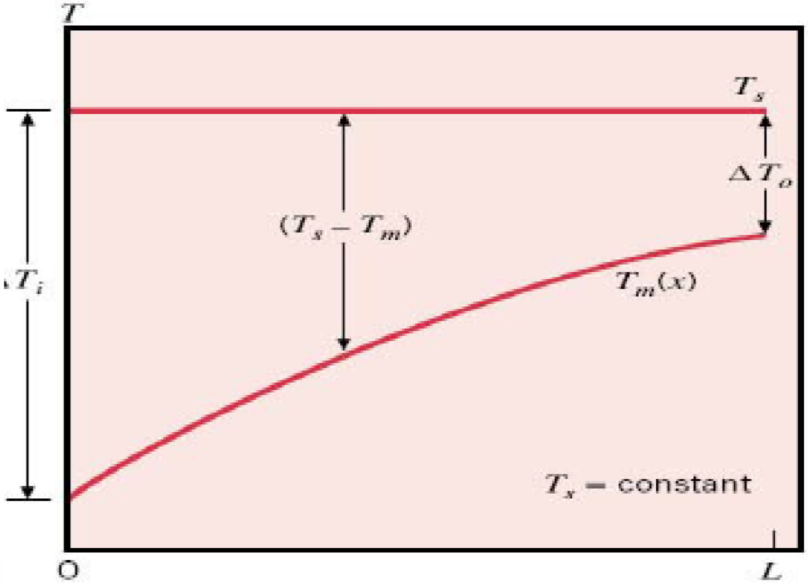
The driving force for corrosion is due to
Hot zone depletion – Cold zone deposit

Two locations for temperature gradients:
Solar flux tubes: constant flux
HTF temp, T_m (x), increases
Tube surface, T_s (x), increases



Heat Exchanger (HX):
HTF temp (T_s) constant for large mC_p
Steam temp (T_m) increases





Temperature profiles from Incropera et al., 5th Ed. John Wiley & Sons, Inc., NJ, Chapter 8, 2007.

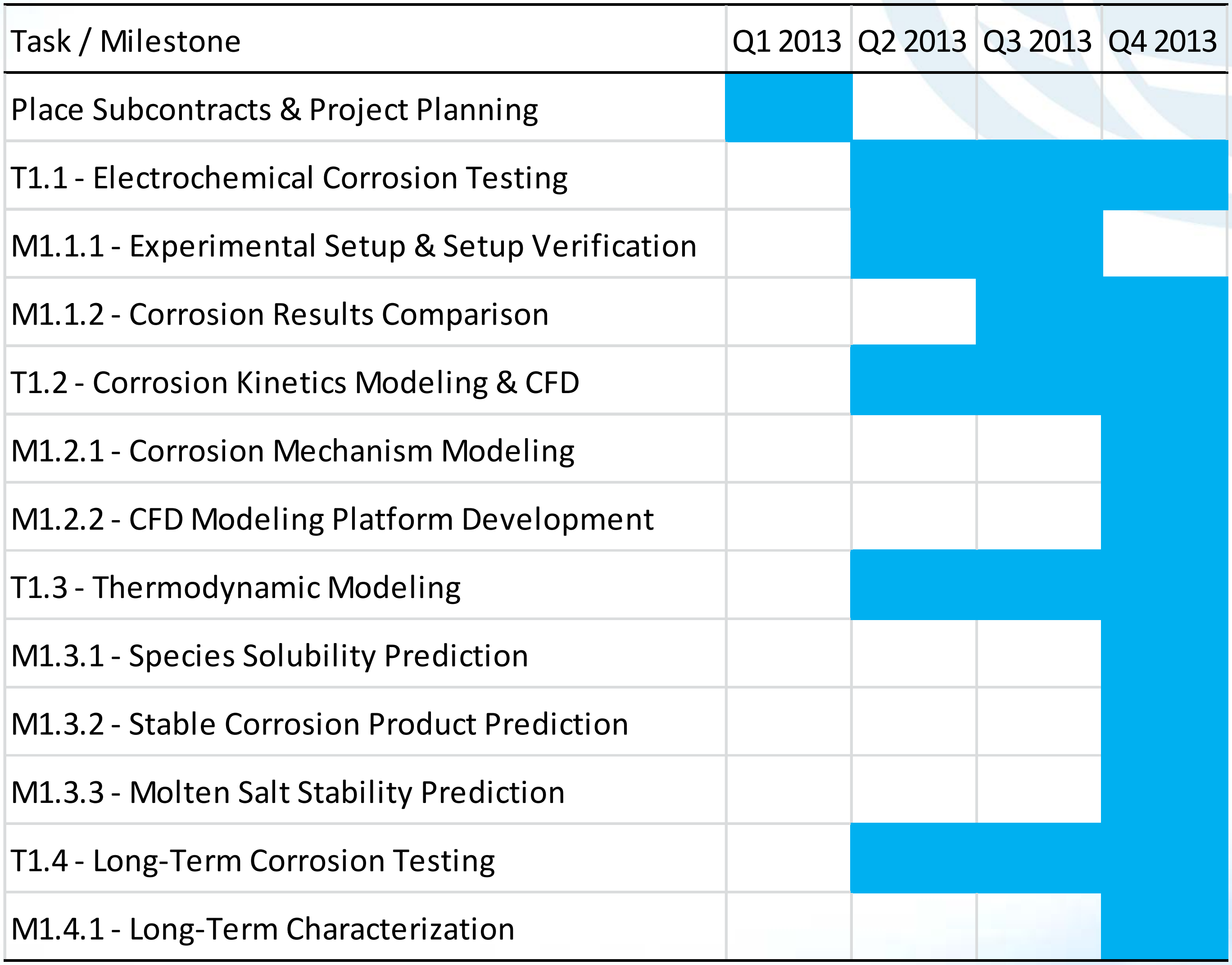
Summary: Fluid/Electrochemistry/Corrosion Models

- Methodology
  - Choose a geometry for the fluid side
  - Solve for local velocity and temperature profiles
  - For thermodynamically predicted species
    - Include transport of redox and solubility chemistry
      e.g. Cr(II)/Cr(III) and Fe(II)/Fe(III))
  - Include temperature gradients/profile
  - Include transport through oxide layer
  - Solver for potential drop in solution
  - Include rate kinetics (e.g. Tafel or mixed potential)
  - Calculate current density
  - Convert current density to weight loss or film thickness
- <u>Complexity of Corrosion Models with Computational Fluid Dynamics (CFD) will be used for the most complex models</u>

Future Work

- Characterize corrosion in FLiNaK and KCl-$MgCl_2$
- Identify novel materials and salts that enable long service life based on mechanisms
  - Advanced Ni-Fe-Cr Alloys
  - Refractory Alloys & Composites
  - High fluoribasicity salts to reduce corrosion
- Thermodynamic modeling of corrosion products, alloys, salts
- 0-D, 1-D and multidimensional CFD electrochemical modeling of CSP system utilizing alloy/salt combinations
- Investigate corrosion inhibitors and cathodic protection

Project Plan



Task / Milestone	Q1 2013	Q2 2013	Q3 2013	Q4 2013
Place Subcontracts & Project Planning	■			
T1.1 - Electrochemical Corrosion Testing		■	■	■
M1.1.1 - Experimental Setup & Setup Verification		■	■	
M1.1.2 - Corrosion Results Comparison			■	■
T1.2 - Corrosion Kinetics Modeling & CFD		■	■	■
M1.2.1 - Corrosion Mechanism Modeling				■
M1.2.2 - CFD Modeling Platform Development				■
T1.3 - Thermodynamic Modeling		■	■	■
M1.3.1 - Species Solubility Prediction				■
M1.3.2 - Stable Corrosion Product Prediction				■
M1.3.3 - Molten Salt Stability Prediction				■
T1.4 - Long-Term Corrosion Testing		■	■	■
M1.4.1 - Long-Term Characterization				■

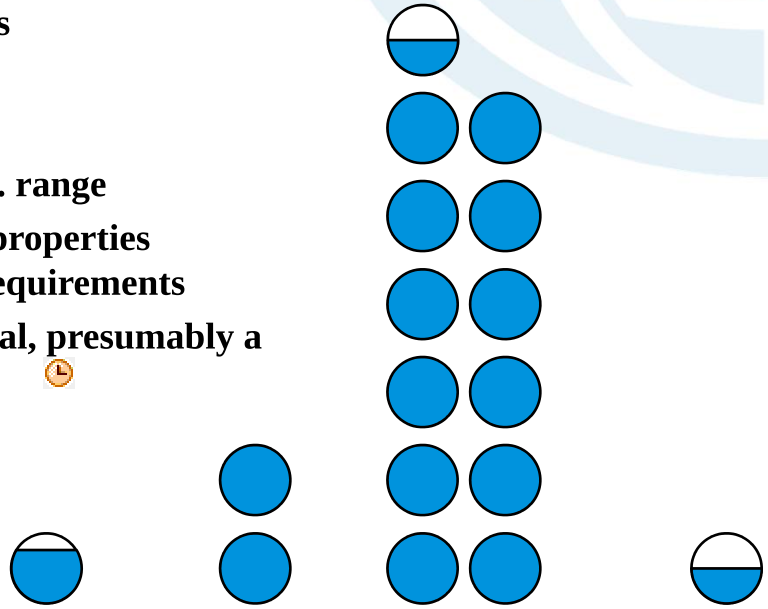
Thank You

QUESTIONS?

Extra Slides

Motivation for Study of Corrosion Inhibition in Molten Salts

- **Coolant properties determine equipment size and costs**
- **Shown is the pipe area needed to transport an equivalent amount of heat of several heat transport fluids**
- **Necessary attributes in working fluids**
  - **Thermally stable**
  - **Low vapor pressure over working temp. range**
  - **Adequate heat transfer/hydrodynamic properties without excessive recirculation power requirements**
  - **Relatively non corrosive to some material, presumably a metal**
- **Desired attribute**
  - **Cheap**
  - **Easy to handle**



	Water (PWR)	Sodium (LMR)	Helium	Molten Salt
Pressure (MPa)	**15.5**	**0.69**	**7.07**	**0.69**
Outlet Temp (°C)	**320**	**540**	**1000**	**1000**
Coolant Velocity (m/s)	**6**	**6**	**75**	**6**

Slide Source: Charles W. Forsberg, (June 7, 2006) High-Temperature Reactors for In Situ Recovery of Oil from Oil Shale, Presentation for ICAPP'06; Paper 6104

Salt Selection

- Nitrates, sulfates, carbonates (oxygen containing salts) [1]:
  - Lack high temperature thermal stability
    - e.g. Nitrates decompose into nitrites with usable temperature range of <95 - 600 C [2, 3]
  - Carbonates decompose into oxides (calcination)
  - Release oxygen during decomposition → can rely on mature oxide passivation layer paradigm
- Fluorides, chlorides, alkali fluoroborates:
  - Chemical stability above 800 C, melt below 525 C and not volatile, compatible with high temp alloys and ceramics [1]
  - Appear to have suitable traits, but corrosion mitigation via oxide passivation layers likely not possible

---

[1]: Williams, D., Assessment of Candidate Molten Salt Coolants for the NGNP/NHI Heat-Transfer Loop, ORNL/TM-2006/69.
[2]: Bradshaw et al., Patent No.: US 7,588,694 Bl
[3]: Bradshaw et al., High-temperature stability of ternary nitrate molten salts for solar thermal energy systems, Solar Energy Materials 21 (1990) 51-60.

Salt Selection

- Fluorides, chlorides, alkali fluoroborates:
  - Melting point is most important physical property
  - Melting point <400 C for use with steam Rankine power cycles, above for use with other power cycles such as supercritical CO_2 or Brayton
  - Single components → too high of melting point → multicomponenet mixture needed
    - Most binary systems of interest have been measured as have many ternary systems
    - Primary lowering of freezing point (as much 500 C) comes from first salt addition to pure component. Further additions are lower order (~50 C reduction in T_M) [1]
- Due to higher vapor pressures of fluoroborates, and boiling points near 1000C, initial focus will be on fluorides and chlorides

---

[1]: Williams, D., Assessment of Candidate Molten Salt Coolants for the NGNP/NHI Heat-Transfer Loop, ORNL/TM-2006/69.

Materials Investigated for Molten Salt Compatibility

Alloy	Cr	Mo	W	Al	Ti	Fe	C	Co	Ni	Mn	Zr	Si	Nb
Ni-201*					**.02**	**.05**	**.02**	**.02**	**99.4**	**.19**			
Incoloy-800H*	**20.4**			**0.5**	**0.6**	**42.3**	**.07**		**31.6**	**0.8**			
Hastelloy-N*	**6.31**	**16.1**	**0.06**	**<.01**	**<.01**	**4.03**	**.03**	**.15**	**72.2**	**0.53**	**<.01**		
Haynes-230*	**22.5**	**1.2**	**14.1**	**0.3**		**1.8**	**0.1**	**0.3**	**59**	**0.5**			
Haynes-NS-163*	**28**			**0.5**	**1.3**	**21**	**0.1**	**40**	**8**	**0.5**		**0.5**	**1**
TZM*		**99.37**			**0.5**		**0.03**				**0.1**		
Mo-30W*		**70**	**30**										
SiC/SiC Composites													

***New heat compositions need to be input, these compositions are from previous work**

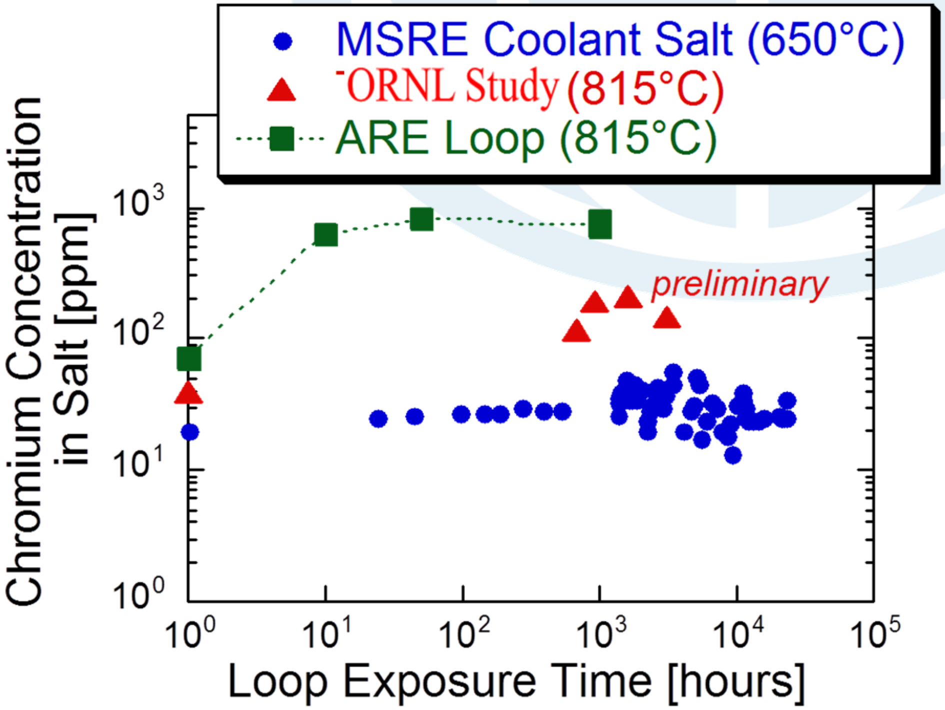
- Mostly code-certified alloys selected
- Compositions in wt.%

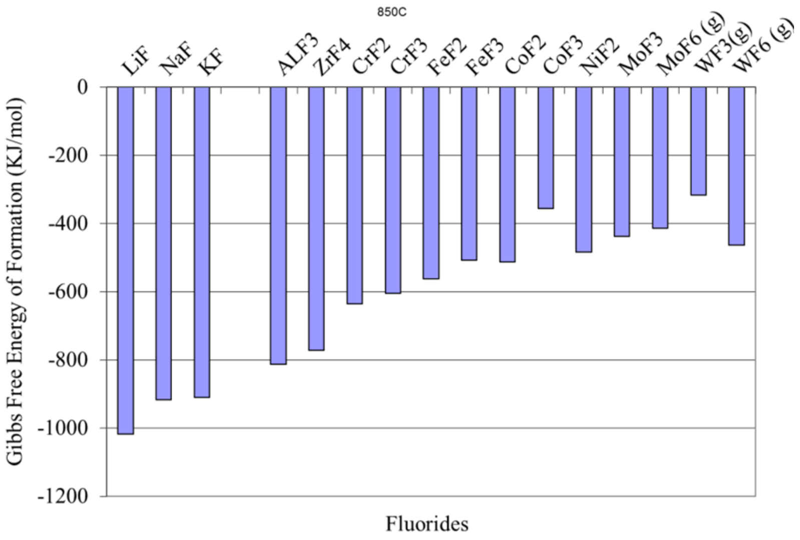
Material Selection: Chemical/Morphology Considerations

- SiC oxidation and dissolution resistant
  - SiC/SiC composite (physical properties such as thermal expansion and UTS can be tailored to needs by adjusting fiber orientation, thickness, weave, etc…)
  - May react with some corrosion inhibitors
- Ni, Mo, W very dissolution resistant
  - Ni-201, TZM, Mo-30W
  - Refractories very susceptible to oxidation, some are easily embrittled
  - May react with corrosion inhibitors, different class of alloy compared to Fe-Ni-Cr base
- Fe-Ni-Cr and Ni-Mo-Cr alloys
  - Incolloy-800H, Hastelloy-N, Haynes-230
  - Commercially available now with long history of use
  - Cr very prone to dissolution, Fe less so but still, Ni immune
    - Ni-201<Hastelloy-N<Haynes-230
  - Higher C contents correlated to higher corrosion rates, hypothesized to be due to different connectedness of grain boundary carbides
    - <<<C → unconnected carbide network → little intergranualr corrosion
    - <<C → connected spider web like network → Spider web like voiding seen from alloy surface into alloy
    - <C → carbide film around grains → Complete intergranular voiding from surface into alloy

Corrosion Mechanisms Chlorides

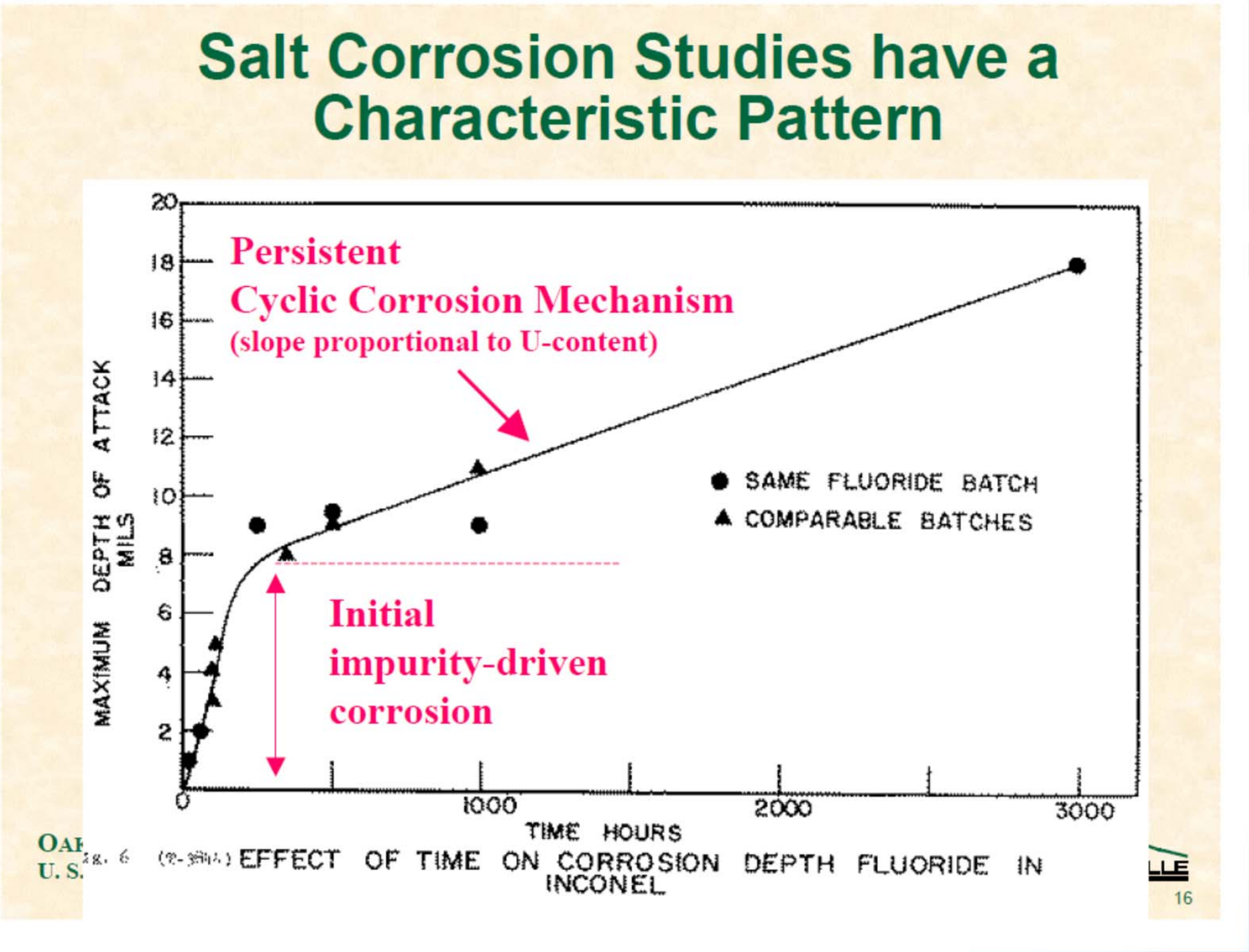
- Gibbs free energy of formation of alloy and salt components can predict non corrosion prone alloy components and alloy incompatibility.





Sources: [1] D. Wilson, Corrosion Issues In Molten Fluoride Salts, 2006 ANS Annual Meeting Reno, Nevada, June 8, 2006

Corrosion Mechanisms



Salt Corrosion Studies have a Characteristic Pattern

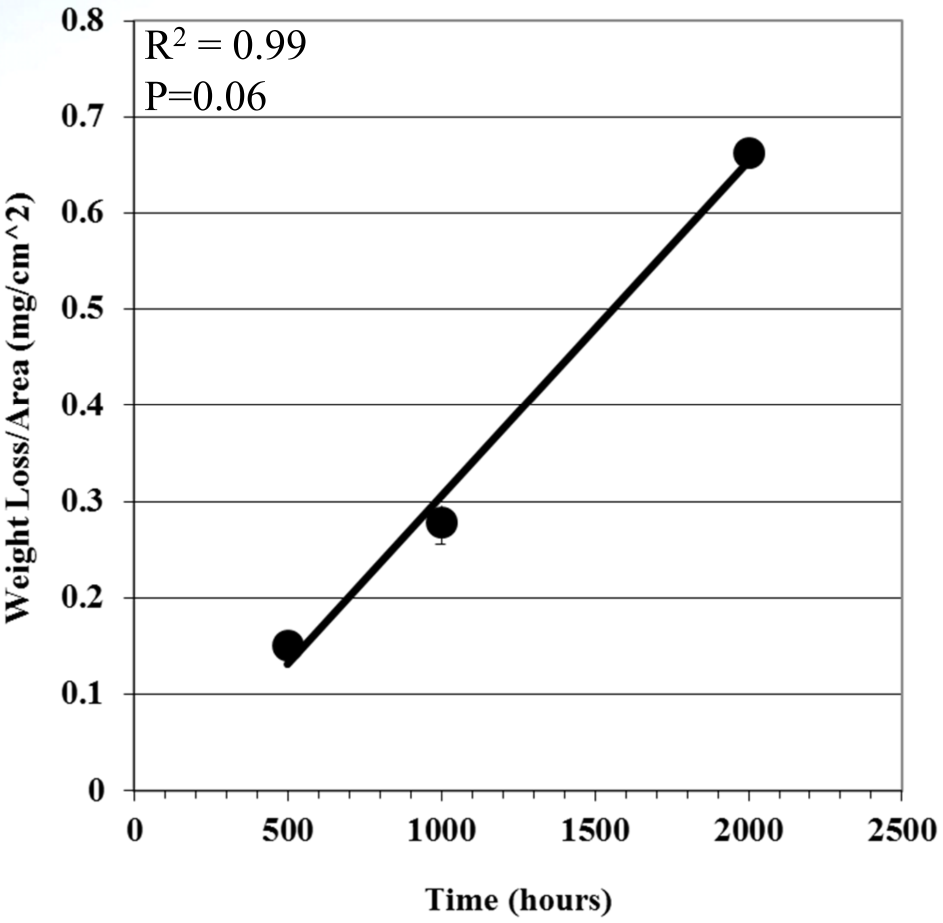
ig. 6 [illegible] EFFECT OF TIME ON CORROSION DEPTH FLUORIDE IN INCONEL

Slide copied from: Williams, D., Molten Fluorides as High Temperature Coolants for Nuclear Reactors, January 21, 2003 Nuclear Engineering Design, University of Tennessee , Knoxville 308 Pasqua Hall.

Alloy Selection:
Chemical Considerations

- Time/budget permitting, other alloys that may be investigated that can potentially have different corrosion behavior include
  - Alumina forming Fe-Ni-Cr alloys
    - Haynes HR-224
  - Higher temperature fluoride compatibility
    - Haynes-242
  - Precipitation hardened alloys
    - Haynes-282
  - Nitride precipitation hardened Co-base alloys
    - Haynes-NS-163

Influence of Corrosion Container Materials



All capsules were tested at 850C. 800H crucibles.

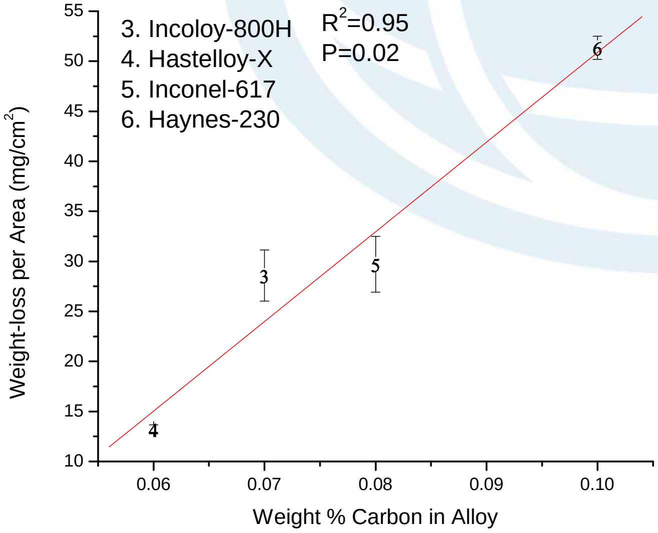
- Cr dissolution less severe in alloy versus graphite crucibles (500 h)
  - Weight-loss/area: ~0.15 versus ~ 29 mg/cm^2
  - Cr in salt: ~100 versus ~370 ppm (as determined by NAA)
- Cr dissolution mechanism similar to the graphite capsules (Cr depletion from grain boundaries)
- The pure alloy weight-loss appears to be approximately linear until at least 2000 hours

---

[1] L. Olson, J. Ambrosek, K. Sridharan, M. Anderson, T. Allen, "Materials corrosion in molten Lif-NaF-KF salt," Journal of Fluorine Chemistry, Vol. 130, No. 1, pp. 67-73, Jan. 2009.

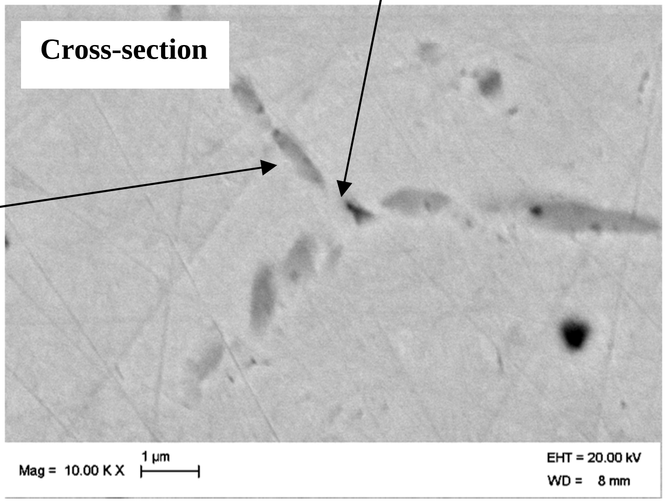
High Cr Alloy Weight-Loss Correlated with C Content

- Weight-loss/area shown to correlate with C content in alloys with ~20% Cr [1]
- Cr is concentrated in carbides in GB leading to GB attack

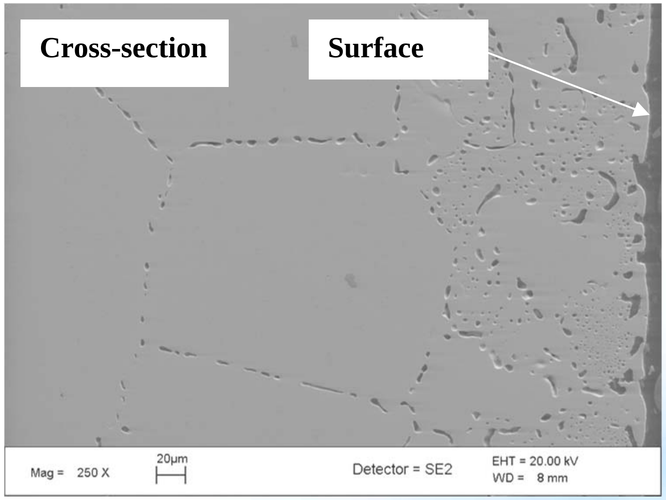


Grain triple point

Cr Carbides



800H 500 h 850C Heat Treatment, no salt exposure



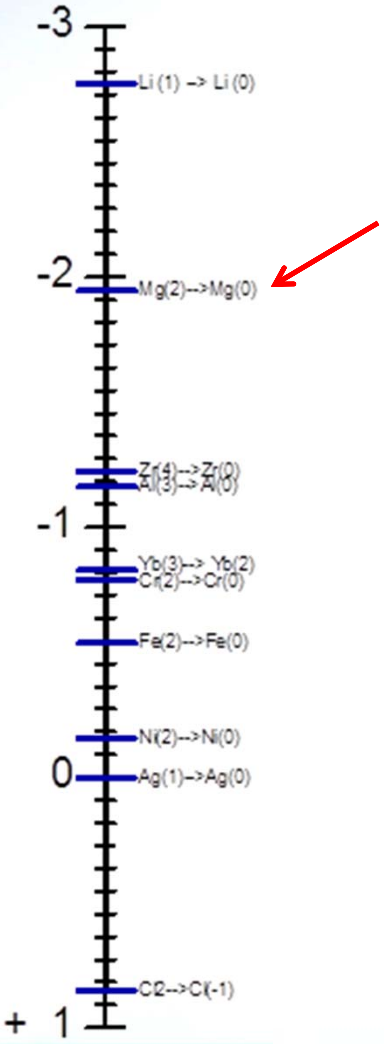
800H 500 h 850C Heat Treatment, FLiNaK exposure

---

[1] "Intergranular Corrosion of High Temperature Alloys in Molten Fluoride Salts", L. Olson, K. Sridharan, M. Anderson, T. Allen, Materials at High Temperatures, vol. 27, No. 2, pp. 145-149, (2010).

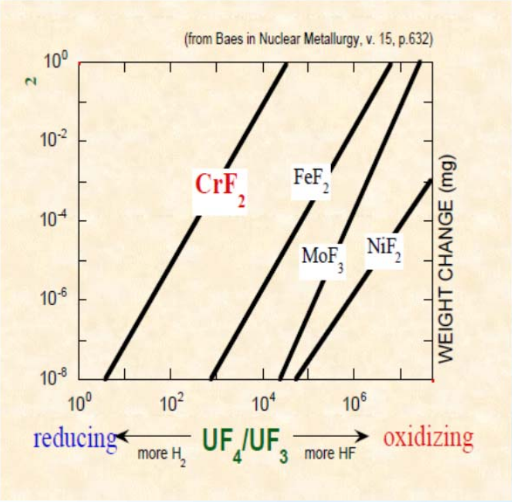
Corrosion Inhibitor Strategies

Reduction potentials of various elements in LiCl-KCl [1, 2, 3]



If Mg metal is added to LiCl-KCl, and the salt reaches a thermodynamic equilibrium with Mg, as long as there is some Mg left in the metallic state, the chemical potential will be fixed at this point, making the reactions below unfavorable. I.E. Cr and other alloys will not dissolve into solution.

- Change acidity/basicity of salt, A.K.A. Redox Control
  - Chemical potential of salt is fixed until addition is exhausted
  - Add a metal to scavenge F^- ions (Zr, Mg)
  - Add Rare earth salts (Tm(III/II), Sm(III/II), Yb(III/II), V(III/II) and Eu(III/II) [1]
- Change chemical activity of material surface
  - Chemically alter surface (nitride/carburize)
  - Plate surface or use bimetallic piping
  - Cathodic protection

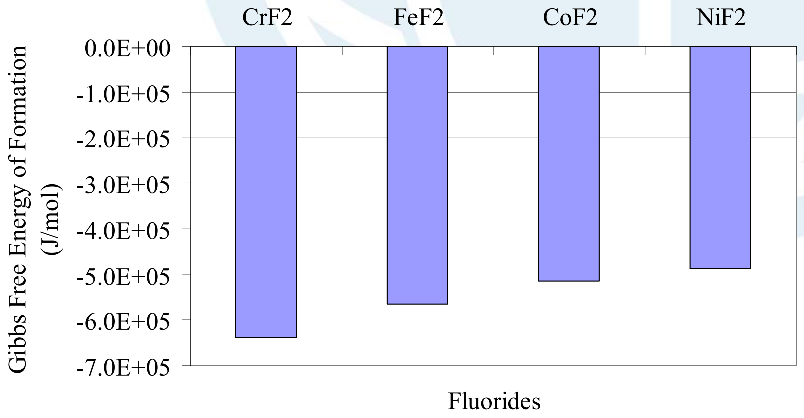

(from Baes in Nuclear Metallurgy, v. 15, p.632)

---

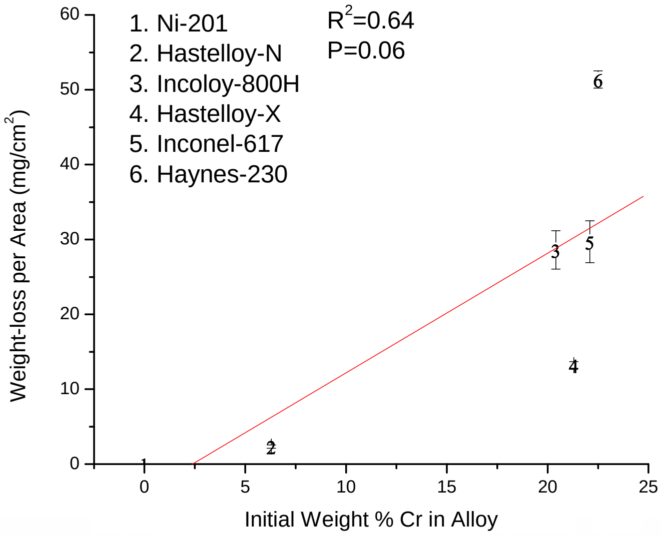
[1] Del Cul, et al., Redox Potential of Novel Electrochemical Buffers Useful for Corrosion Prevention in Molten Fluorides, http://www.ornl.gov/~webworks/cppr/y2001/pres/112728.pdf
[2] J. Plambeck, Electromotive Force Series in Molten Salts, in Journal of Chemical and Engineering Data, Vol. 12, No. 1, January 1967, pg. 77-82.
[3] Williams, D., Molten Fluorides as High Temperature Coolants for Nuclear Reactors, January 21, 2003 Nuclear Engineering Design, University of Tennessee , Knoxville 308 Pasqua Hall.

Correlation Between Cr Content and Alloy Weight-Loss

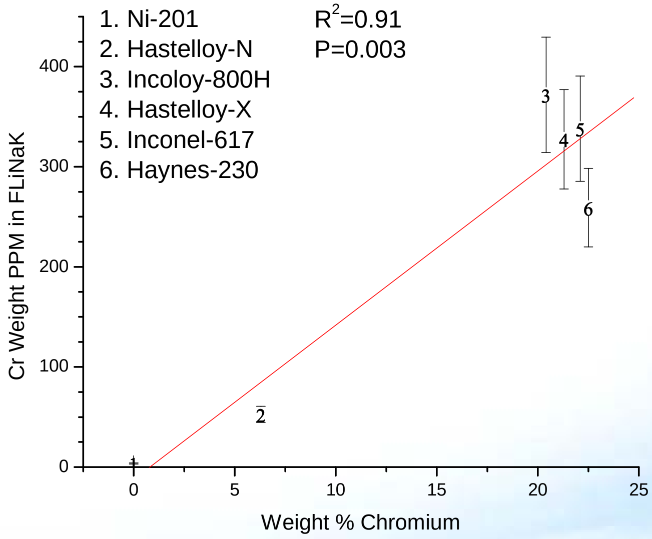
- Most stable fluorides formed by elements in alloy will be selectively attacked
- In Ni-Fe-Cr alloys, Cr is most active
- Weight-loss per area generally correlates with Cr content of alloy [1]
- Cr in salt correlates with Cr content of alloy



Weight-loss/area results



NAA salt analysis results



---

[1] L. Olson, J. Ambrosek, K. Sridharan, M. Anderson, T. Allen, "Materials corrosion in molten Lif-NaF-KF salt," Journal of Fluorine Chemistry, Vol. 130, No. 1, pp. 67-73, Jan. 2009.