An Overview of the Material-Salt Compatibility Program at ORNL

Stephen Raiman

with J. Keiser, N. Gallego, C. Contescu, J. McMurray, A. Willoughby, J. Startt, J. McDuffey, D. Ezell-Bull, S. Sham, and others

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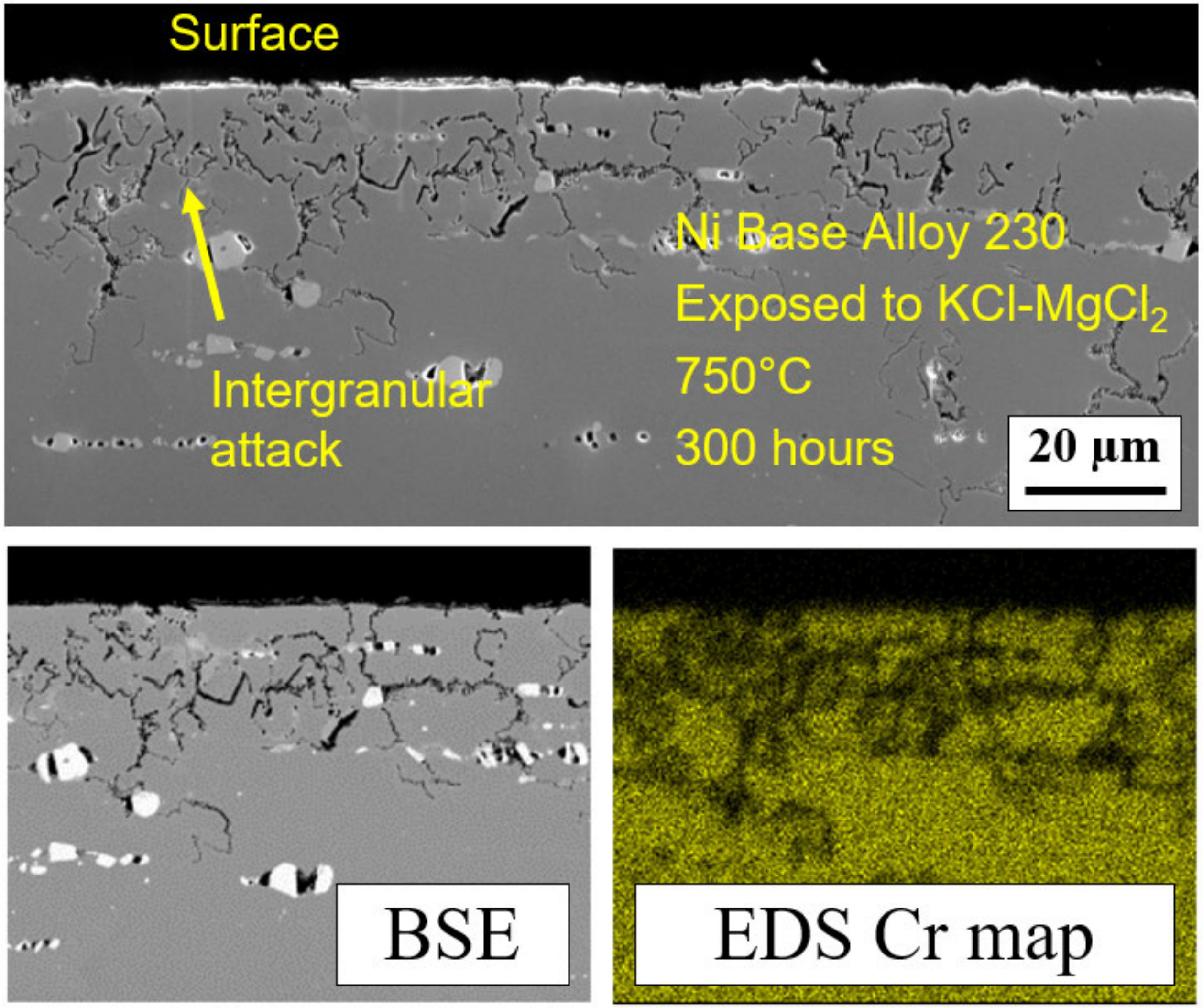
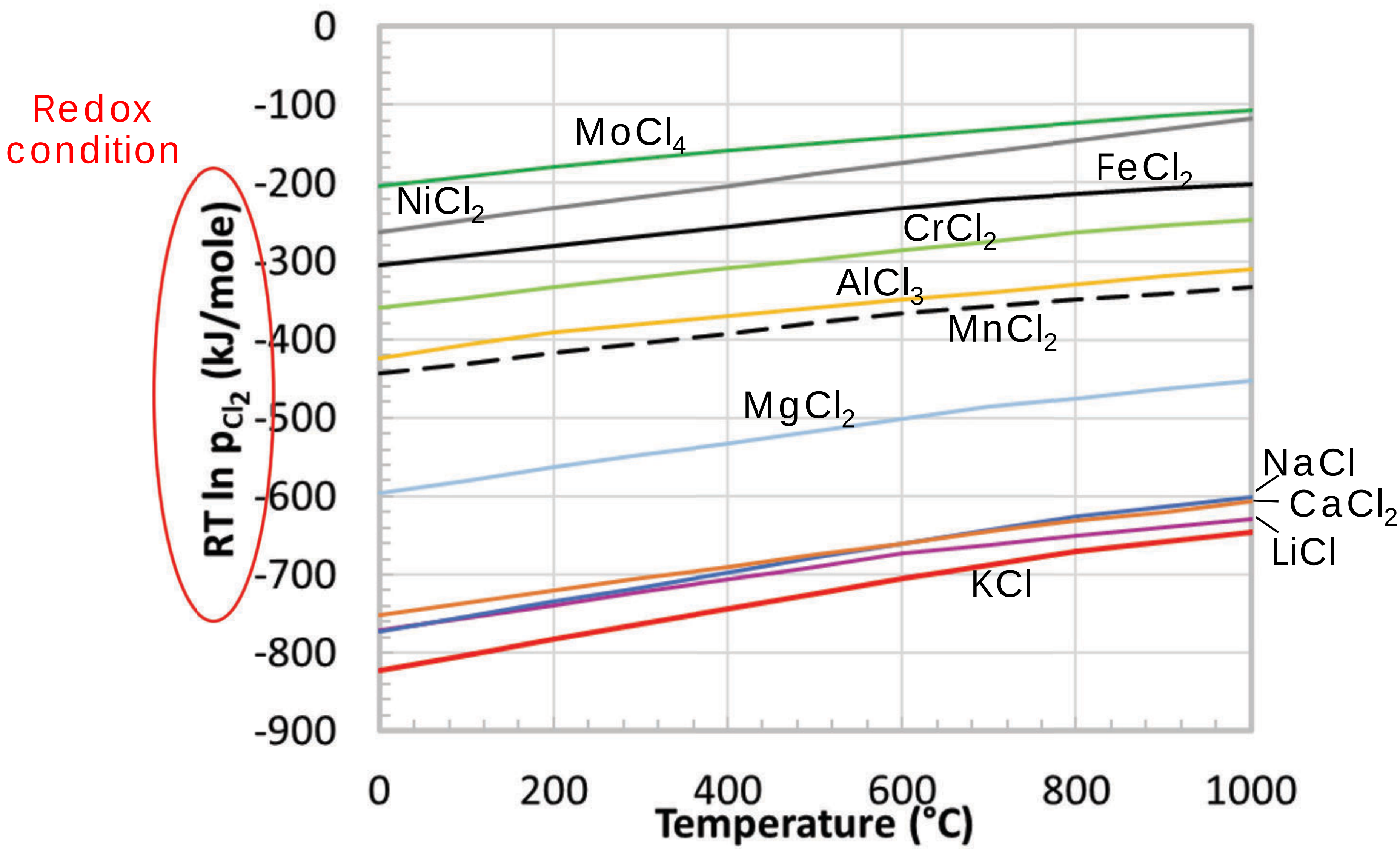
Materials in molten salts degrade by chromium depletion



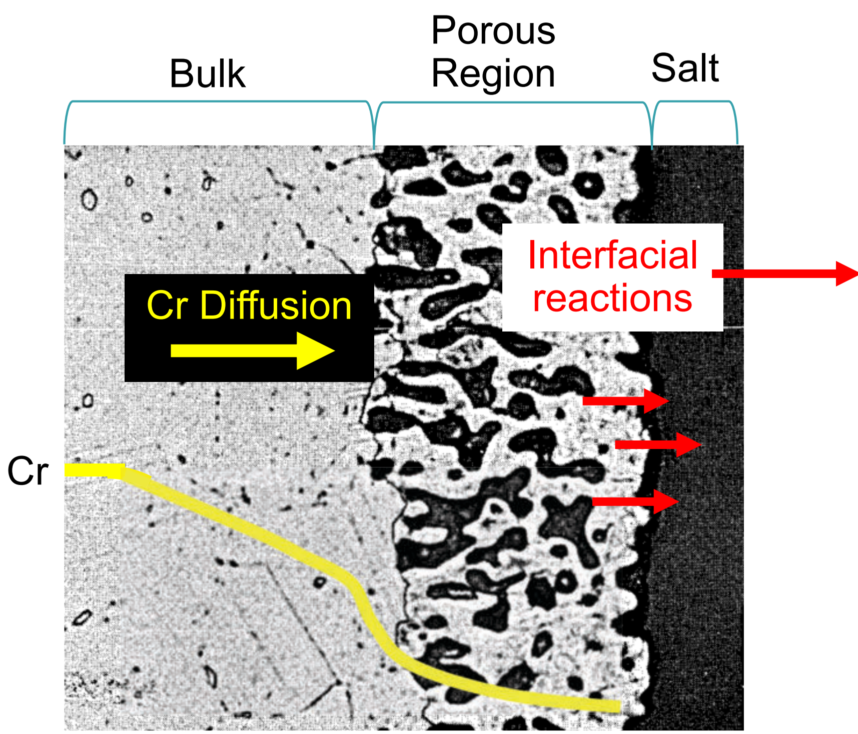
S.S. Raiman (unpublished)

Stability of Metals in Chloride Salts



J.W. McMurray (unpublished)

Chromium reacts at salt-metal interface, diffuses outward from bulk, and leaves porous layer



- Salt impurities react with structural alloys

$$2HF(d) + Cr(s) \rightarrow CrF_2(d) + H_2(d)$$

- Metallic halides

$$Cr(s) + FeF_2(d) \rightarrow CrF_2(d) + Fe(s)$$

- Fuel

$$Cr(s) + 2UF_4(d) \rightarrow CrF_2(d) + 2UF_3(d)$$

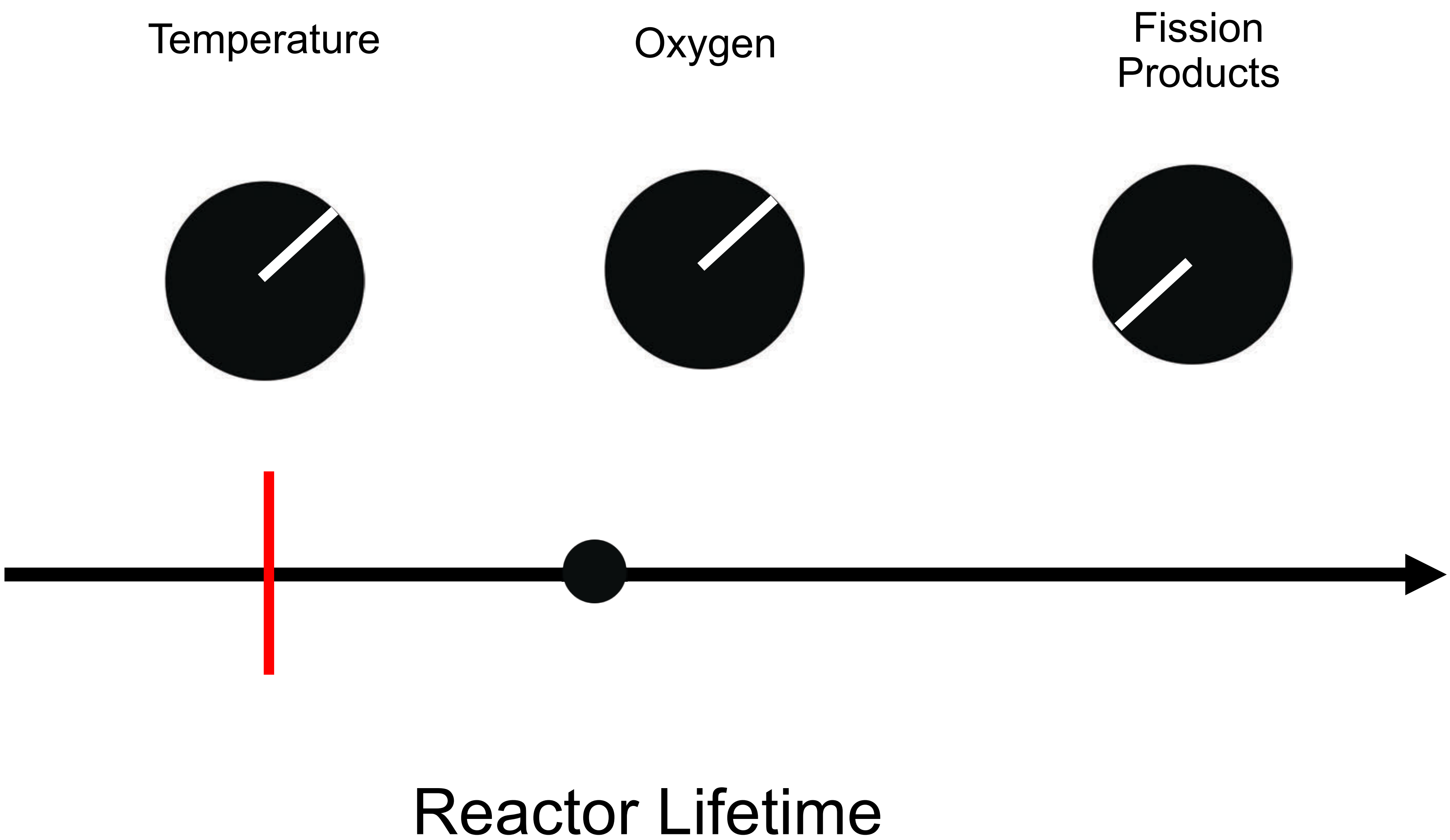
Similar reactions in Cl salt, just replace F with Cl

Our objective is to understand degradation of structural alloys in molten salts

Enabling…

- Optimized chemistry-material choices
- Accurate models of in-reactor behavior
- Development of advanced materials

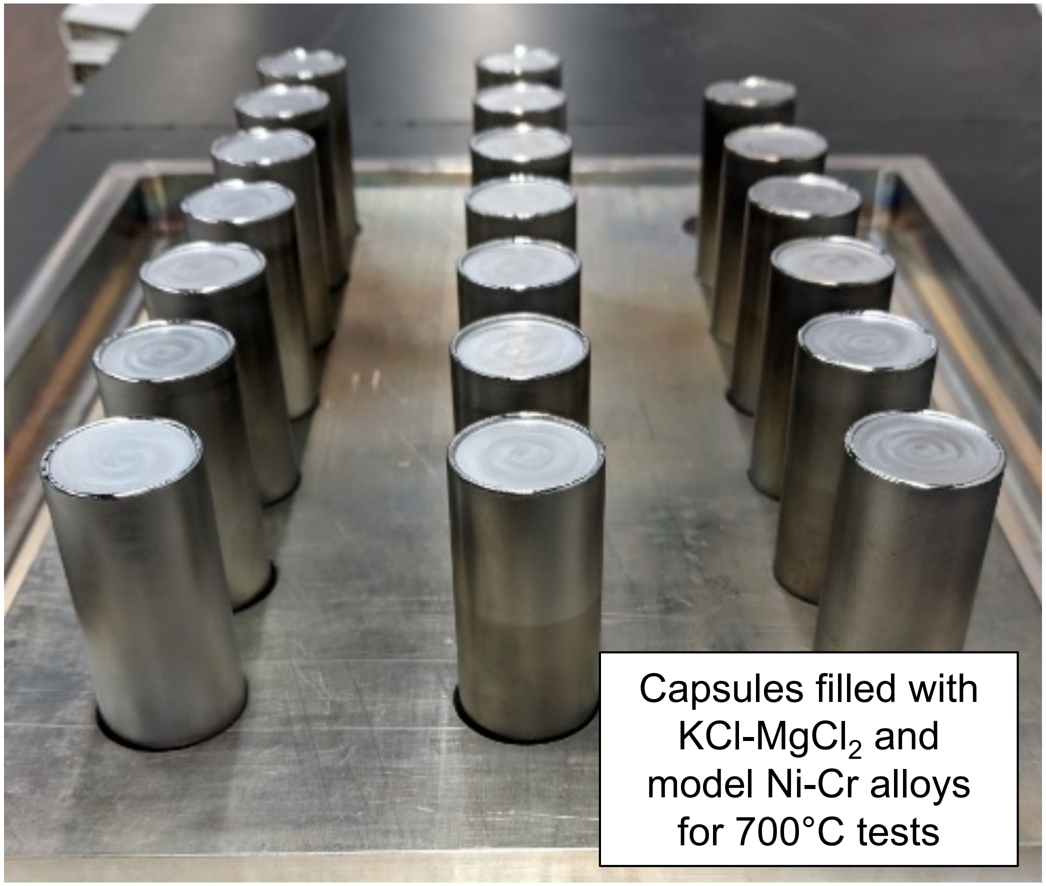
"Calibrating" how salt chemistry affects the lifetime of salt-facing components



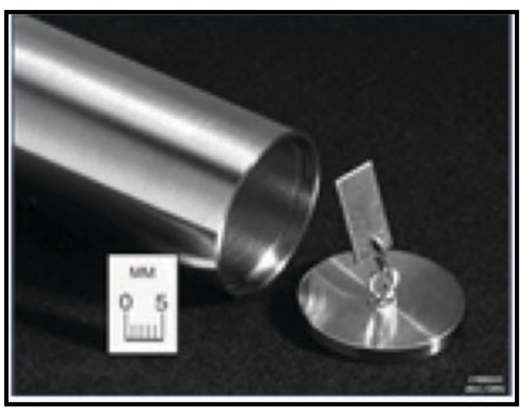
Outline

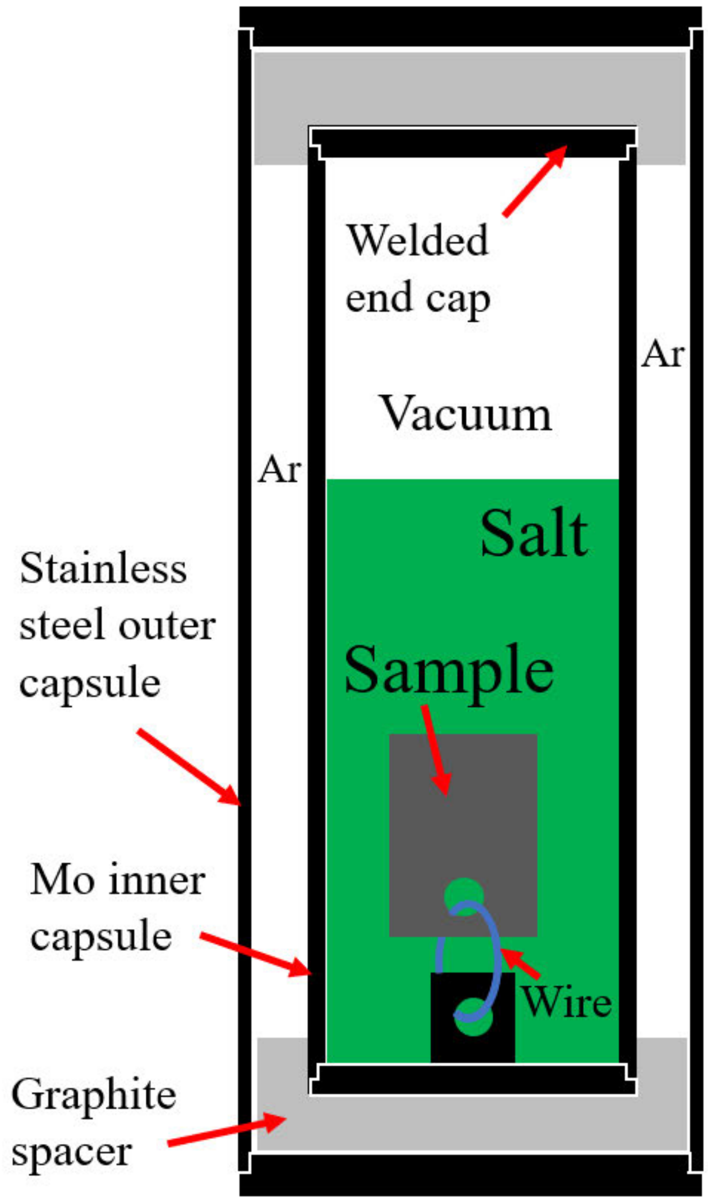
- Corrosion testing methods
- Advanced material development
- Graphite and SiC compatibility
- Modeling
- Irradiation accelerated corrosion
- Infrastructure development and future plans

Capsule testing



Capsules filled with $KCl-MgCl_2$ and model Ni-Cr alloys for 700°C tests





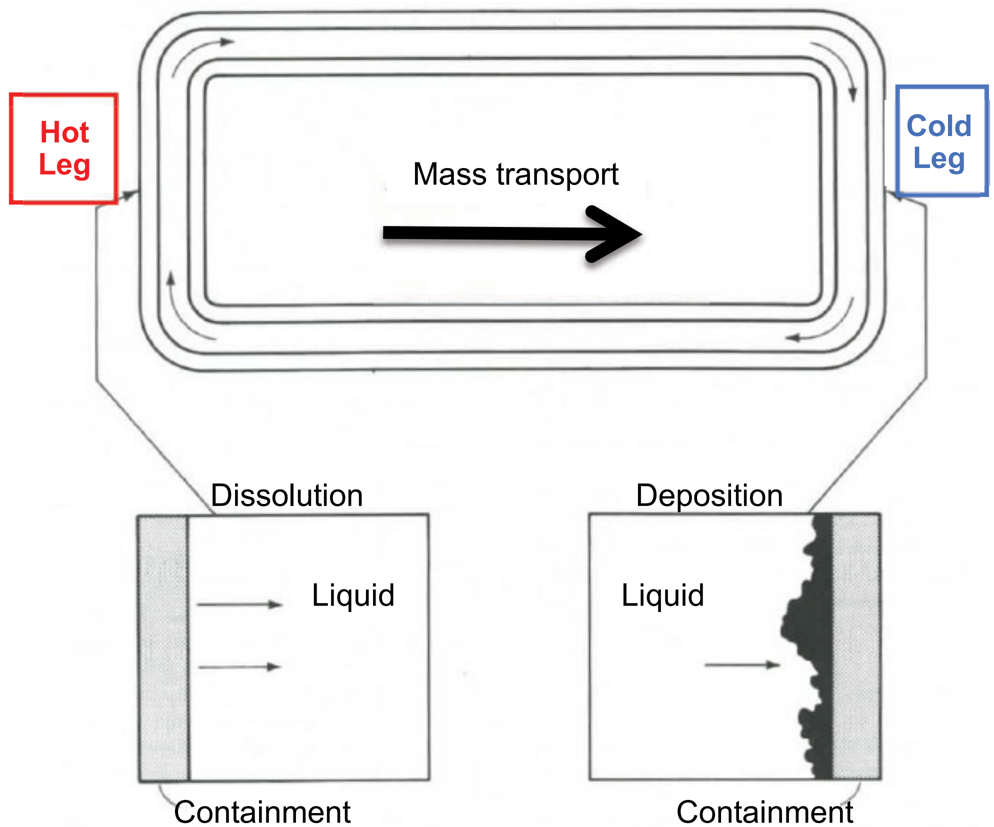
Flowing salt with a thermal gradient is required to accurately reproduce MSR conditions

- Temperature-dependent equilibrium constants drive mass transfer

$$Cr + 2F^{-} \leftrightarrow CrF_2$$

Hot leg: reaction moves to right (dealloying)

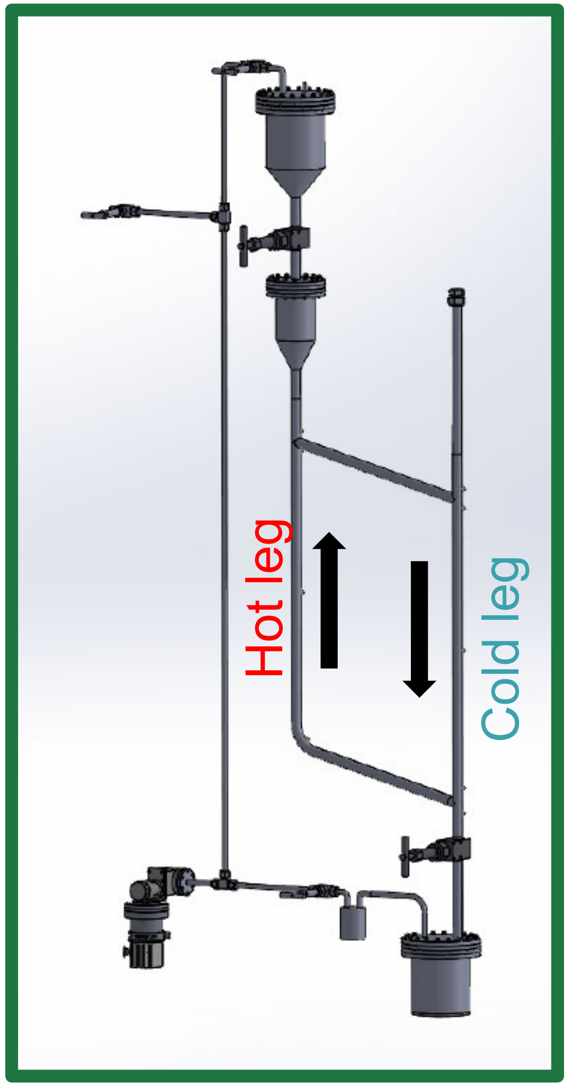
Cold leg: reaction moves to left (deposition)



(Source: J. Keiser)

Thermal convection loops have been used at ORNL since the MSRE days

- Salt is introduced at top
- Flow is driven by thermal gradient
- Coupons are hung in both the hot leg and cold leg



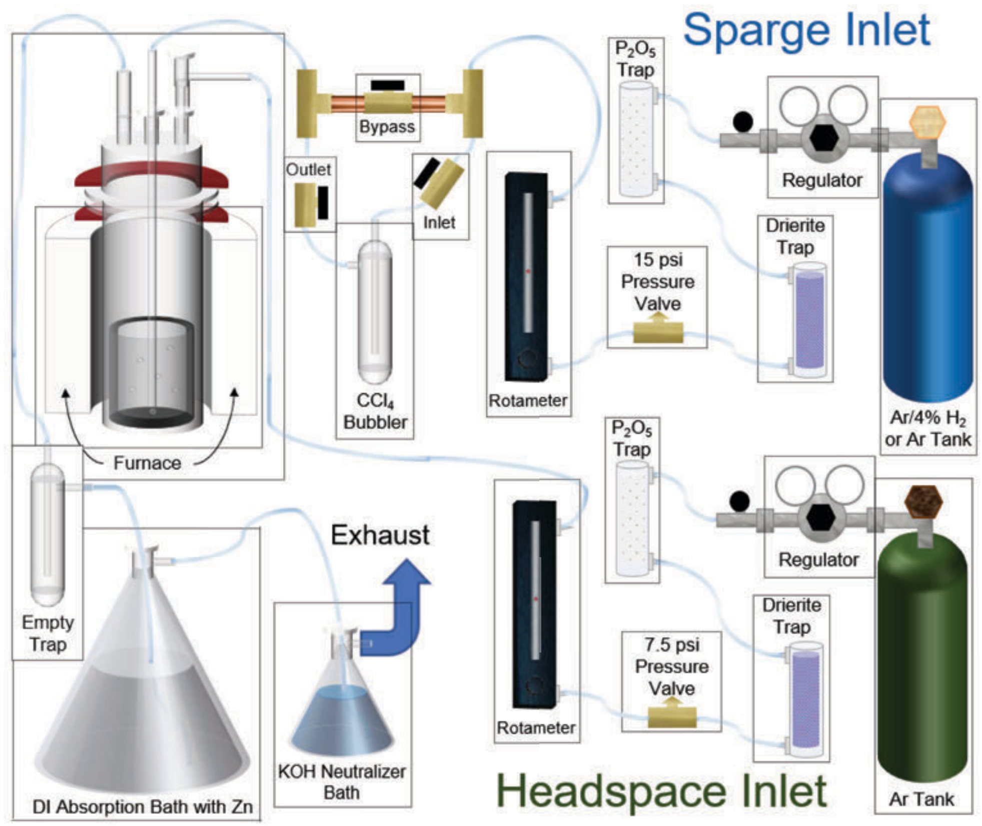
Fluoride salt preparation

- Hydrofluorination process
- Capacity of ~ 3.3 L (6.6 kg) per batch
- Ability to produce a variety of salts including fuel salts and FLiBe

Source: K. Robb

Chloride salt preparation

- Dehydration
  - Carnallite method (NH_4Cl)
- Carbochlorination
  - CCl_4 @ T = 750°C
- Metal & oxide content verified analytically
- Capacity:
  - Current: 0.5 L (0.8 kg) /batch
  - Expanding to 1.5 L / batch



Salt Purification Reactor

Source: R. T. Mayes & J.M. Kurley

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Understanding how commercial alloys perform in molten chlorides and fluorides

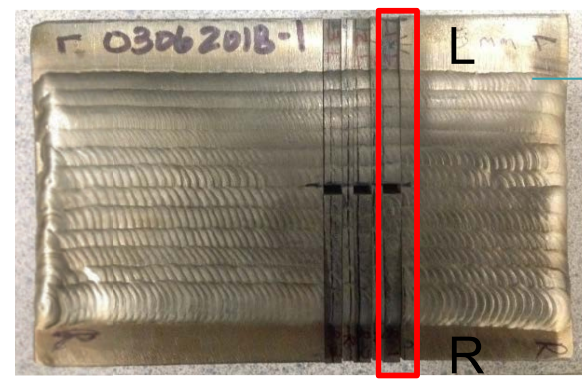
Alloy	Ni	Fe	Cr	Mo
316H SS	10	68	17	3
Hastelloy N	71	4	7	16
Alloy 800H	33	45	20	0
Haynes 230	57	3 max	22	2
Inconel 600	75	7	15	0
Hastelloy C-276	61	4	22	9
Haynes 242	57	5	16	16

Advanced materials

- New alloys with enhanced properties
  - Includes Hastelloy-N variants
- Cladded materials
  - Corrosion resistant materials cladding joined to code-qualified structural materials

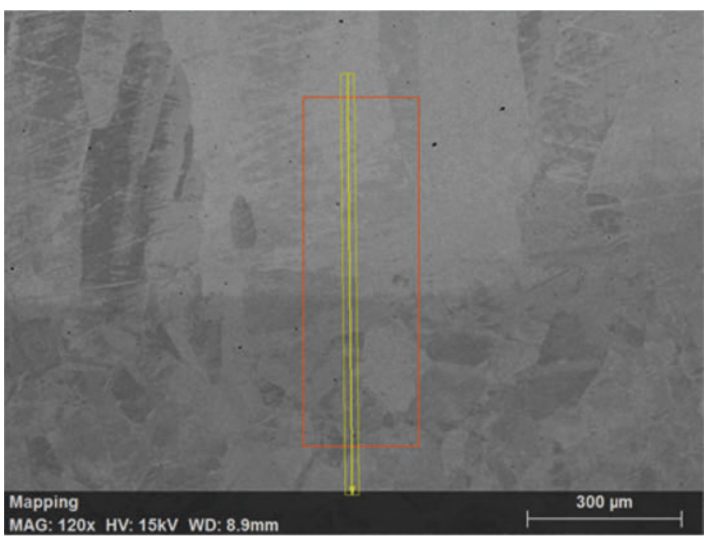
Fusion Welding of Ni on 316H Stainless

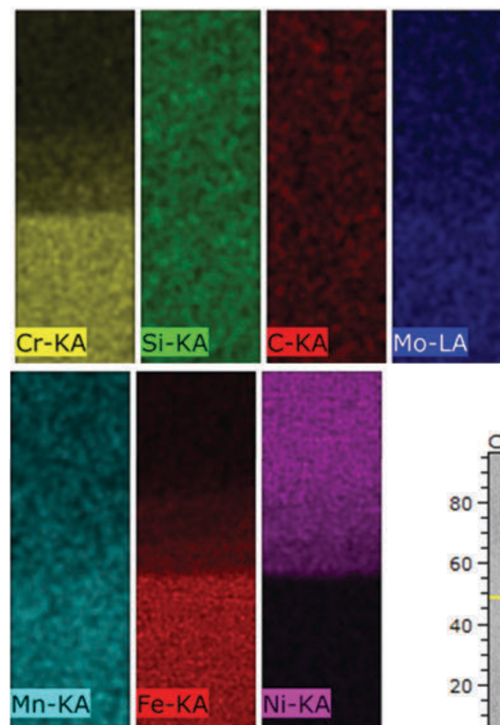
- Nickel cladding on 316H steel
- Total 12 passes, 50% overlay
- High quality arc welding cladding of Ni on 316H is relatively easy to achieve
- Multiple layers of cladding will be carried out next

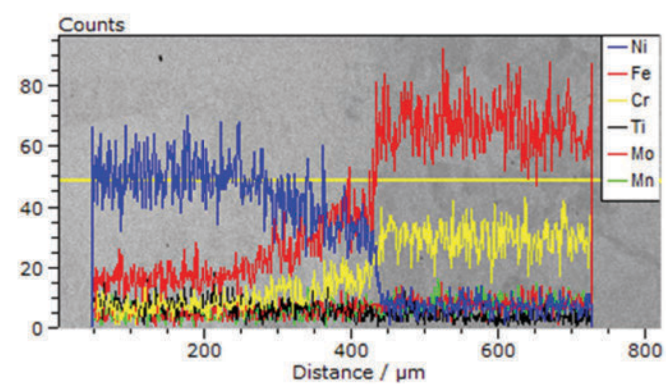


1st

Characterization

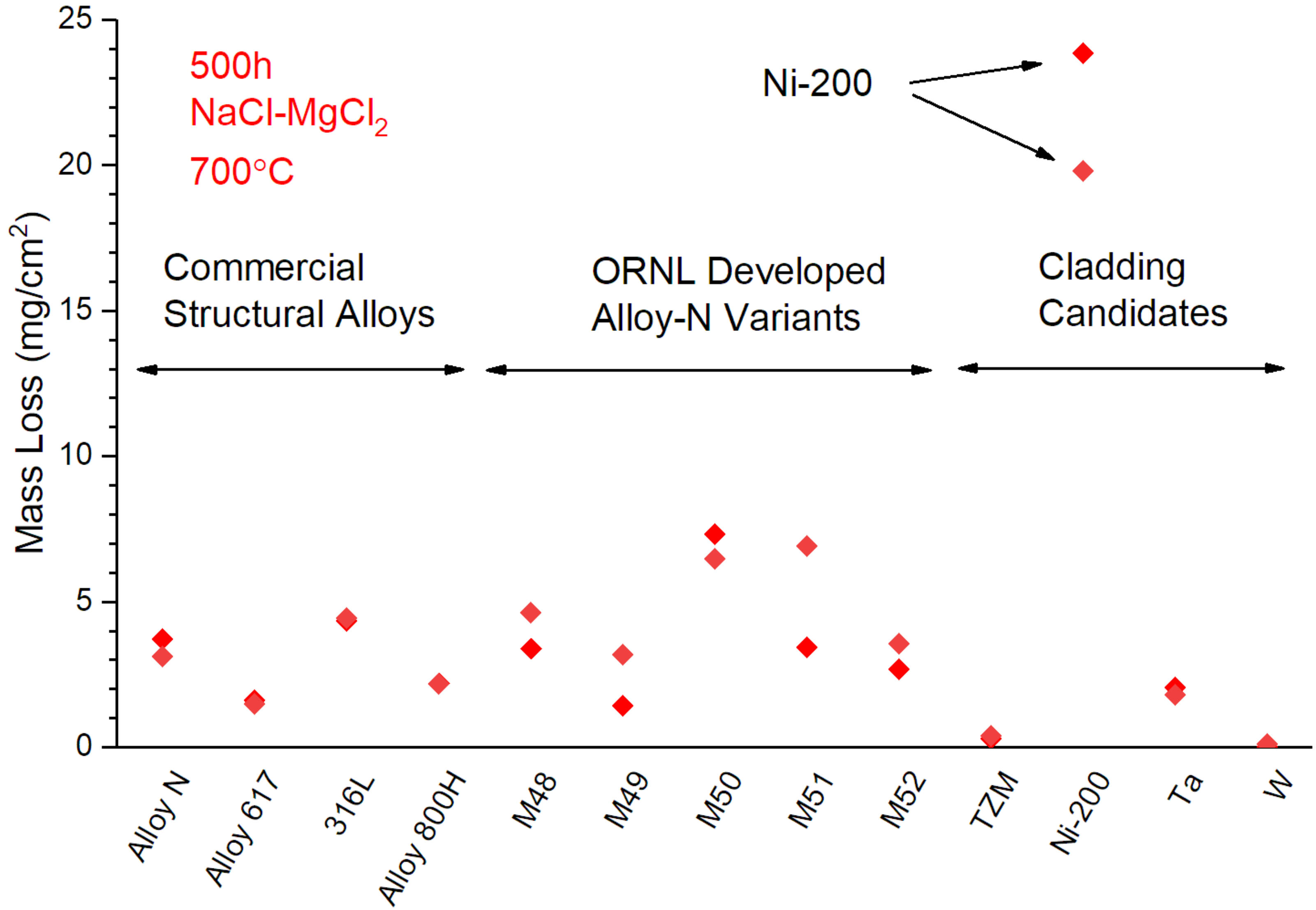






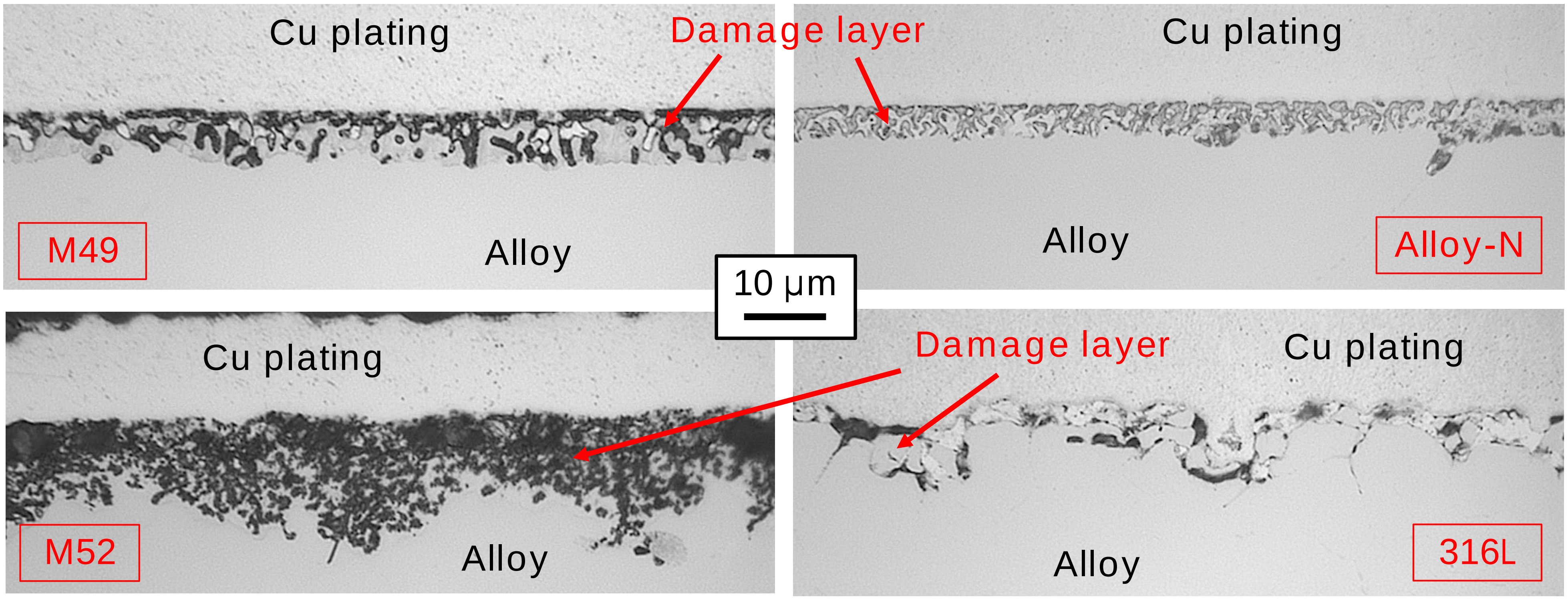
Source (Sam Sham)

Capsule testing of alloy-N variants and potential cladding materials



Raiman, (*unpublished*)

Metallography of samples



Raiman, (*unpublished*)

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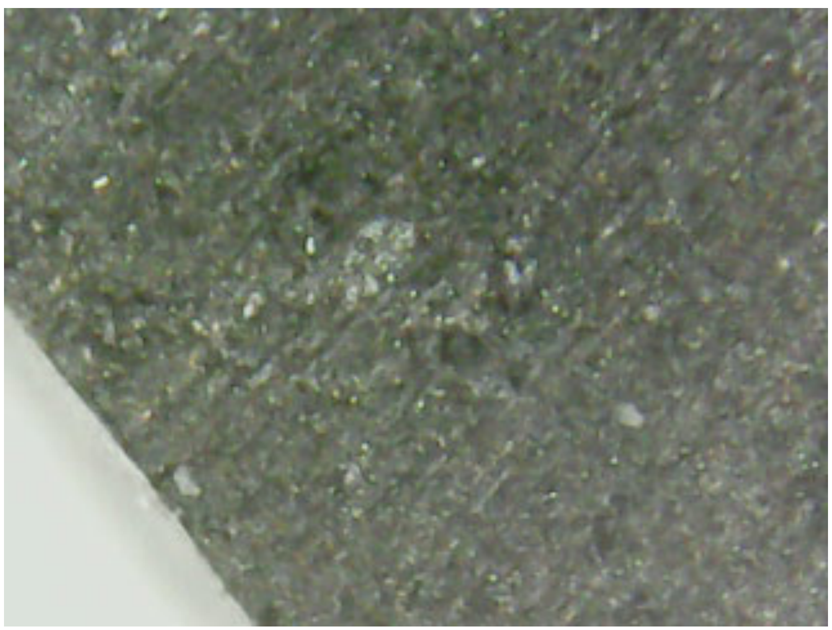
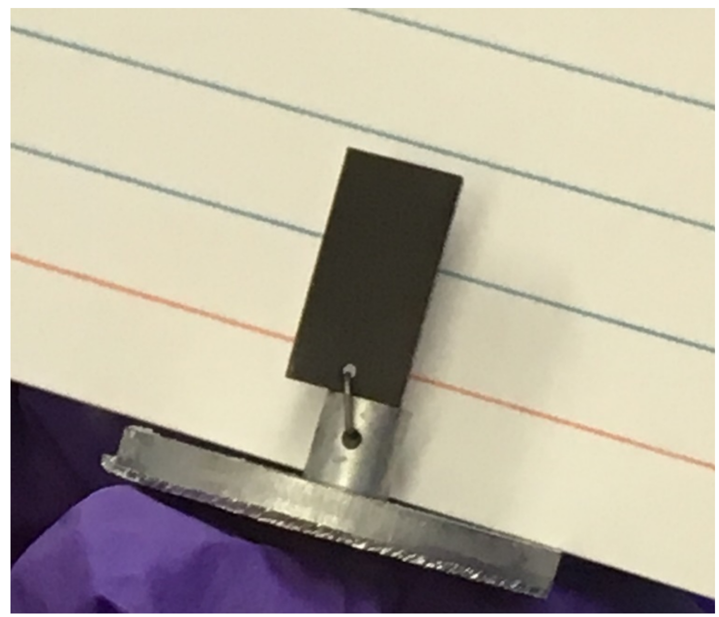
Nuclear graphite requirements

- High purity: Neutronics (low B content), oxidation resistance
- High density: Greater neutron moderator capacity
- High irradiation stability: Low dimensional changes
- High thermal conductivity, high strength, low elastic modulus, low CTE
- Low anisotropy: Less than 1.1 defined by ratio of thermal expansion
- Low salt infiltration
- Small grain size/pore size: Ultrafine (<10 μm) / microfine grains (<2 μm)
- Low gas fission products permeation
- Chemically inert: low tritium and fluorine chemisorption
- Electrochemically passive: need to minimize galvanic corrosion of metals/alloys in the presence of graphite
- Low cost

Low wettability observed on fine-grained graphite

- Sample surfaces were relatively clean
  - no major visible salt concentrations in graphite surfaces after removing from capsule
- Small drops of salt on surface (very small bright spots)
  - Appear spherical, indicating low wetting, limited adhesion to surface

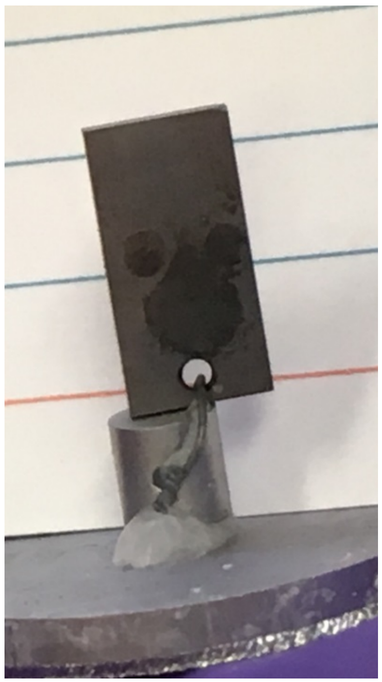




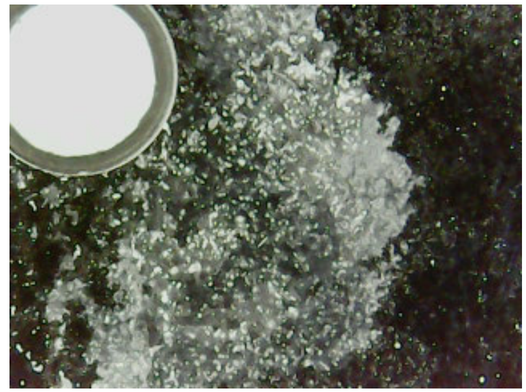
Exposed to FLiBe for 500 hours at 700°C

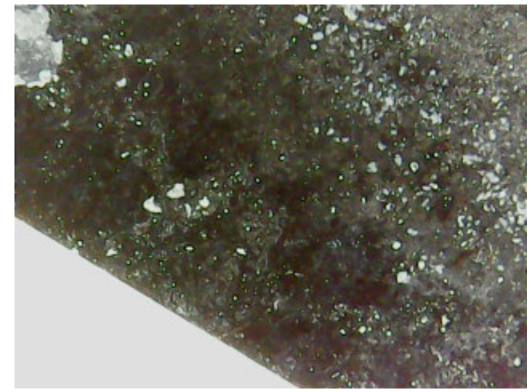
Gallego, et al.

Significant wetting observed on SiC sample exposed to FLiBe

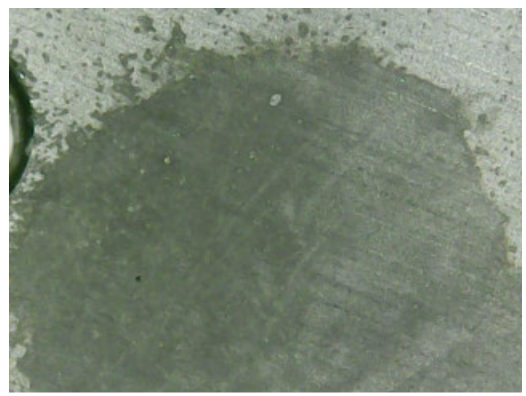


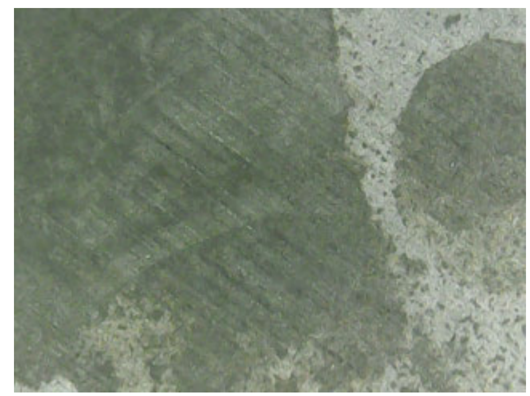
Shiny side





Dull side

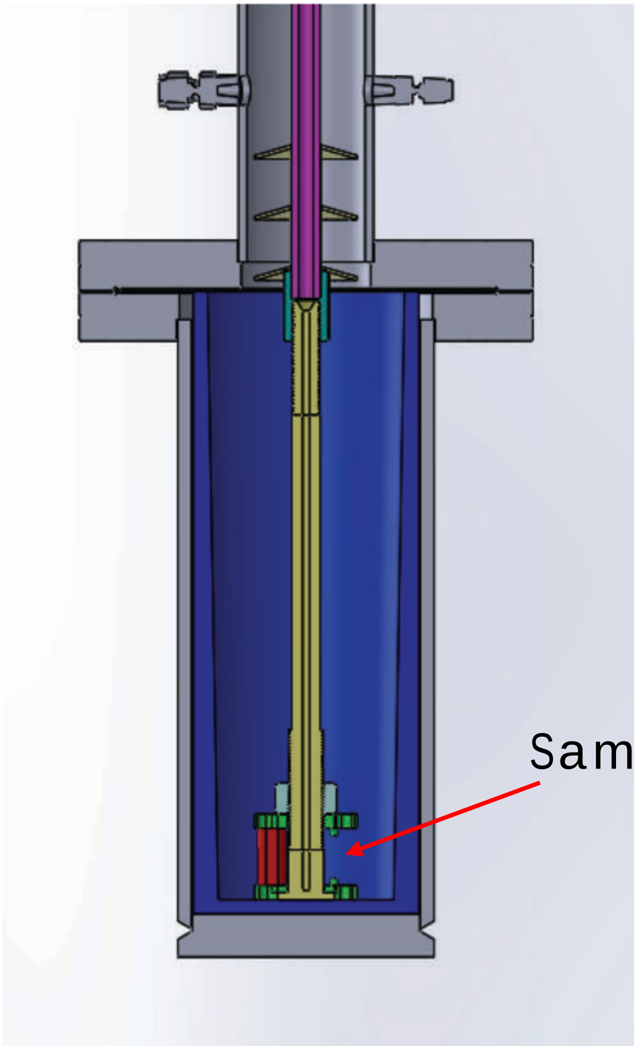


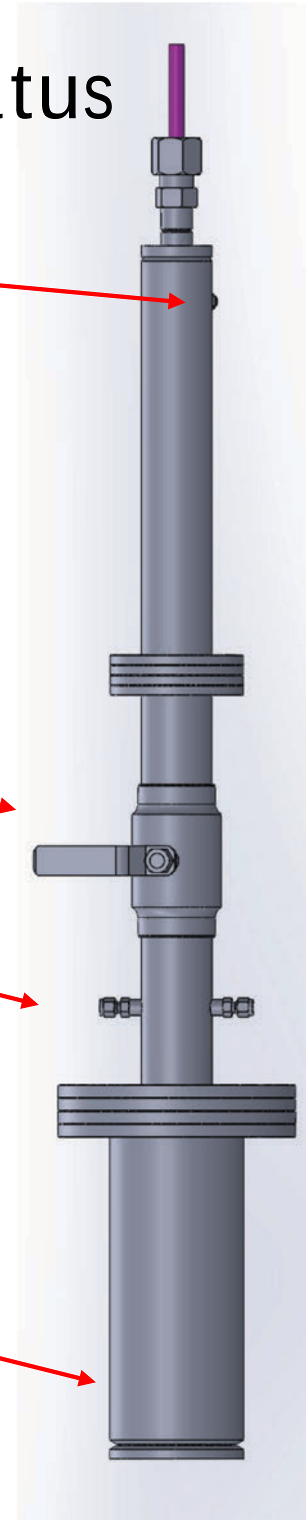


Exposed to FLiBe for 500 hours at 700°C

Gallego, et al.

New pressure-vessel testing apparatus with antechamber





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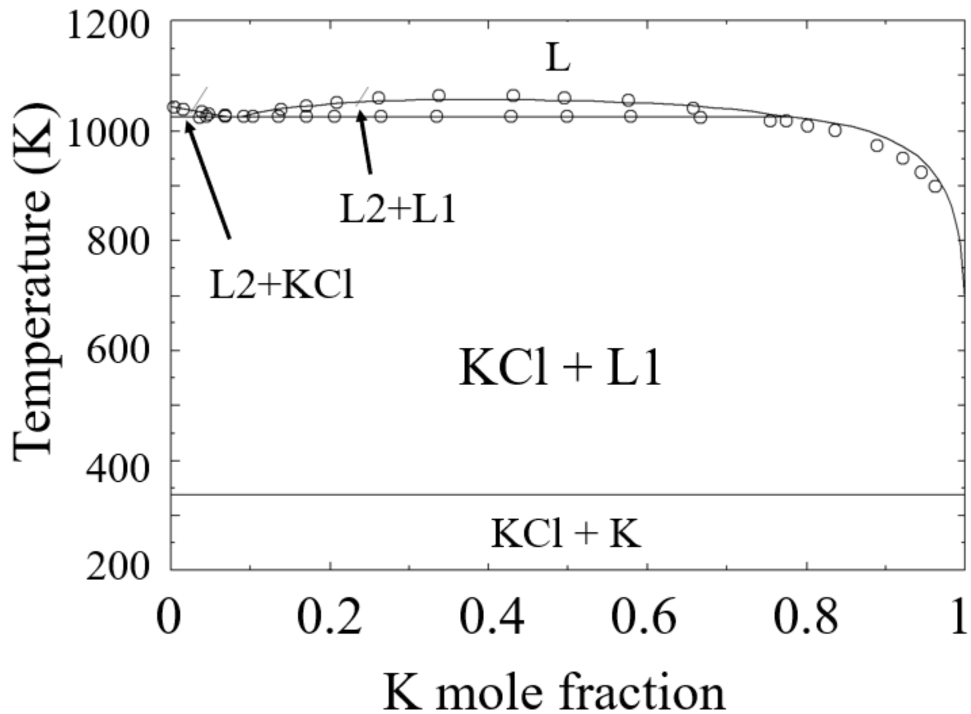
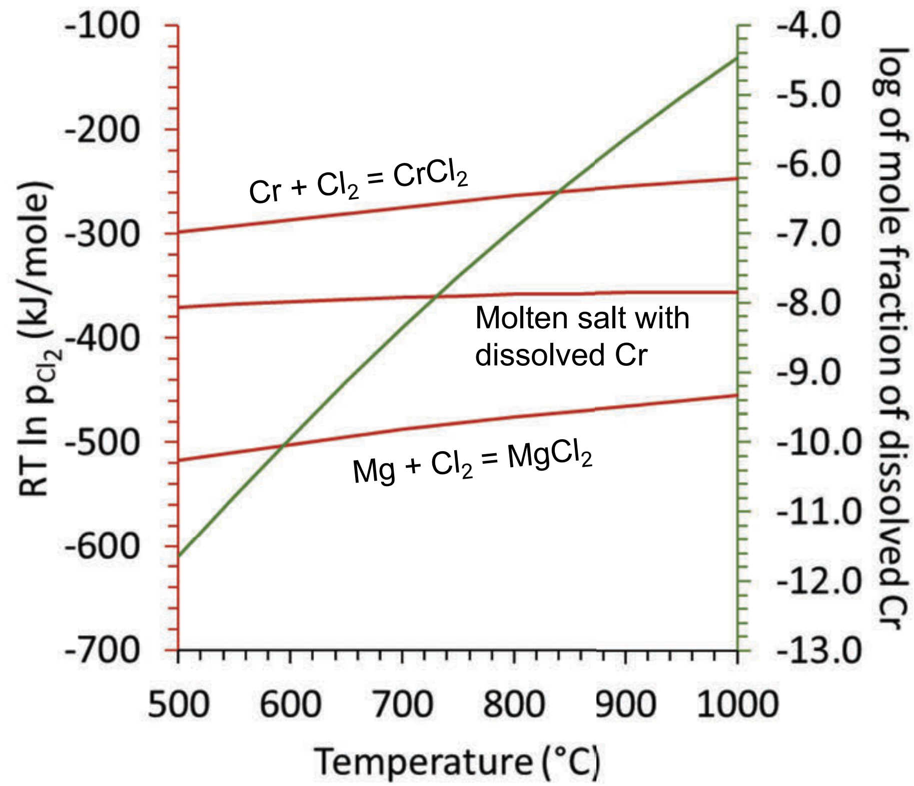
Development of thermodynamic models

Computed phase diagram for the K-KCl binary
Using the quasichemical model



McMurray, Raiman, *Solar Energy* (*2018)*

Computed equilibrium concentration of $CrCl_2$ in $KCl\text{-}MgCl_2$ based on
$Cr + MgCl_2$ (liq) → $CrCl_2$ (liq) + Mg (liq)

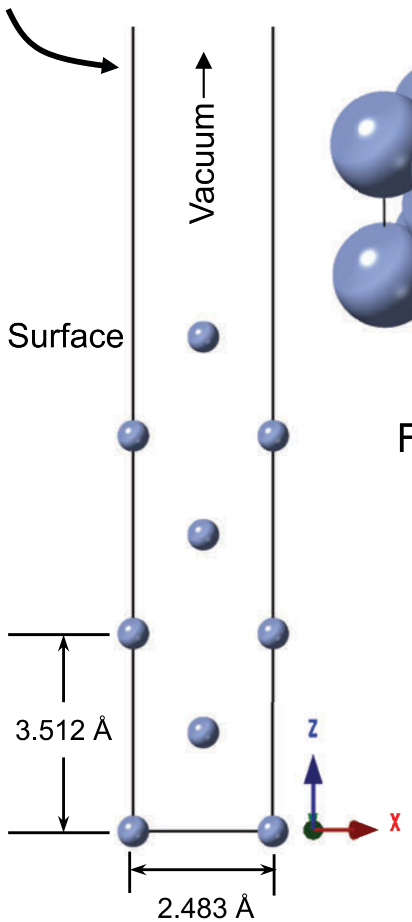


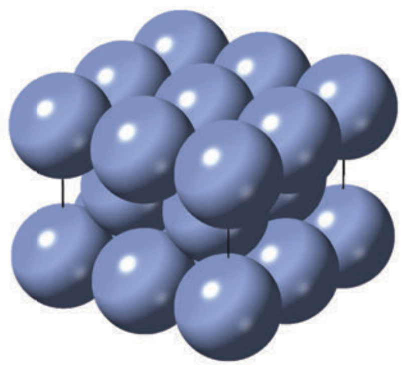
McMurray, (*unpublished)*

Basic models will be extended to include the highly multicomponent systems that inevitably occur with MSRs.

Modeling surface energy at the alloy-salt interface with density functional theory (DFT)

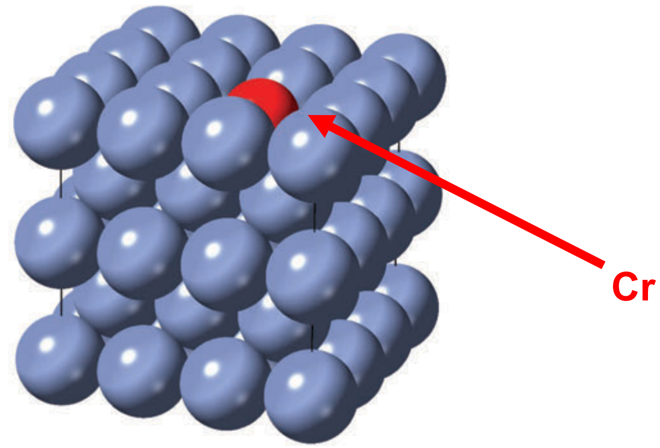
1. Initial models of unalloyed nickel in vacuum



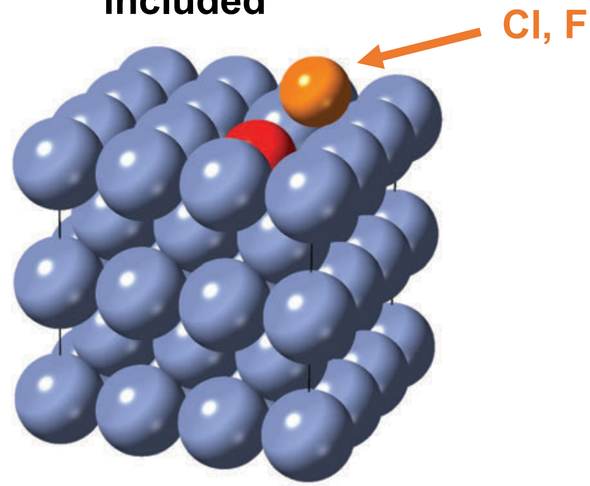


FCC (001)

2. Models expanded to include alloyed chromium

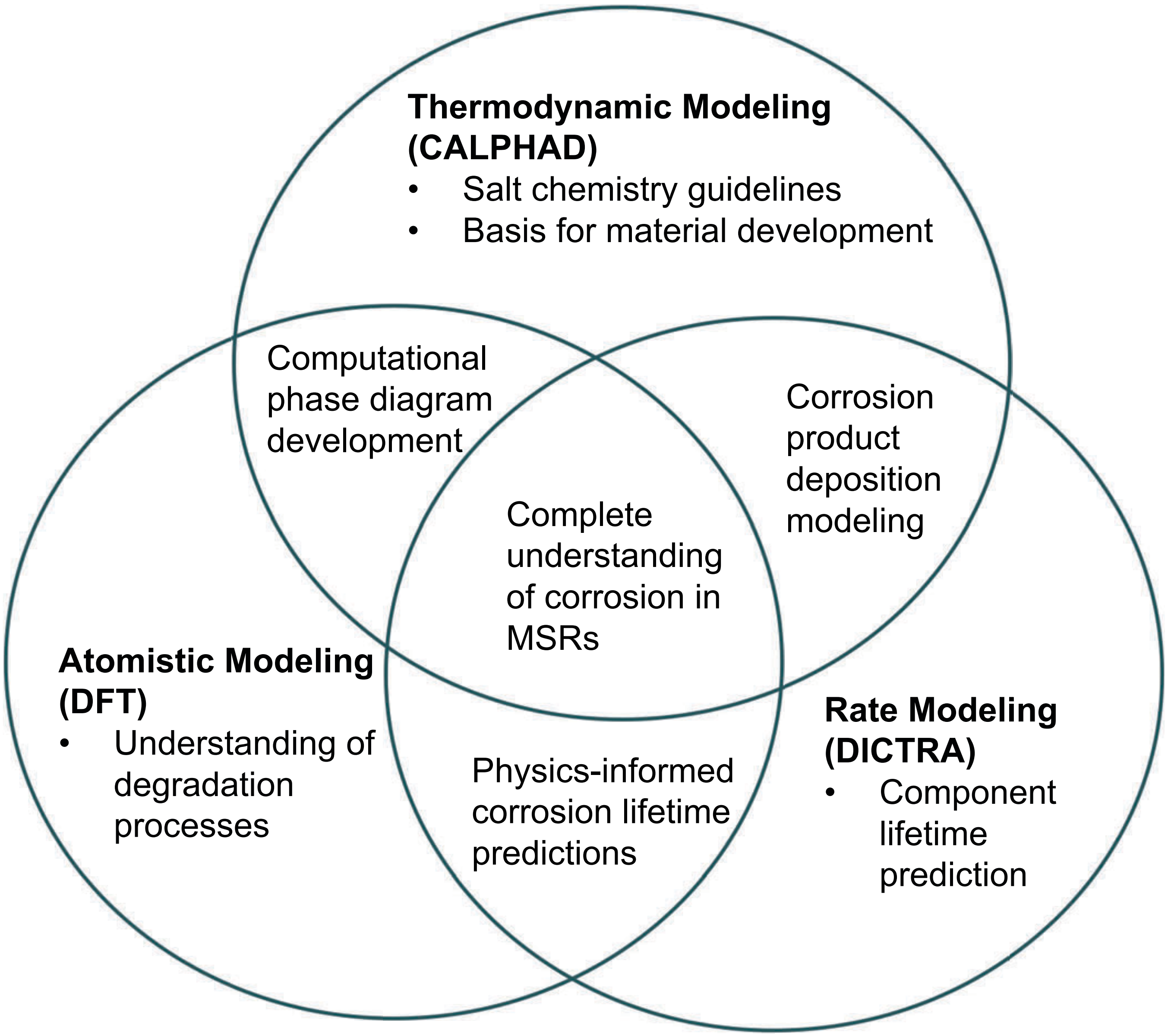


3. Adsorbed atoms are included



J. Startt

Corrosion modeling framework



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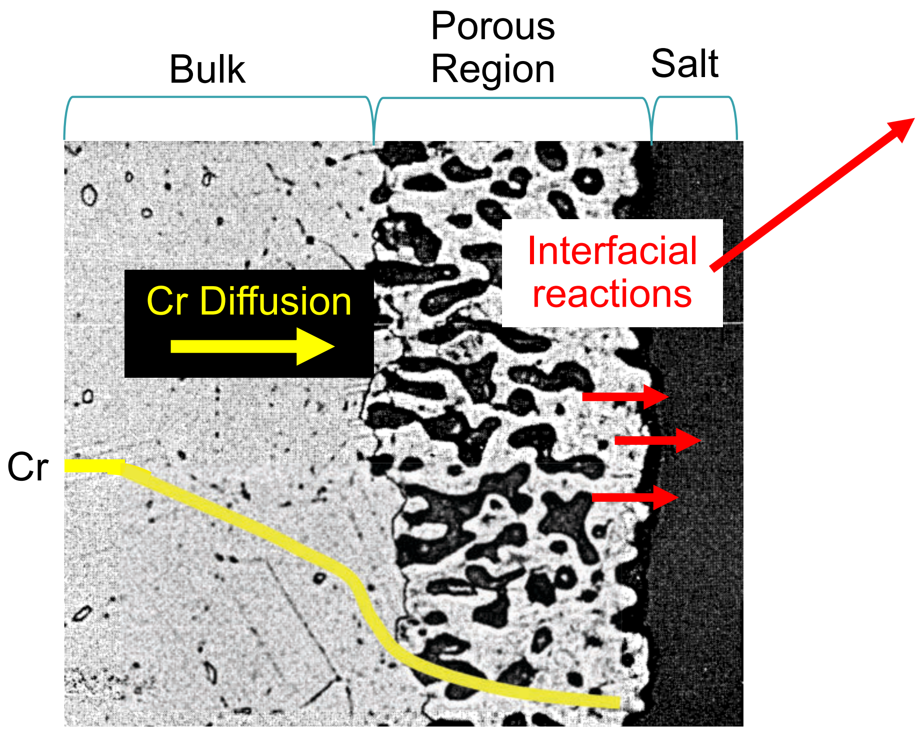
Irradiation effect on corrosion

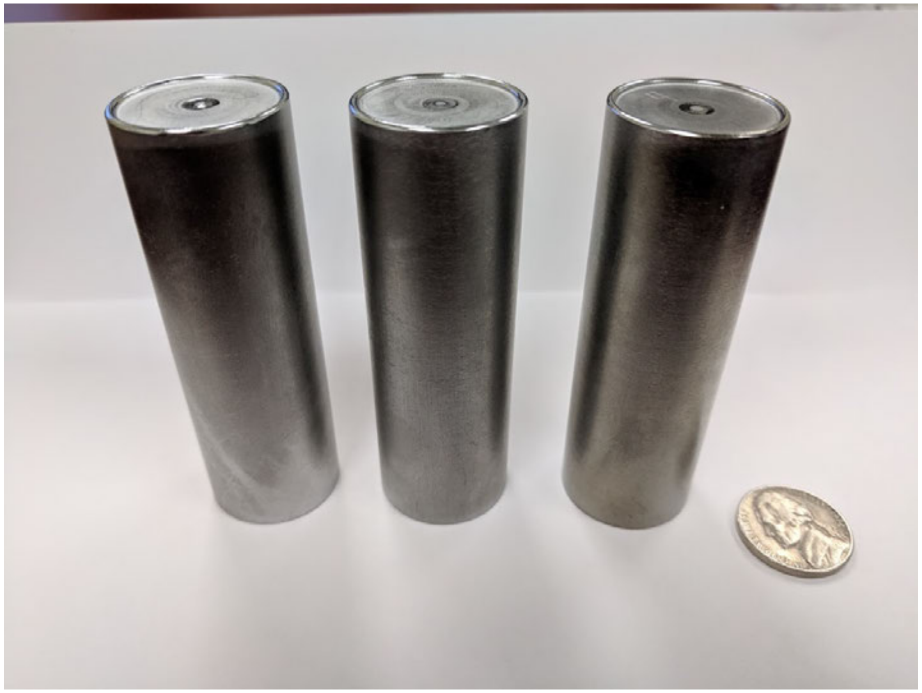


Likely no radiolysis effect in salt

Possible effect of radiation enhanced diffusion

Capsule irradiation in OSU reactor

- KCl-$MgCl_2$ salt
  - "aggressive" salt with ~1% oxide to ensure measurable corrosion during short exposure
  - "clean" salt with <30 ppm oxide to ensure impurity effect doesn't mask irradiation



	Irradiated		Unirradiated	
Aggressive salt	Alloy N	316 SS	Alloy N	316 SS
Clean salt	Alloy N	316 SS	Alloy N	316 SS

Reactor insertion

- Capsules irradiated for 21 hours at 800°C
- Currently awaiting examination at ORNL
- Proof of concept for future irradiations

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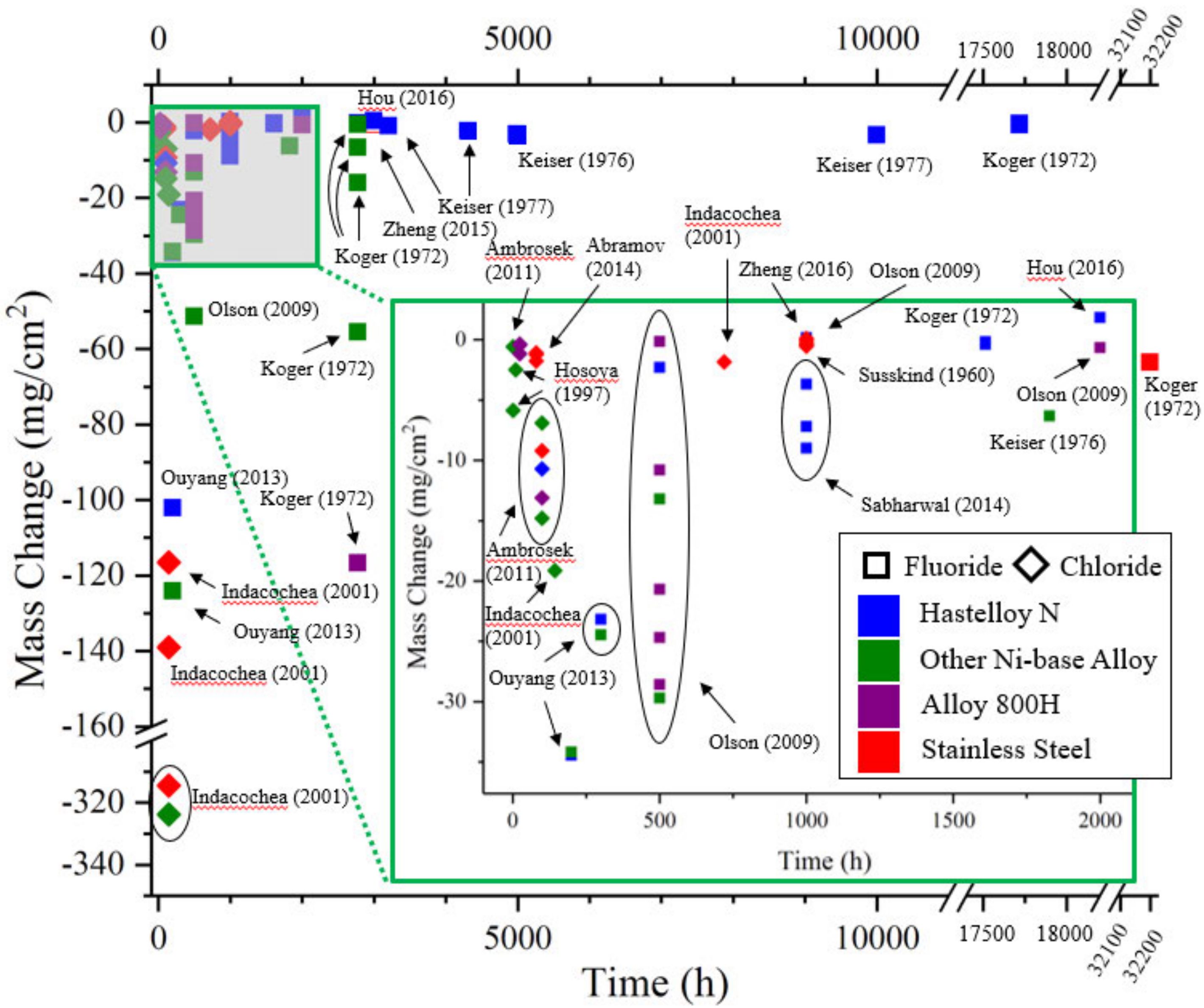
Reliable data on molten salt corrosion?



Raiman, Lee, *J. Nucl. Mater.* (2018)

Data, data, data

- as a basis for salt chemistry guidelines
- to guide material selection and development
- to validate models

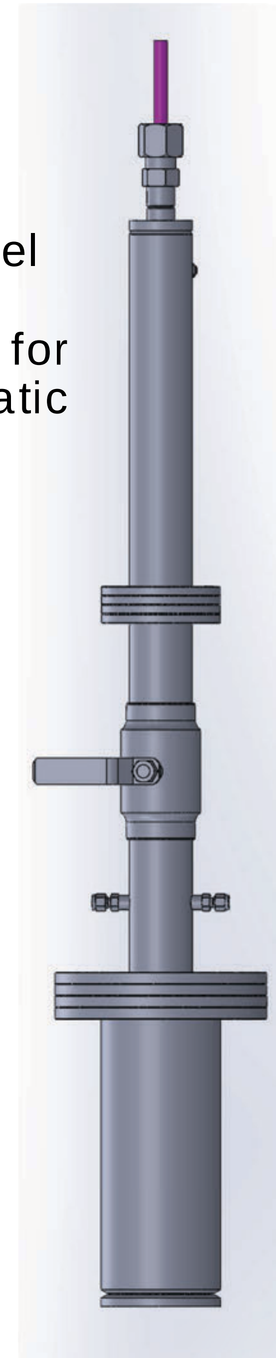
Collected data must be both

- Useful
- Repeatable

Efforts in progress to increase experimental throughput

Furnace banks devoted to capsule testing

Pressure vessel with antechamber for high quality static exposures



Filled and sealed in glovebox

Lots of high quality salt!

Summary

- Multi-faceted program to understand compatibility of structural alloys and graphite with molten salts
- Computational models in development
- Infrastructure improvements to allow data generation with high reliability and high throughput
- Irradiation-corrosion program to understand combined effects in MSR cores

FY19 plans - summary

- Continue exposures of commercial alloys in F and Cl salts
  - Find effect of temperature
  - Impurity effects on corrosion (Redox)
  - Fission product effect
- Corrosion in flowing salt
  - Thermal convection loops
- Model development
  - Atomistic modeling to find interface behavior
  - Thermodynamic modeling to understand salt chemistry effect on corrosion
- Graphite infiltration
- Advanced material studies
  - Advanced Ni superalloys
  - Cladded materials
  - Structural ceramics

Supplementary

Graphites for MSR… “grading”

		Grain size [µm]	Pore size (um)	Density	Billet size	Purity	Cost	Country of origin	Irradia-tion data	Irradiation lifetime	Isotropic	Still manufac-tured
AGC-Campaign	H-451	Medium	5-100	1.71				SGL USA	Low dose		Extruded	
	NBG-17	Medium	8-30	1.86	Large	< 5 ppm	$	SGL (Germany/ France)	Low dose		Vibro-molded	
	NBG-18	Medium	5-50	1.87	Large	< 5 ppm	$	SGL (Germany/ France)	Low dose		Vibro-molded	
	PCEA	Medium	5-100	1.79	Large	< 5 ppm	$	GrafTech (USA)	Low dose		Extruded	
	IG-110	Fine < 100	<1	1.76	Large	< 5 ppm	$	Toyo (Japan)	Low dose		Iso-molded	
	IG-430 (dropped)	Fine < 100	<1	1.80	Large	< 5 ppm	$	Toyo (Japan)	Low dose		Iso-molded	
	2114 (added)	Fine < 100			Large	< 5 ppm	$	Mersen (France-USA)	Low dose			
MSRE	CGB	Medium		1.86	Small			Union Carbide (USA)			Extruded	
OTHER fine grain graphites	POCO-ZXF-5Q	Microfine < 2	0.3	1.78	Small	< 5 ppm	$$	USA	Low dose		Iso-pressing	
	POCO-AXF-50	Ultrafine < 10	0.8	1.78	Small	< 5 ppm	$$	USA	Low dose		Iso-pressing	
	POCO-TM	Ultrafine < 10	1.5	1.82	Small	< 5 ppm	$$	USA	Few data		Iso-pressing	
	G347A	Ultrafine < 10		1.85	Large	< 5 ppm		Tokai (Japan)	High dose		Iso-pressing	
	IGS743NH	Superfine < 50		1.80	Large			Nippon (Japan)	Low dose		Iso-molded	
	ITU10	Fine < 100						Ibiden (Japan?)				

Experiment Types

	Crucible	Sealed Capsule	Thermal Loop	Pumped Loop
Sealed from contaminants	No	Yes	Yes	Yes
Access for instrumentation	Yes	No	Yes	Yes
Hot and cold sections	No	No	Yes	Maybe
Precise flow control	No	No	No	Yes