Generic topics on Compatibility Between Coolants and Materials in Fusion & Fission

Bruce Pint, Interim Section Head, Materials in Extremes

Materials Science and Technology Division
Oak Ridge National Laboratory

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SAVE THE DATE

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Mail address : htcpm2024@utc.fr

HTCPM 2024

HIGH-TEMPERATURE CORROSION AND PROTECTION OF MATERIALS

Acknowledgments

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- ORNL team
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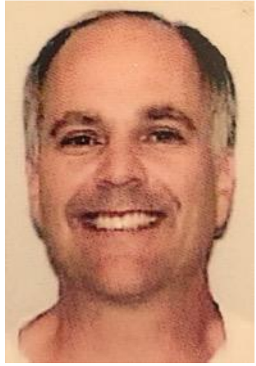
  - Shane Hawkins, Kelsey Hedrick: tensile testing
  - Characterization: Tracie Lowe, Victoria Cox, Ercan Cakmak, Yi-Feng Su (TEM)
- Mentors: Jack DeVan, Jim DiStefano, Peter Tortorelli, Steve Pawel

DeVan 1929-2000

DiStefano 1935-2013



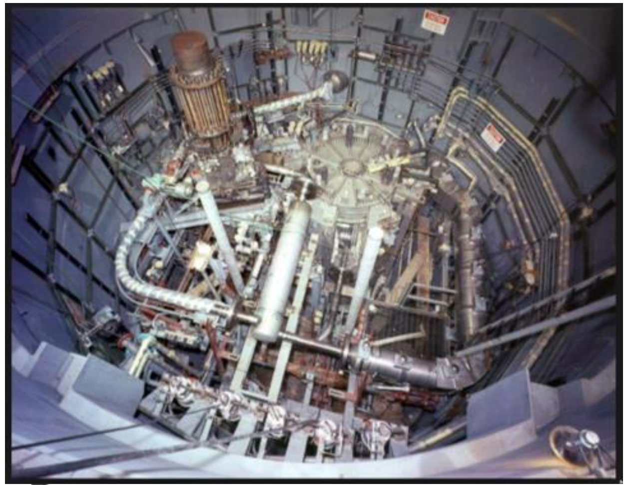
2013 APMT TCL design

OAK RIDGE National Laboratory

Many potential applications for molten salts

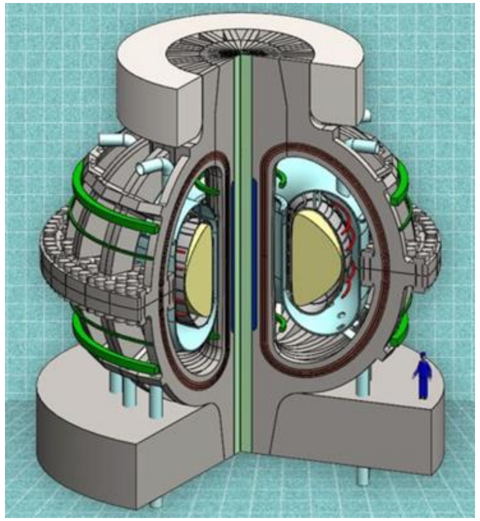
Fission Energy: Fuel or Coolant Salt

- Molten salt reactors
- 1966-1970 ORNL molten salt reactor experiment (MSRE)
  - FLiBe ($2LiF$-BeF_2) coolant
  - LiF-BeF_2-ZrF_4-UF_4 fuel
  - Structural alloy (Hastelloy N)
    - Ni-7Cr-16Mo-5Fe



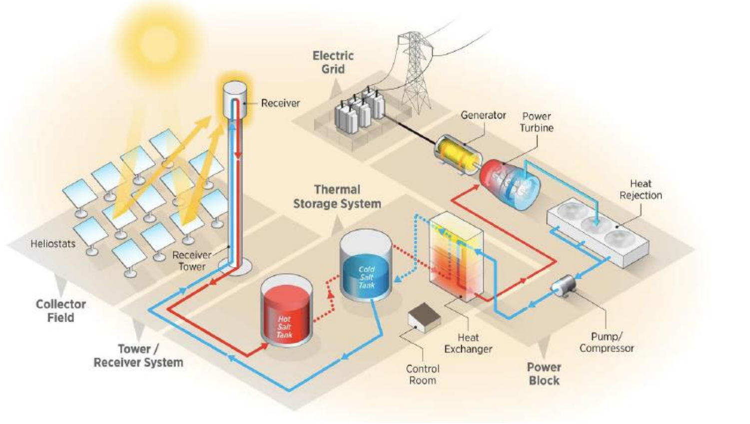
Fusion Energy: FLiBe Blanket

- ARC reactor proposed by Commonwealth Fusion Systems renewed interest
- FLiBe ($2LiF$-BeF_2) extracts heat/breeds T
  - $^{6}Li + ^{1}n \rightarrow ^{4}He + T$
- Issue with T breeding ratio



Solar Energy Thermal storage (Cl)

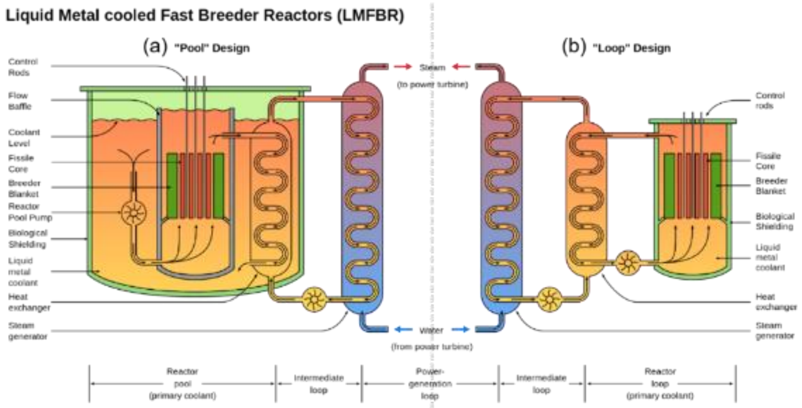
- Gen. 3 concentrating solar power: KCl-$NaCl$-$MgCl_2$
- Replace nitrate salts (Gen.2)
  - Nitrates limited to <600°C
- Dried Cl salt not as corrosive as reported
- Salt concept not down-selected for Gen. 3 by US DOE



Many potential applications for liquid metals

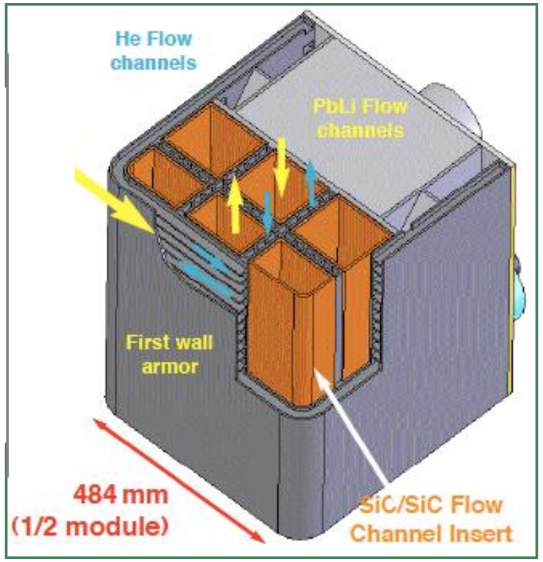
Fission Energy: Na or Pb/PbBi

- Decades of experience with liquid metal cooled reactors
- Na: especially for fast breeder reactors
  - Natrium 345MW by TerraPower under development
- Pb: current interest
  - Westinghouse and others



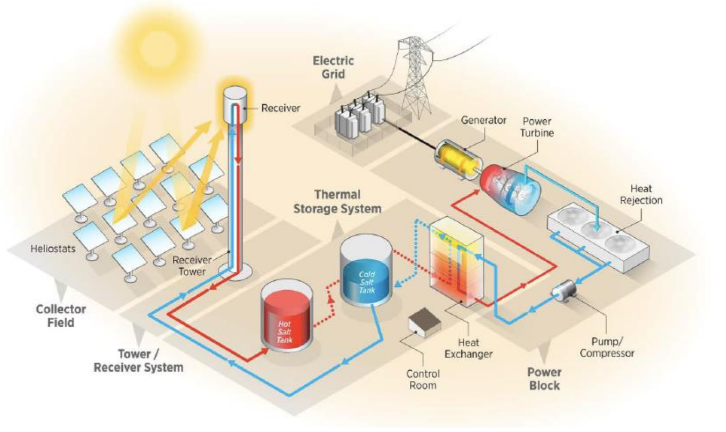
Fusion Energy: Li or PbLi

- Li need to breed T
  - $^{6}Li + ^{1}n \rightarrow ^{4}He + T$
- DCLL: dual coolant (He+PbLi) is leading US blanket concept
- Renewed interest in Li because of limited ^{6}Li supply



Solar Energy Thermal storage (Cl)

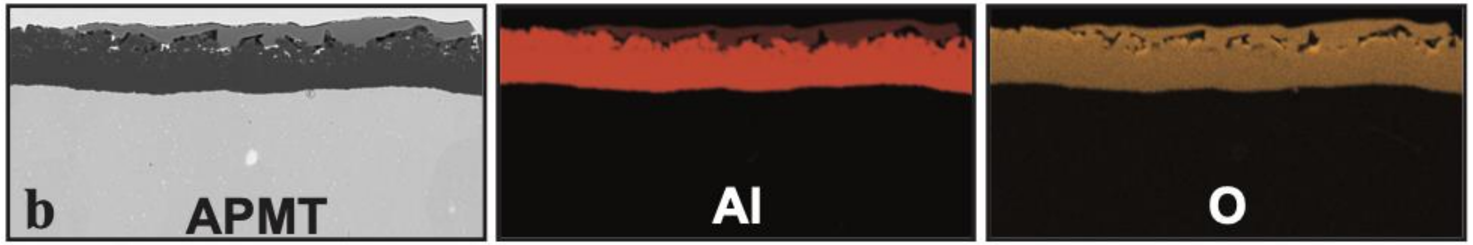
- Gen. 3 concentrating solar power: Na
- Replace nitrate salts (Gen.2)
  - Nitrates limited to <600°C
- Na could enable >700°C
- LM concept not down-selected for Gen. 3 by US DOE



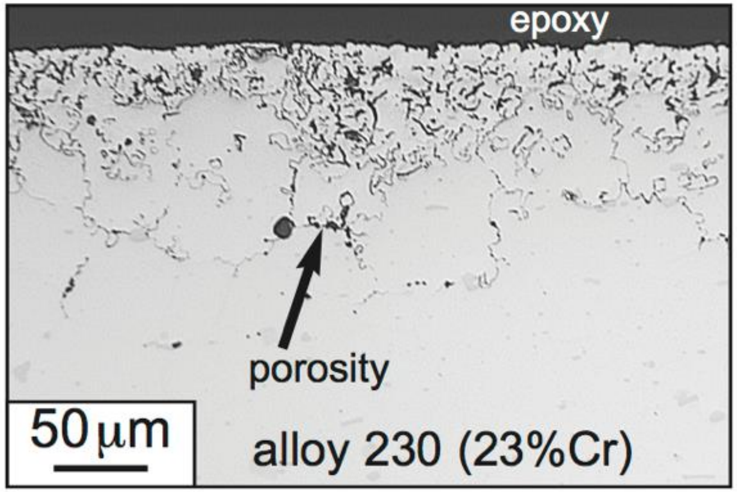
Molten salt/liquid metal compatibility: what is our motivation?

What are we afraid of?

- **High temperature corrosion:** we think of a surface oxide growing:
- **In liquid salt or metal:** we worry about dissolution
  - **BUT, 100µm is inconsequential**

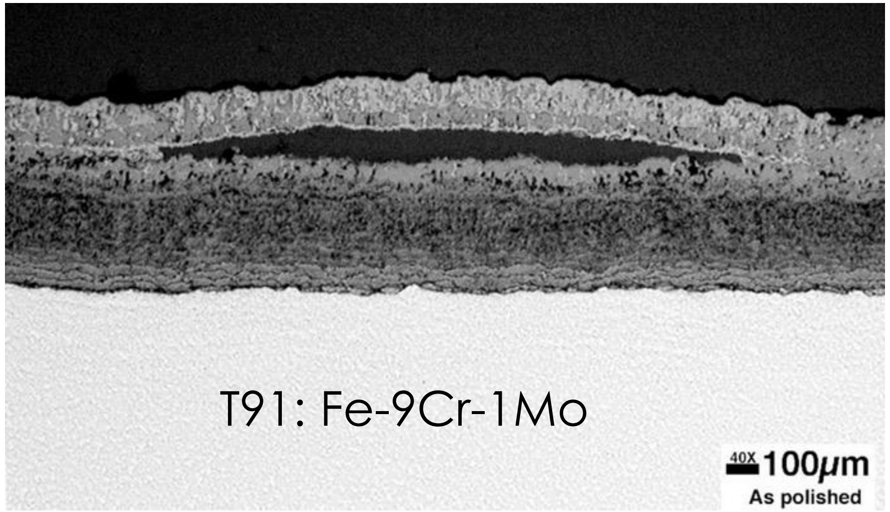


Fe-21Cr-5Al-3Mo



Alloy 230 (Ni-23Cr-14W)
100h at 800°C in (K,Mg,Na)Cl salt

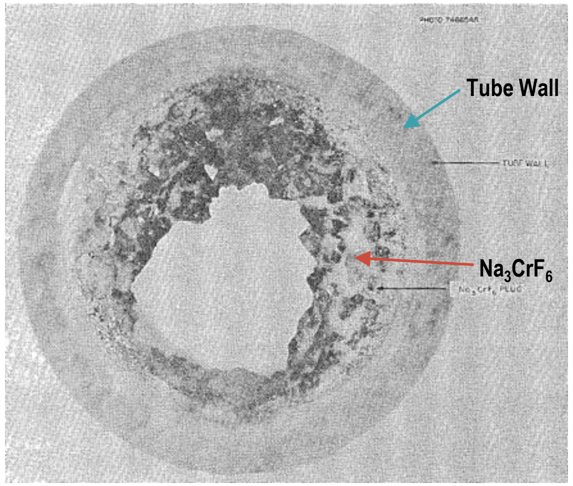
Consider the thick Fe oxides that form on the inside of steam tubes: designers allow for "metal wastage"



Molten salt compatibility: what is our motivation?

What are we afraid of?

- Inconsequential: Cr surface depletion
- **Mass transfer**
  - Block flow in channel!

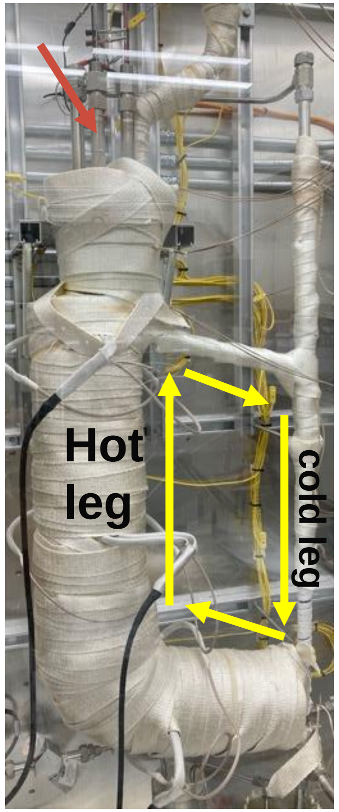


Hastelloy N, $NaBF_4$-NaF-KBF_4
8760 h, TCL 605°-460°C
- J. Koger, Corrosion, 1974

How do we study it?

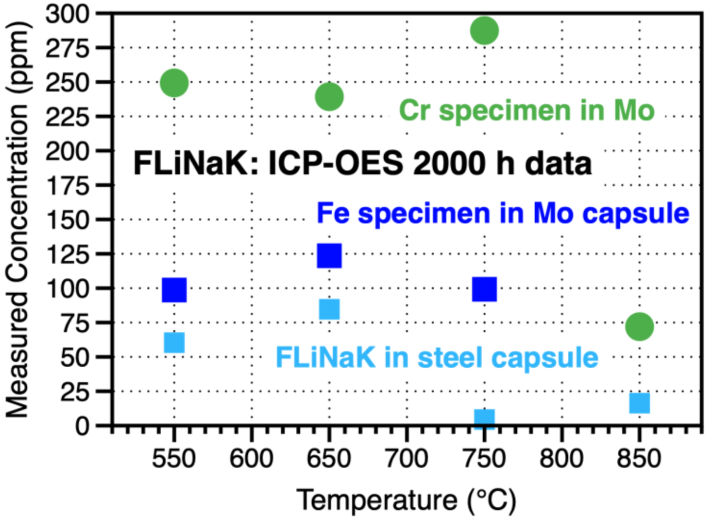
- Flowing salt experiments
  - Forced convection loop
  - Thermal convection loop

2021 ORNL FLiBe TCL



How do we understand it?

- Dissolution experiments
  - Compare Cr and Fe in isothermal salt
  - Experiments in FLiNaK and FLiBe in progress
    - 550°-850°C
    - Temperature effect?



Molten salt compatibility: what is our motivation?

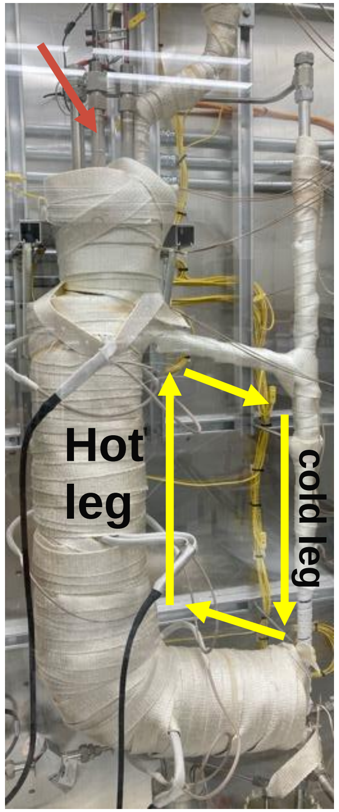
What are we afraid of?

- Inconsequential: Cr surface depletion
- **Mass transfer**
  - Block flow in channel!

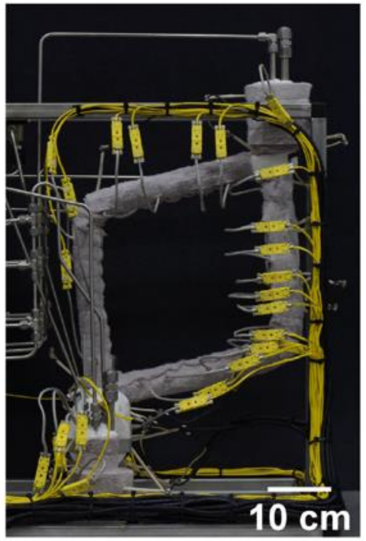
Kelleher 2022 Materials Today
- Ni 200 loop, 14 h at 620°C, unpurified $NaCl$-$MgCl_2$ salt

How do we study it?

- Flowing salt experiments
  - Forced convection loop
  - Thermal convection loop



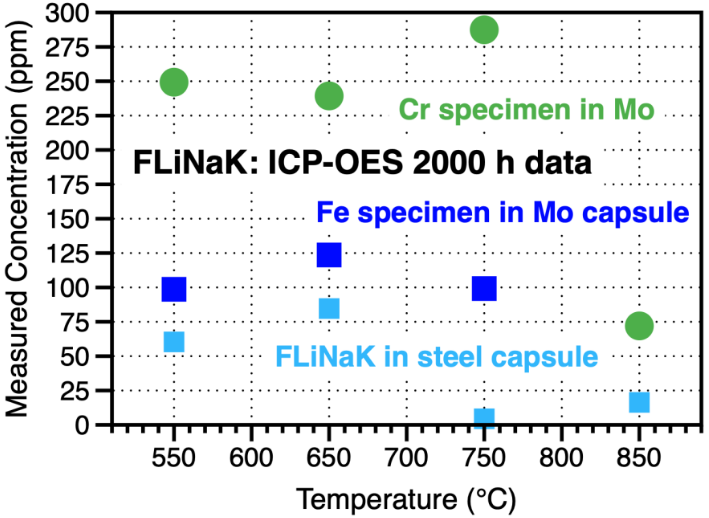
2021 ORNL FLiBe TCL
1 m tall



TerraPower "microloop"

How do we understand it?

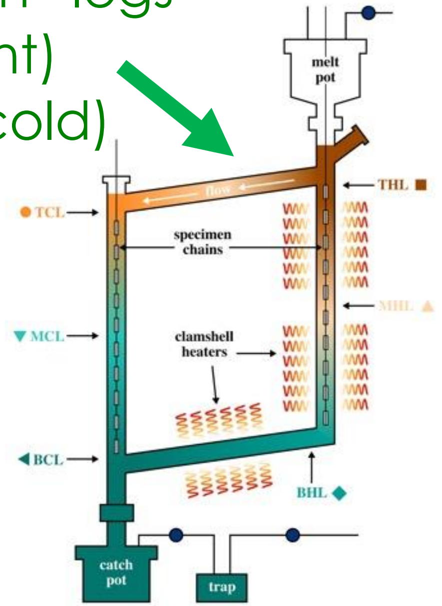
- Dissolution experiments
  - Compare Cr and Fe in isothermal salt
  - Experiments in FLiNaK and FLiBe in progress
    - 550°-850°C
    - Temperature effect?



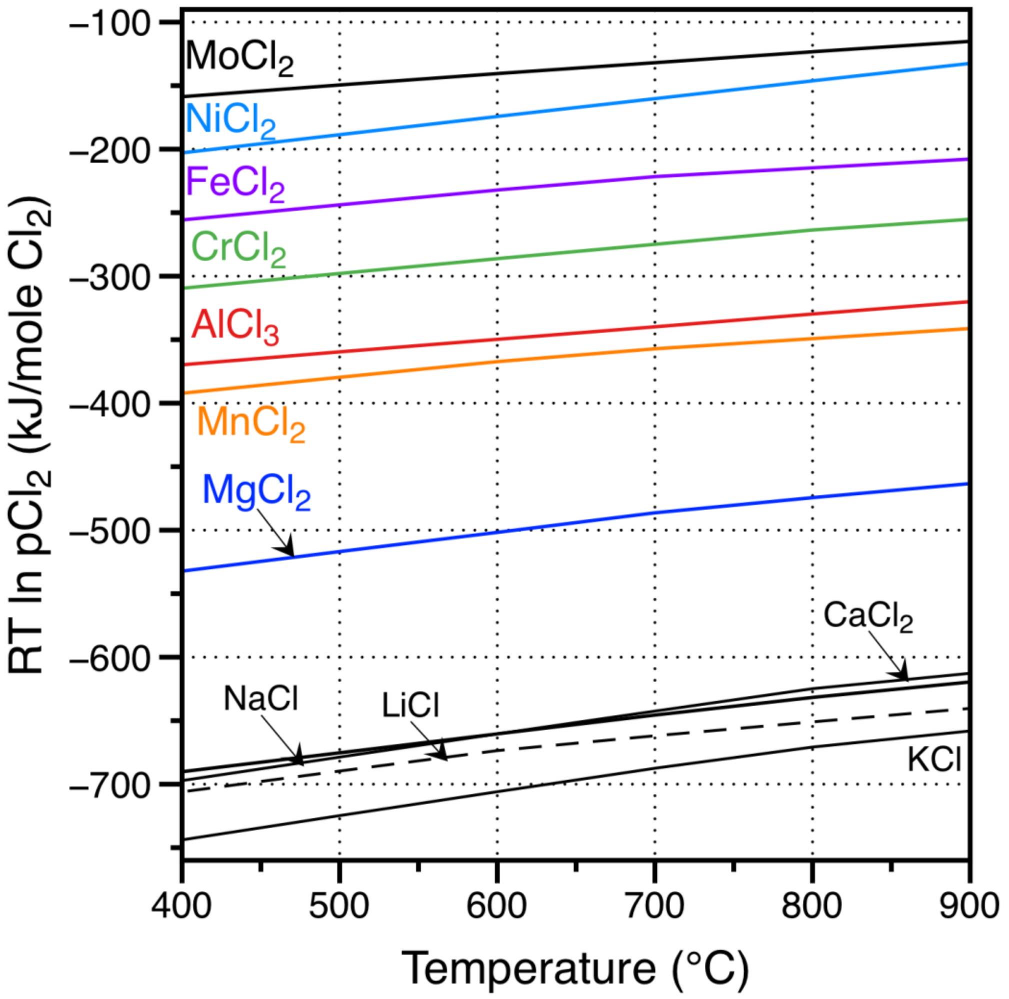
How do we assess and quantify LM compatibility?

- Thermodynamics
  - First screening tool (assessments published, but data is not always available)
- Static capsule/crucible (screening test only)
  - Isothermal test, first experimental step
  - Prefer inert material and welded capsule to prevent impurity ingress
  - **Dissolution rate changes with time**: key ratio of liquid/metal surface
  - **No assessment of mass transfer**

- Flowing thermal convection loop (TCL)
  - Flowing liquid metal by heating one side of "harp" with specimen chain in "legs"
  - Relatively slow flow and ~100°C temperature variation (design dependent)
  - **Captures solubility change in liquid**: dissolution (hot) and precipitation (cold)
    - Dissimilar material interactions between specimens and loop material
- Flowing forced convection or pumped loop
  - Most realistic conditions for flow
  - Historically, similar qualitative corrosion results as TCL at 10+X cost
  - Necessary progression for other aspects of LM blanket development
  - **Fusion needs results ASAP, including with magnets and radiation**

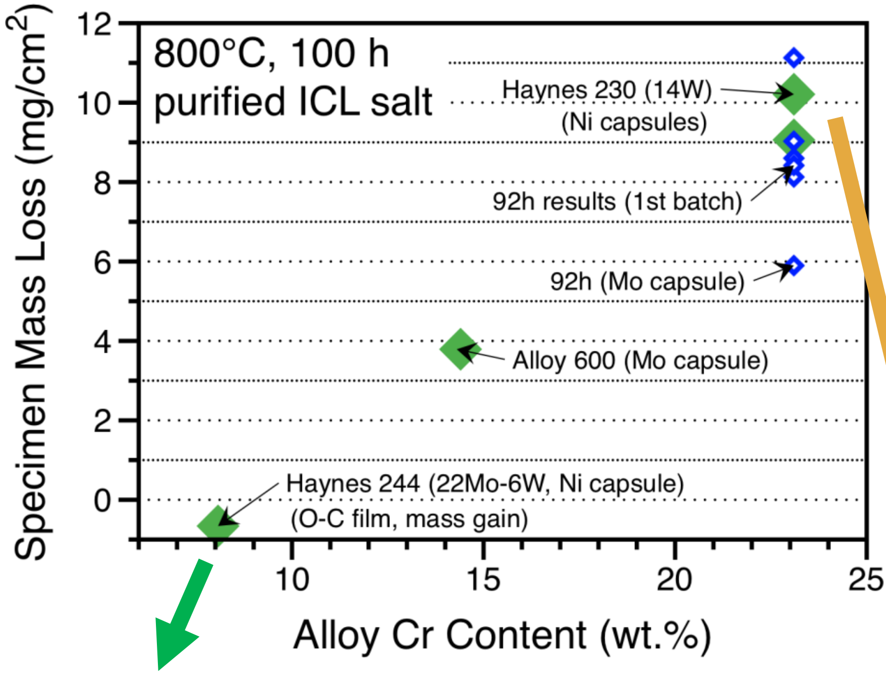


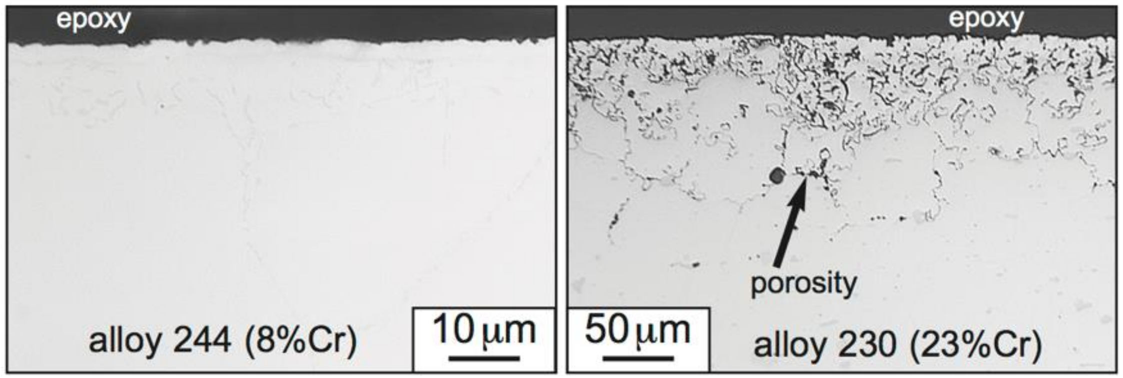
Thermodynamics suggests which elements will be selectively attacked (similar for F and Cl)



Hastelloy N: Ni-7Cr-16Mo~5Fe

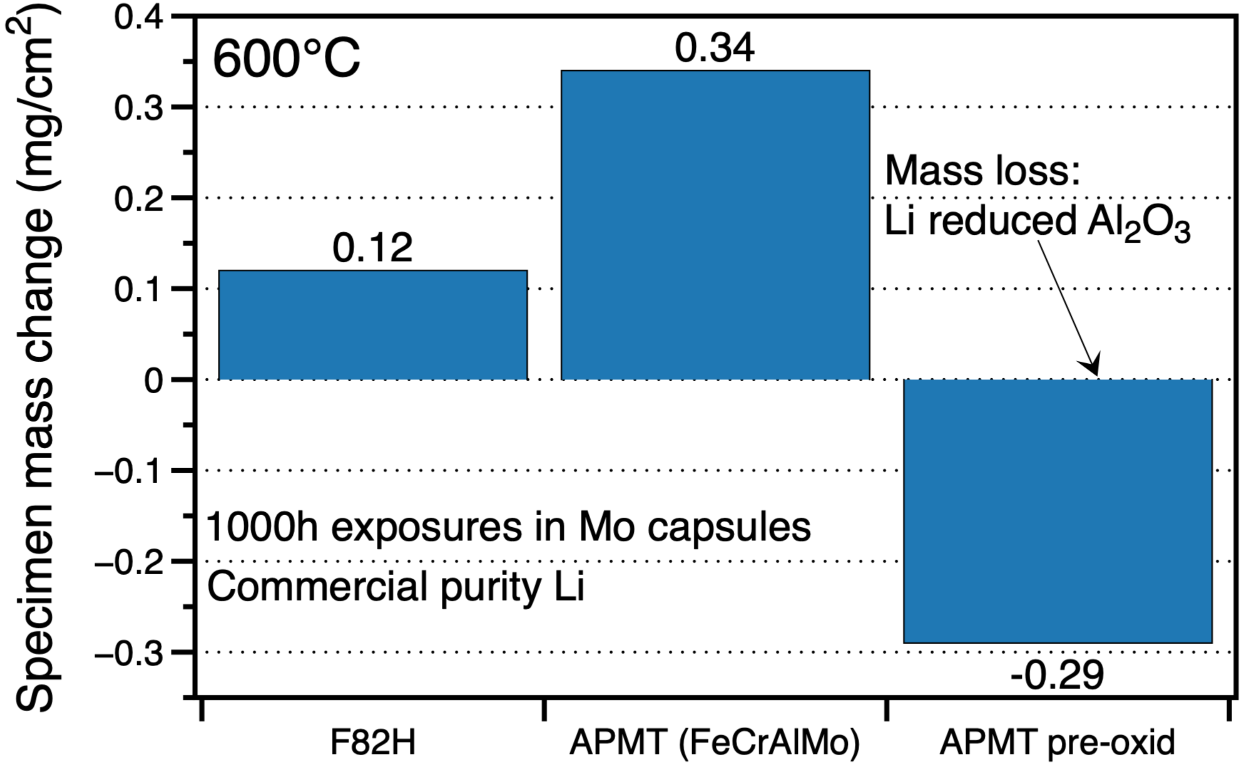
Lots of focus on Cr





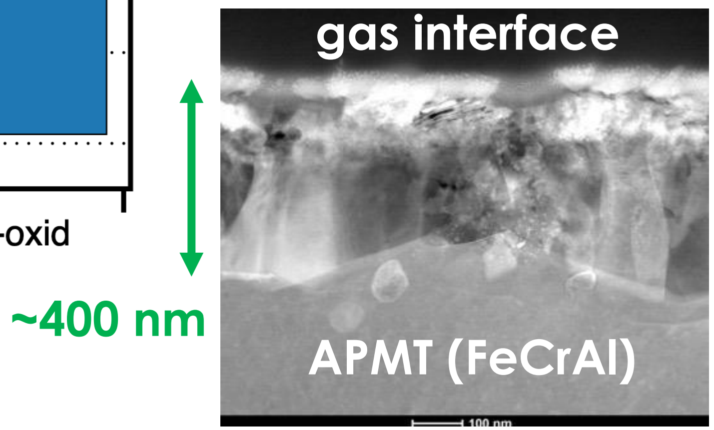
Li capsule testing: minimal mass changes at 600°C/1000 h

Mass change after 1000h in Mo capsule



F82H: Fe-8Cr-2W
APMT: Fe-20Cr-5Al-3Mo+Y,Zr,Hf,Ti,O
Preox = pre-oxidation for 2h at 1000°C

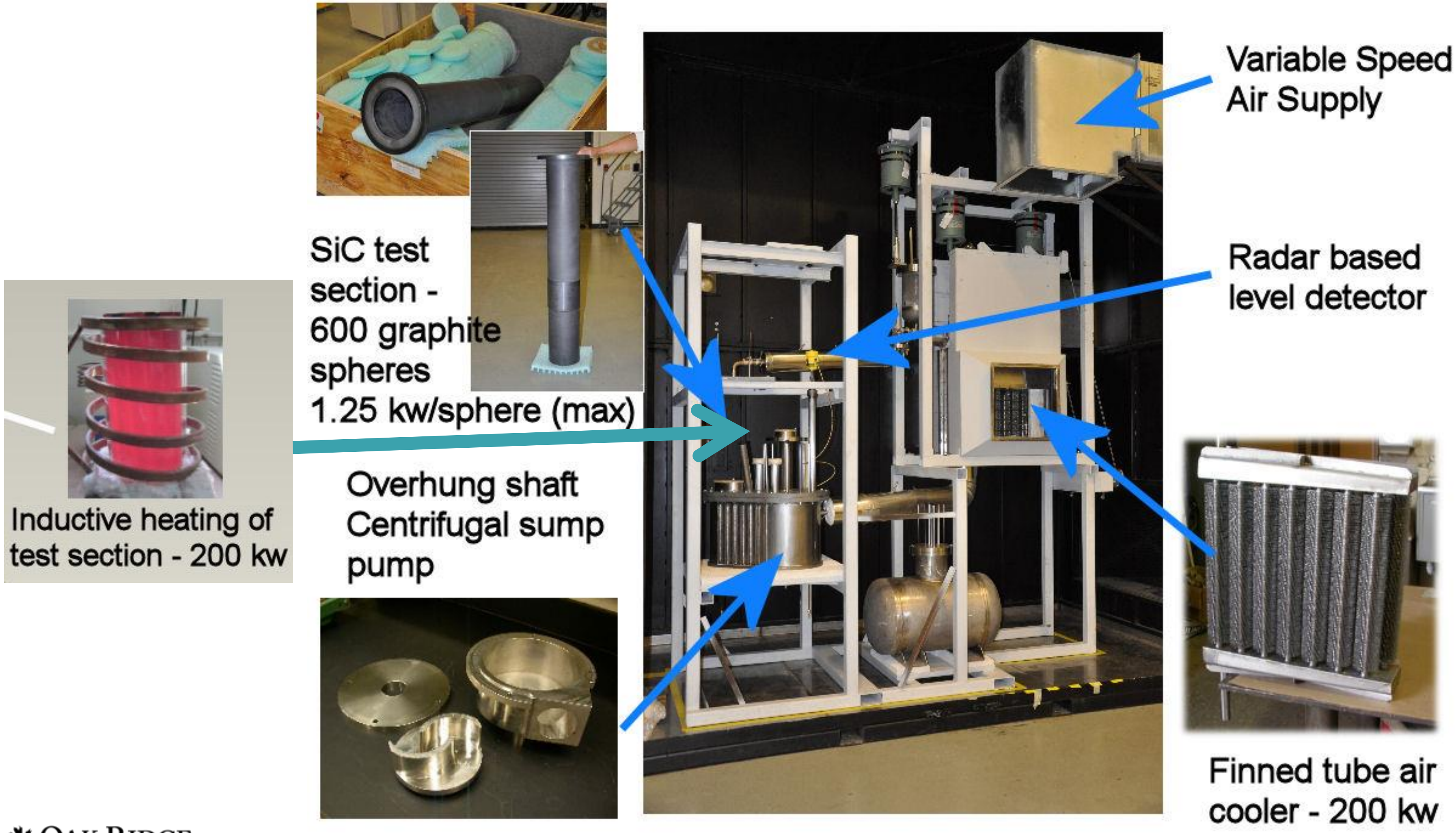
Thermodynamics:
$6Li+Al_2O_3 \rightarrow 3Li_2O+2Al$



Static capsule testing:

F82H: OK with Li at 600°C

ORNL FLiNaK pumped loop: this is where we need to be. But we first learn about compatibility on inexpensive TCLs



ORNL compatibility research has several current tasks

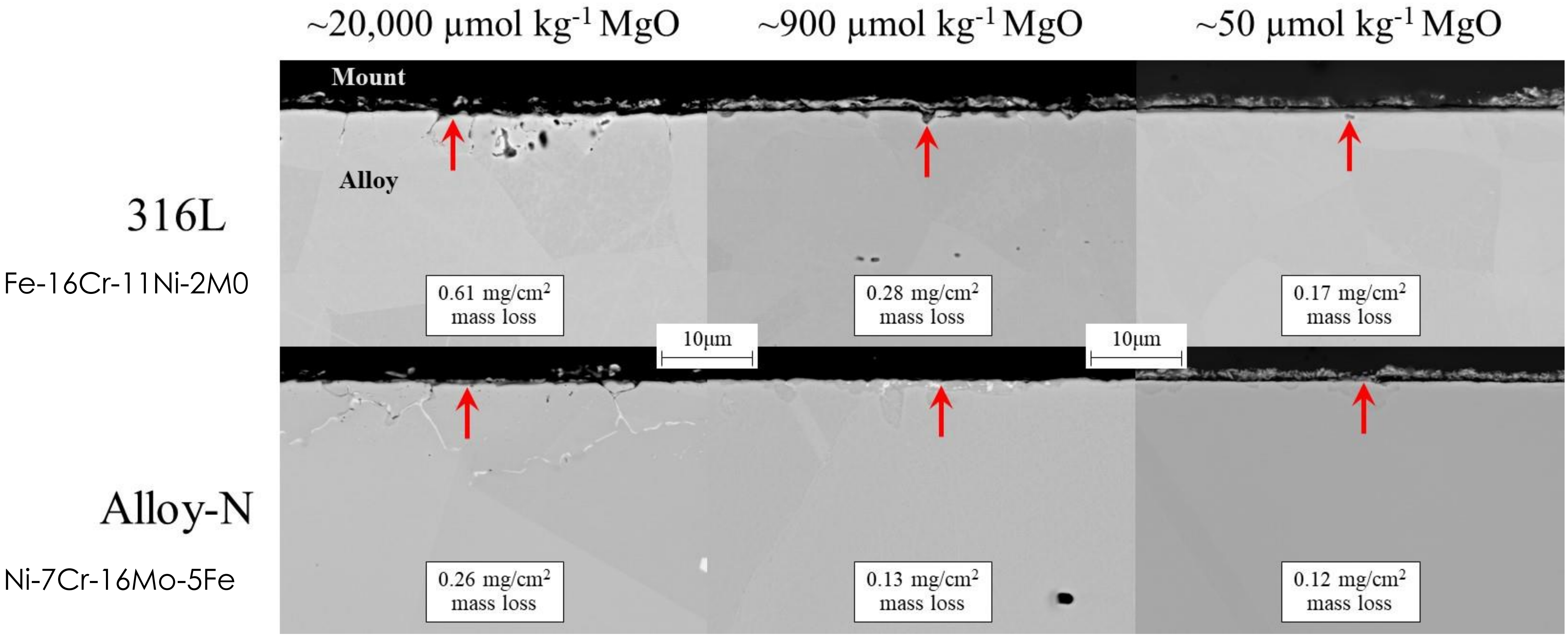
- **US DOE FESS LM PFC project (2020-2025)**
  - Investigating liquid metal **embrittlement of F82H (Fe-8Cr-2W) in Li**
- **US-Japan FRONTIER emphasis on Sn (2019-2024)**
  - Pre-oxidized FeCrAl (ODS, APMT): Sn thermal convection loop (2021)
  - HFIR irradiation pre-oxidized FeCrAl in Sn at 400°C (0.8 dpa in 2022)
- **US DOE Blanket & Fuel cycle project (2019-2024)**
  - ORNL Pb-Li project ended 2019 (4 monometallic APMT (FeCrAlMo) loops)
  - More fusion relevant materials in **flowing Pb-Li** (APMT tubing)
    - TCL #5: SiC, ODS FeCrAl (700°C peak, completed April 2020)
    - TCL #6: SiC, Al-coated RAFM (650°C peak, completed in September 2021)
    - **TCL #7 : SiC, Al-coated RAFM (650°C peak, 2000 h operation completed Sept. 2023)**
- **ORNL SEED: explore steel-$Be_{12}Ti$ interaction in FLiBe (2023)**
  - Initial static capsule testing in FLiBe at 550°-750°C in September 2023

Fusion liquid physical properties and compatibility TRL

Property	Li	Pb-Li	Sn	FLiBe
Melting Temp. (°C)	**181**	235	232	**459**
Density (g/cm^3)	**0.5**	**9.9**	6.5	2.0
Viscosity ($N{\bullet}s/m^2$)	0.0006	**1.4**	0.002	0.07
Heat capacity (J/kg•K)	**4170**	190	248	2414
Thermal Conductivity (W/m•K)	**65**	25	33	**1.1**
Electrical Conductivity (μΩ•cm)	25	1	48	0.4
Compatibility TRL	**high**	**highest**	**low**	**lower**
Thoughts	MHD mitigation, No SiC, No Ni	Radiation? Magnetic field?	Corrosive	??

All concepts are far from where they need to be for designing DEMO/FPP

Please don't study impure halide salts…it is well-known

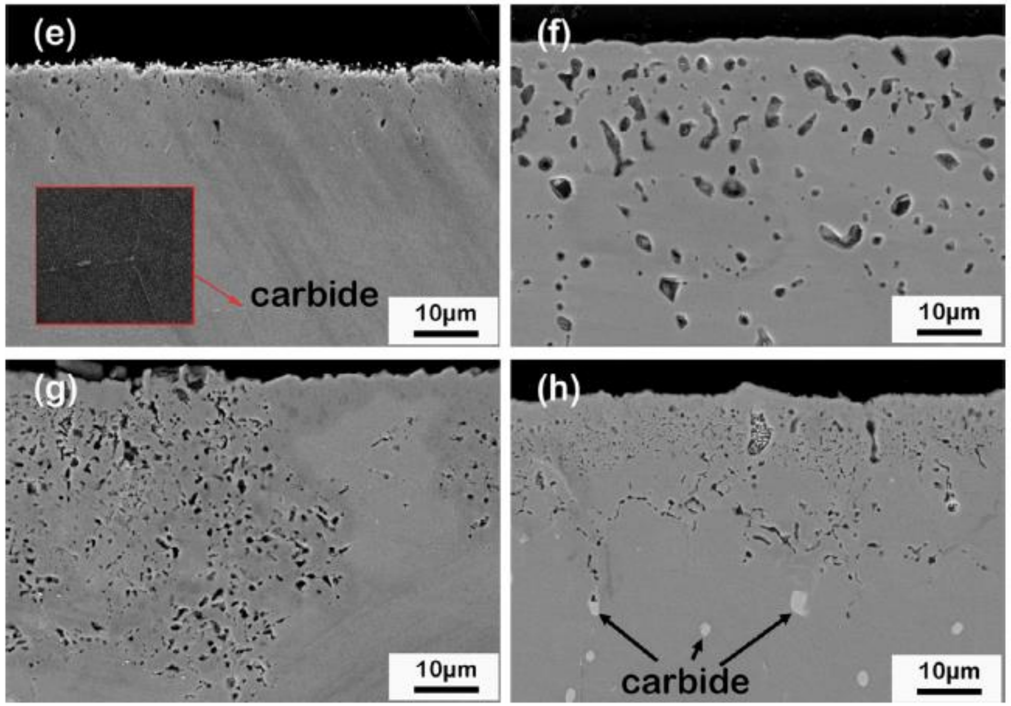


- Water
- Oxygen
- Metals ($NiCl_2$ + Cr -> $CrCl_2$ + Ni)

Are chloride salts really corrosive?

Sun 2018: 700°C/100h Na-K-Mg-Cl

C22: Ni-22Cr-13Mo 600: Ni-16Cr-9Fe



625: Ni-22Cr-9Mo 230: Ni-22Cr-13W

Raiman 2018: data analytics

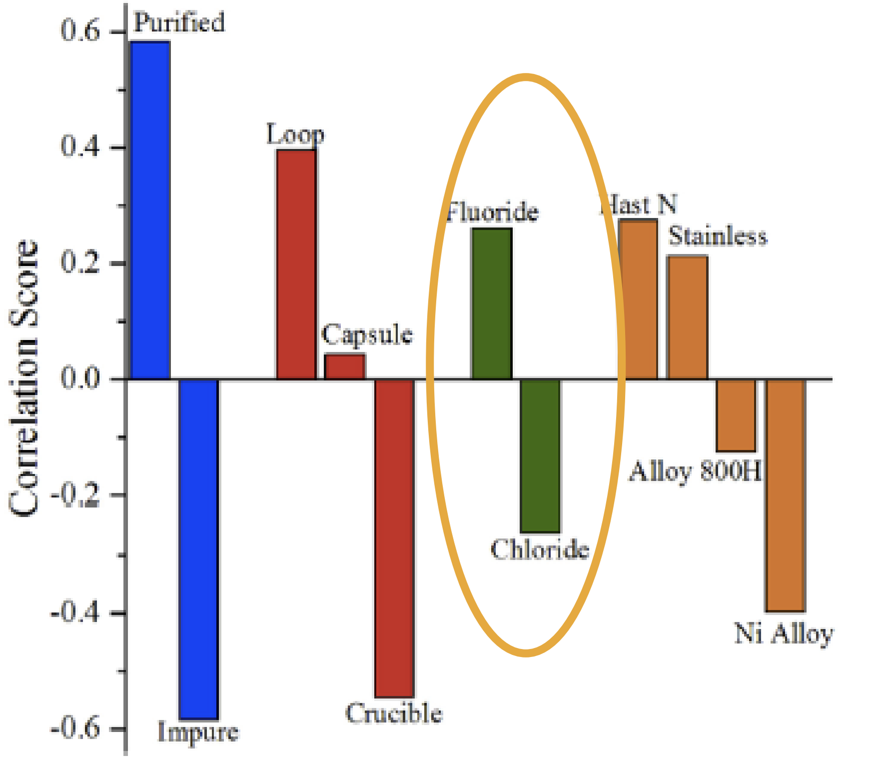
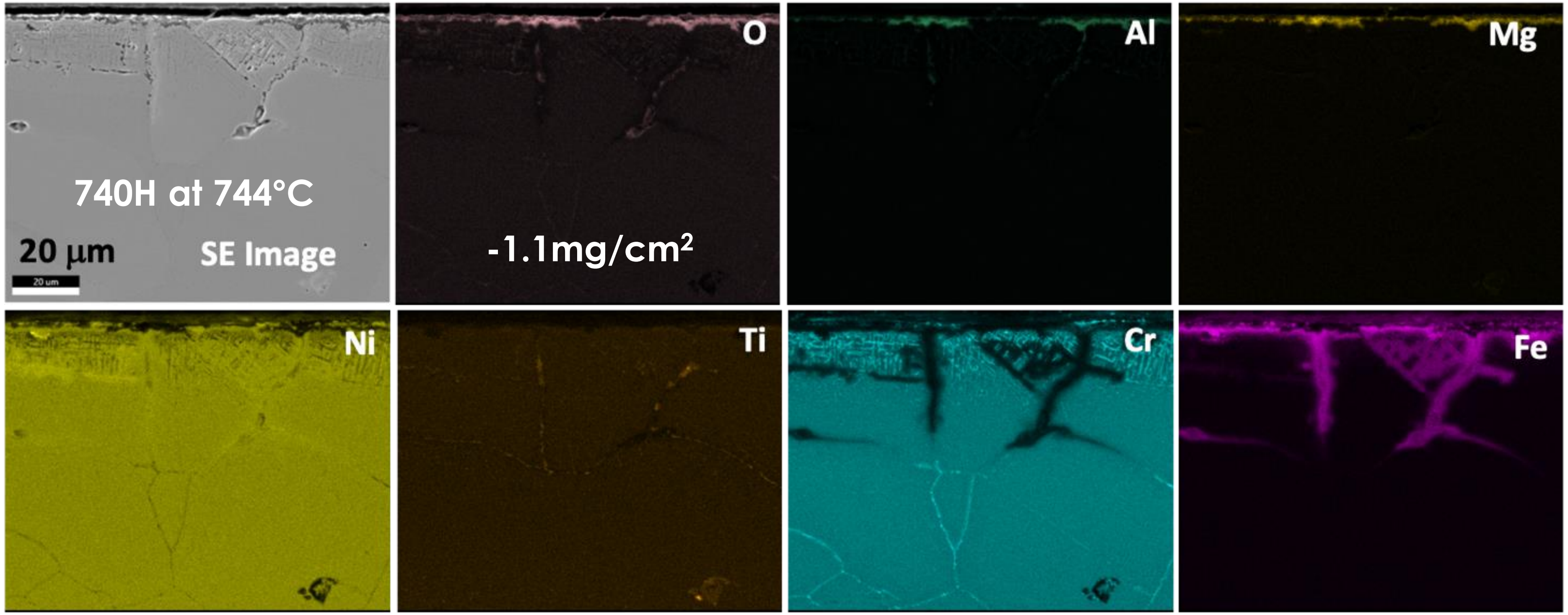


Fig. 8. Correlation analysis result for experimental settings. More positive are correlated with lower corrosion rates, while more negative scores are correlated with higher corrosion rates. The variables depicted are, from left to right: salt purity, experiment type, salt type, and sample material 26.

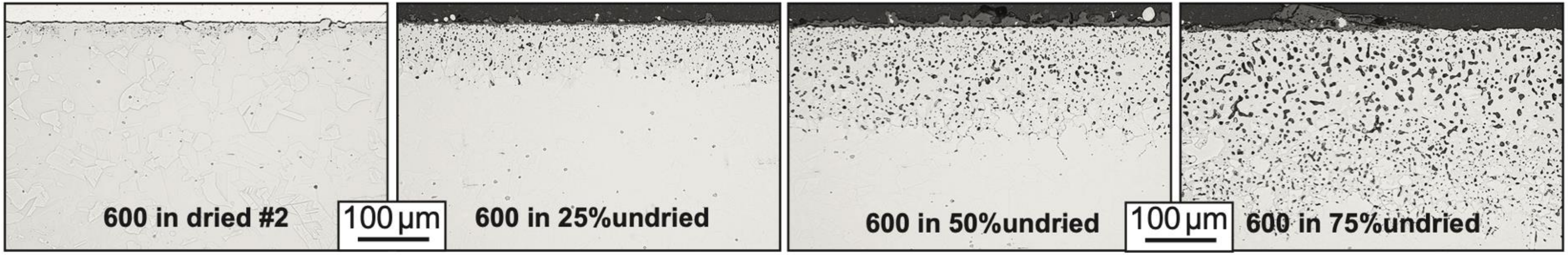
Minimal attack: flowing dried Cl salt ~650°-750°C, 1000h

New TCL design



- 740H: Ni-24.5Cr-20.6Co-1.5Nb-1.4Al-1.4Ti-0.3Mo at 744°C
  - Precipitation strengthened: ~2X strength of conventional Ni-based alloy
- Loop made from C276: Ni-16Cr-15Mo-6Fe-3.5W
  - Fe deposited from Fe-rich coatings in loop (dissolved)
  - Surface Oxide: >50,000 µmol O/kg in dried salt vs. 197 µmol O/kg purified

How do you get deeper attack in static Cl salt? (100h/800°C)



-0.76 mg/cm² | -0.07 mg/cm² | +2.1 mg/cm² | -6.5 mg/cm²

- Alloy 600 capsule + specimen (Ni-16Cr-9Fe): 100h/800°C
  - Welded capsule: no O_2/H_2O ingress during exposure
- Dried commercial salt (20.1%K-12.9%Mg-1.6%Na-65%Cl)
  - Dried at 550°C (below the 650°C recommendation)
  - Adding salt straight from the bucket
  - ~5wt.%H_2O in salt (manufacturer estimate)
  - 100% 'bucket' salt ruptured the capsule at 700°C

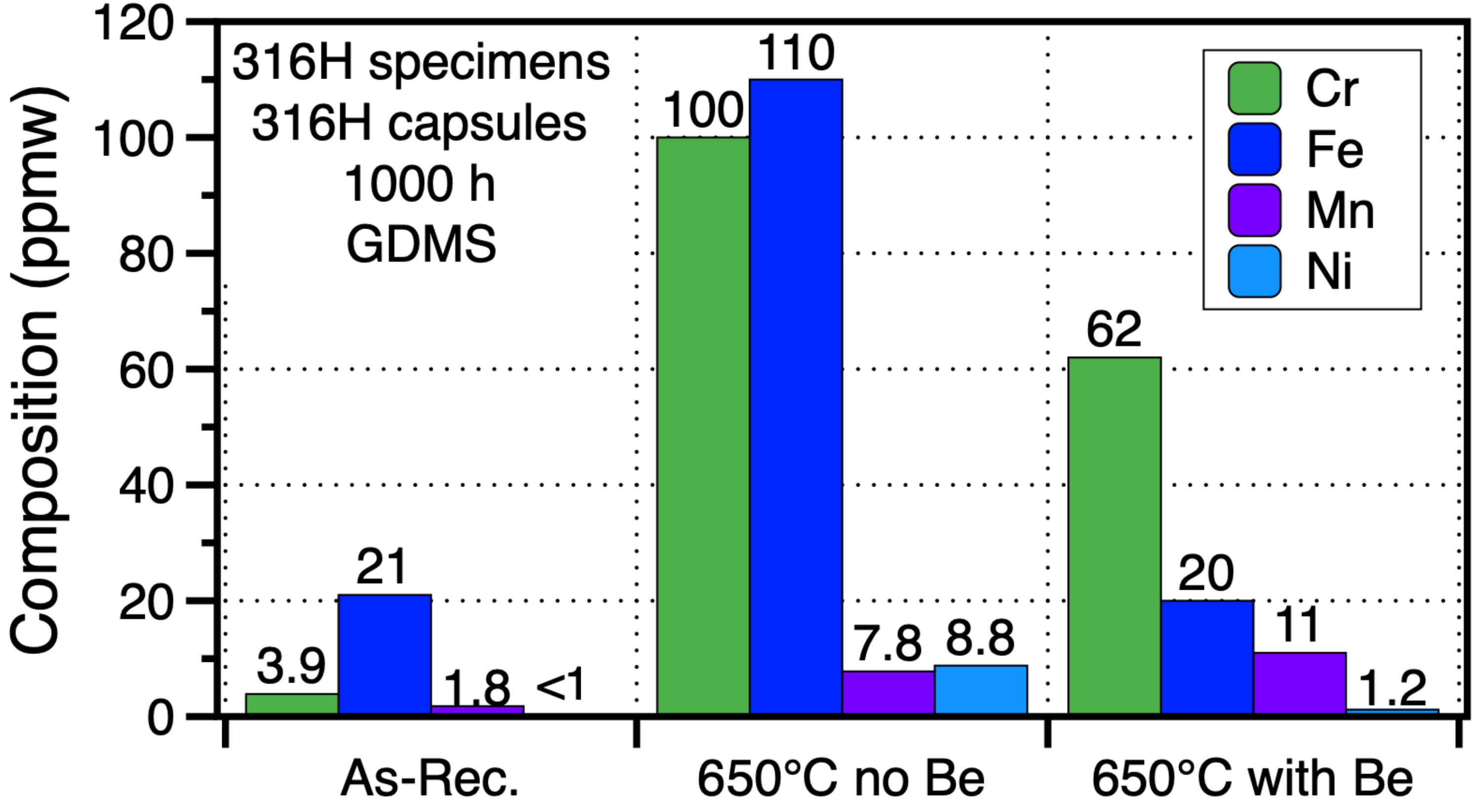
Commercial salt

SS outer capsule

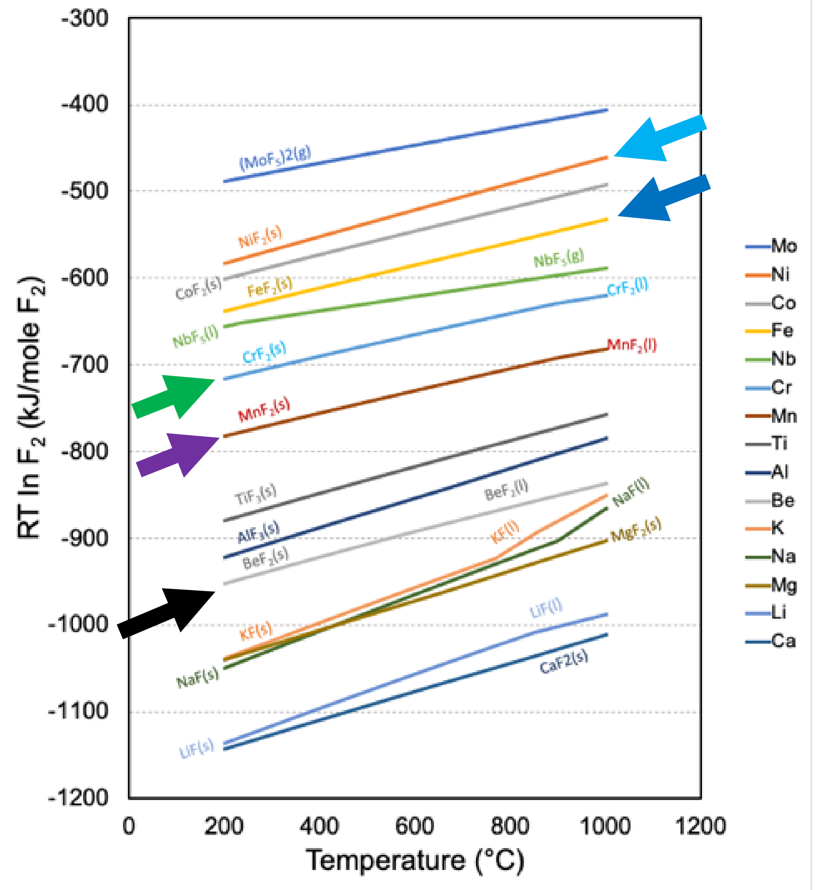
600 in 600

Measuring salt chemistry is essential to understanding effect

316H: 68wt.%Fe-16.5Cr-10.4Ni-1.9Mo-1.5Mn-0.3Si-0.4Cu-0.034C



0.29±0.03 mg/cm^2 0.16±0.04 mg/cm^2



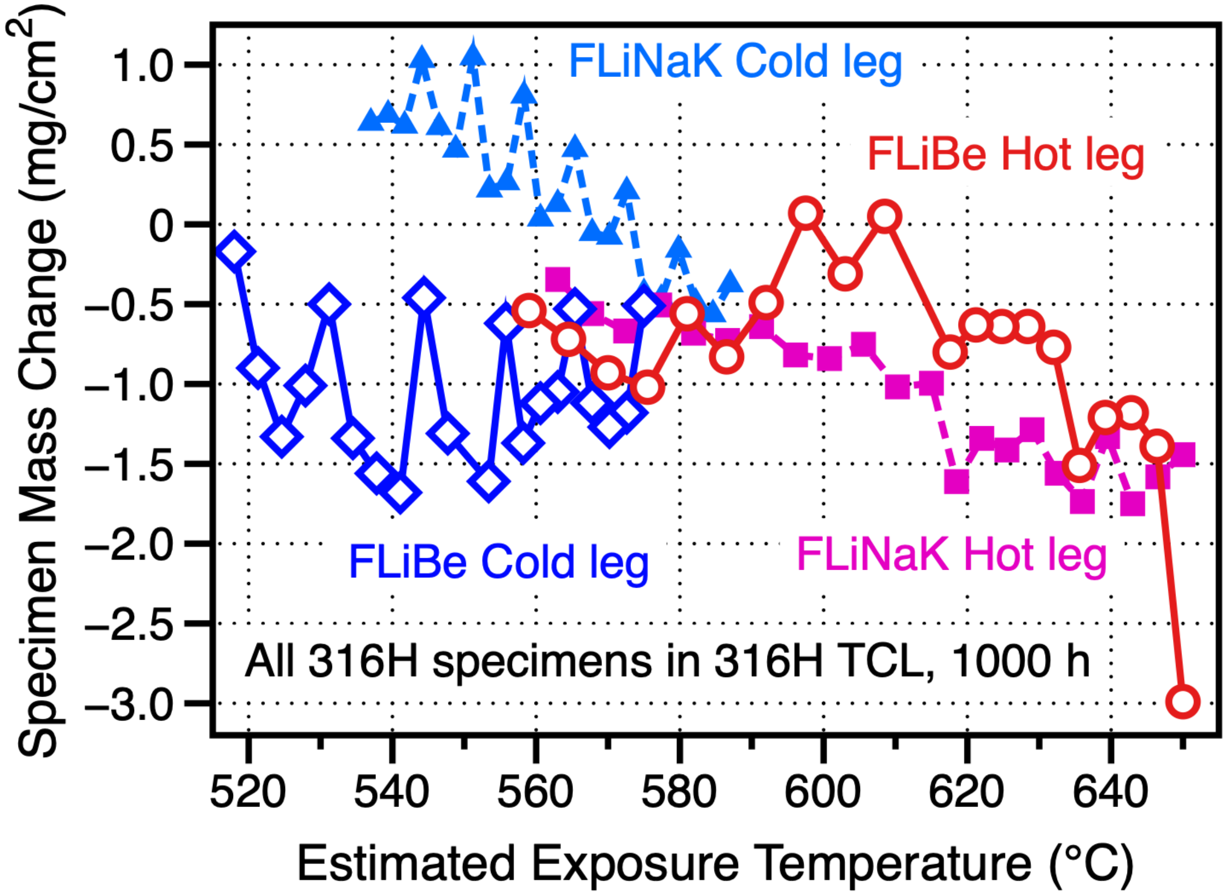
FLiBe: low initial impurities

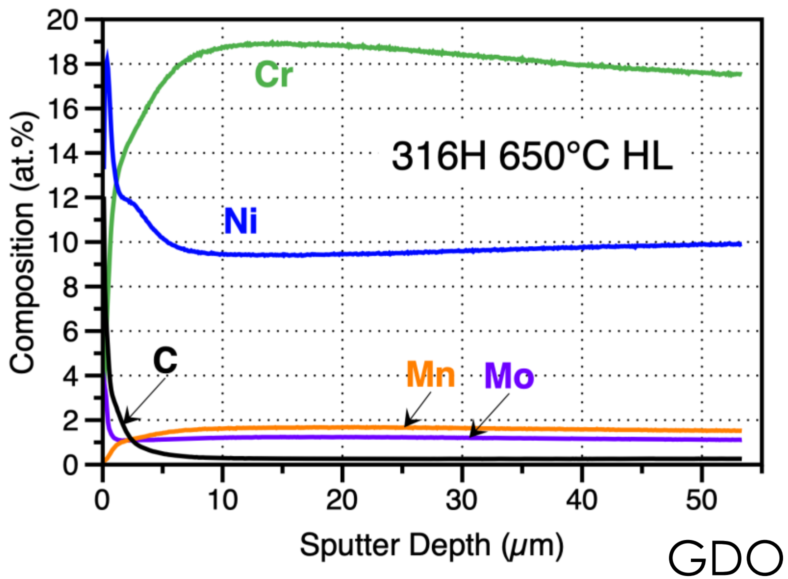
No Be: Cr **and** Fe increase ≥90 ppm, Ni increase

With Be: **no Fe and less Cr** (~45% less mass loss)

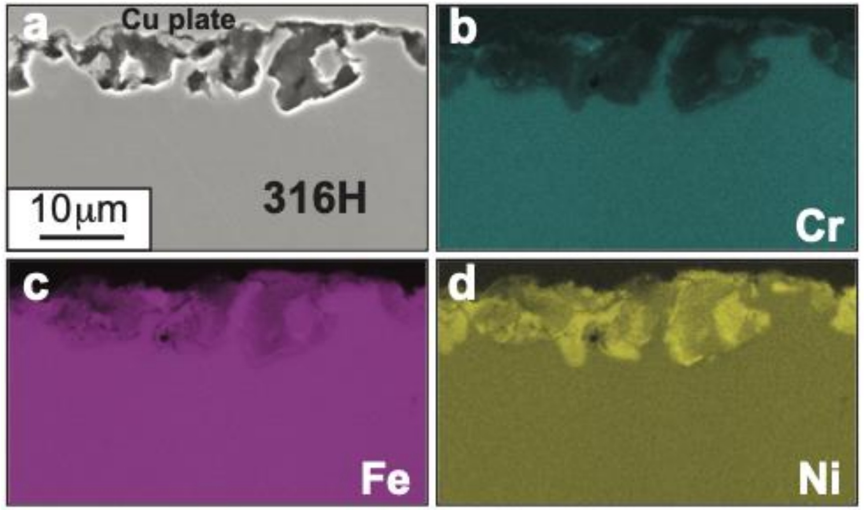
Next phase of modeling: flowing salt conditions
Too many proposed salt combinations for experiments

Mass gain on cold leg





GDOES profiles

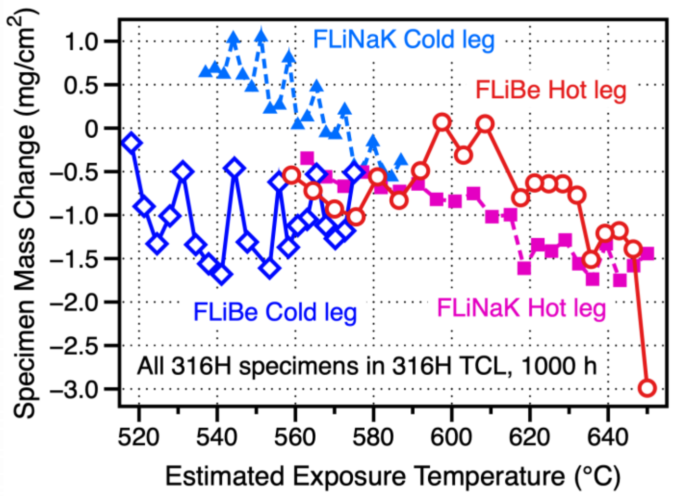


- Similar 316H TCL experiments with 2 salts

Thoughts on 316H in FLiNaK and FLiBe at ~550°-650°C

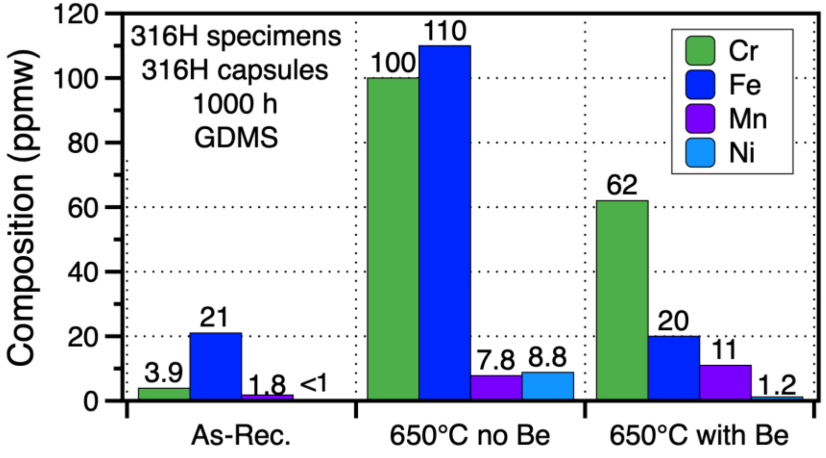
Reasonable compatibility

- Purified salts
- Small mass changes
- Initial results suggest reasonable compatibility with 316H stainless steel



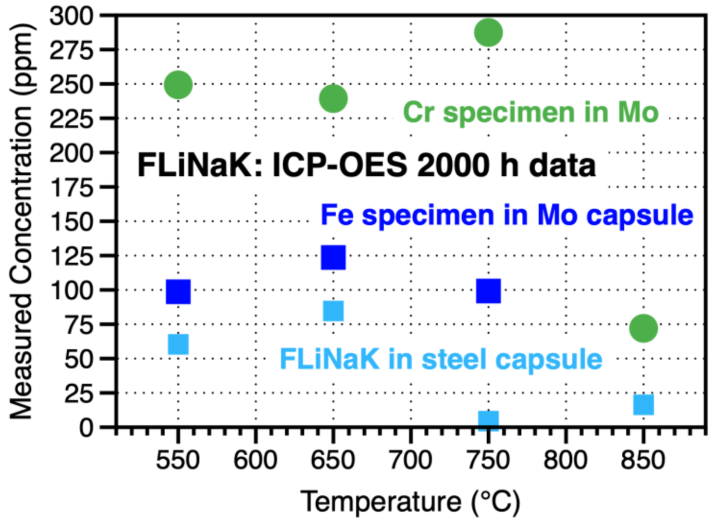
Fe and Cr both dissolving

- Evidence for Fe dissolution in FLiNaK & FLiBe capsules + TCL
- Fe dissolves after Cr depleted
  - Need validation
- Evidence for mass transfer of Fe in FLiNaK TCL

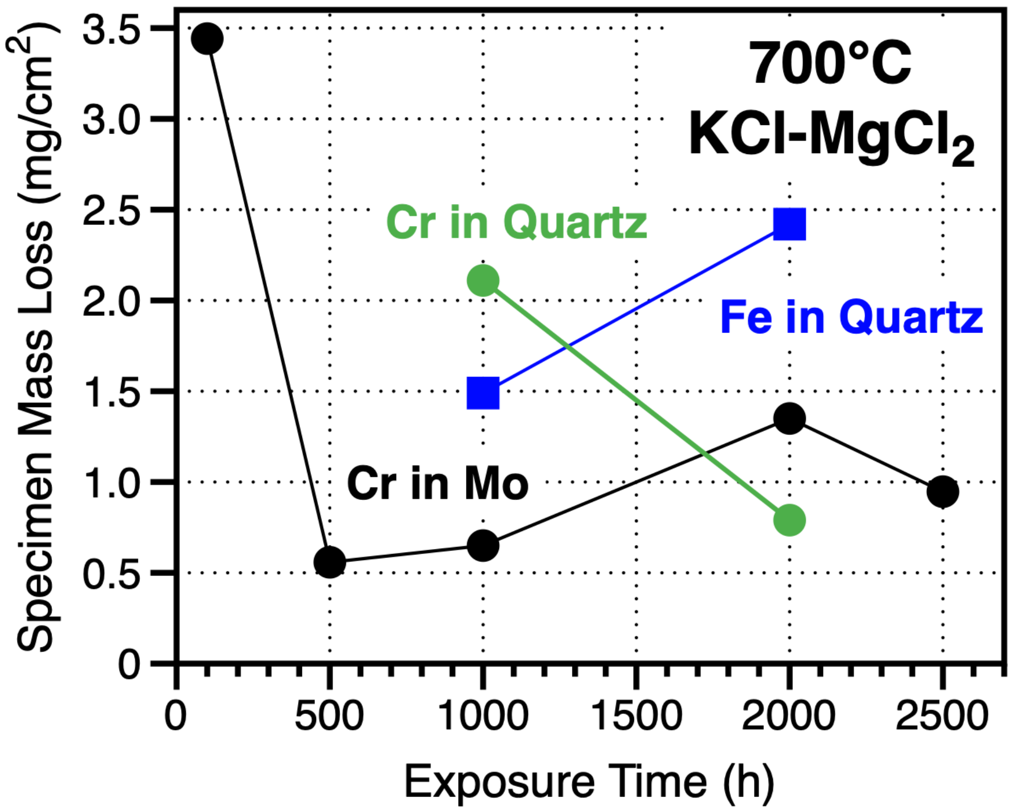


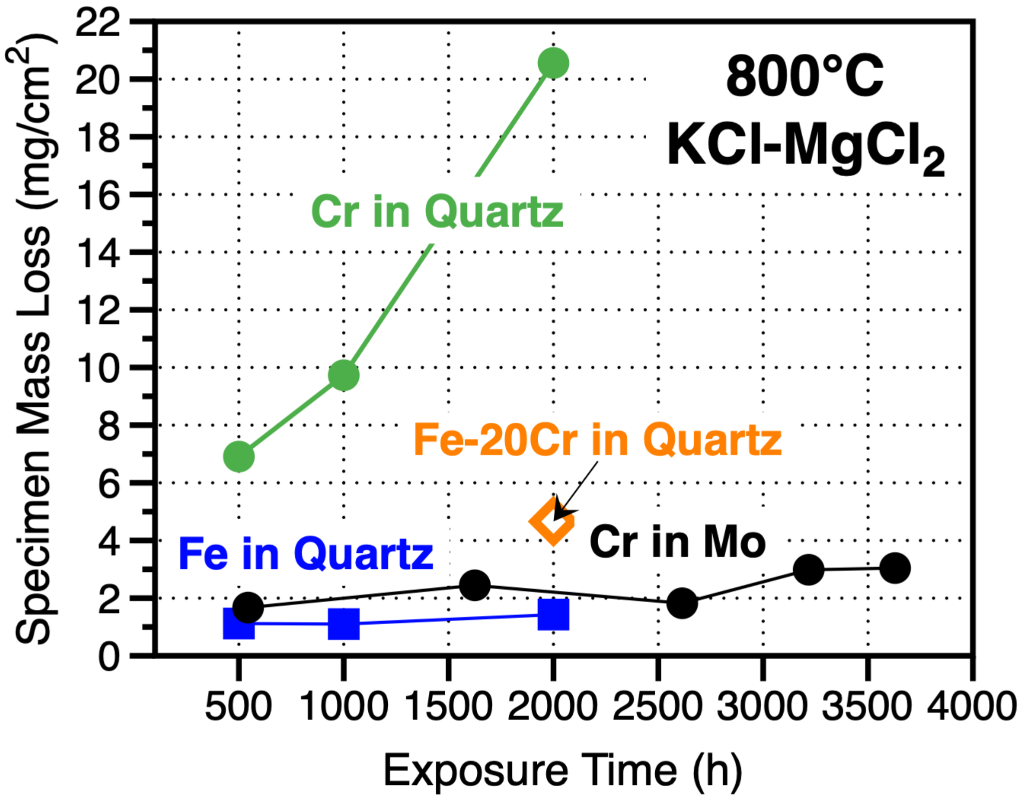
Modeling approach

- Assumes dissolution proportional to activity
- Need dissolution data
  - Both Cr and Fe
  - Impurity effects?
    - Need more data!



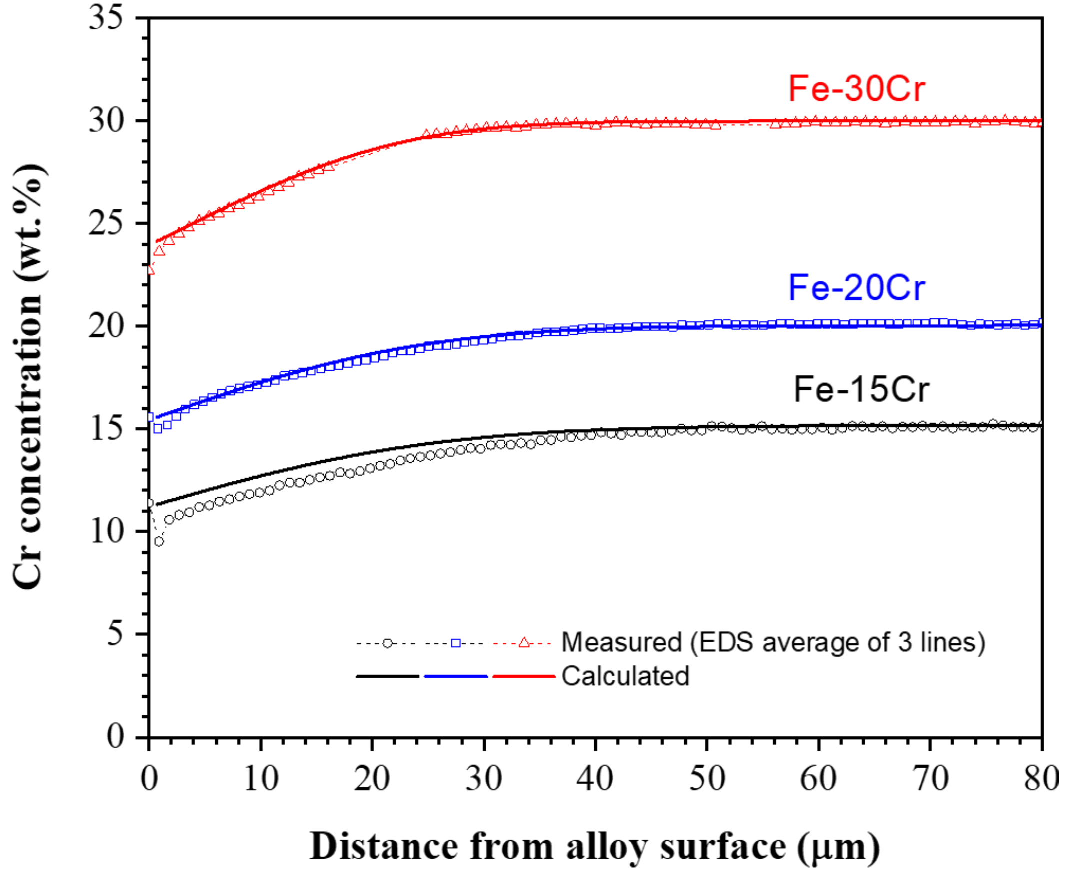
Solubility experiments: Cr and Fe in quartz & Mo capsules
Quartz is easy but you'll be sorry…

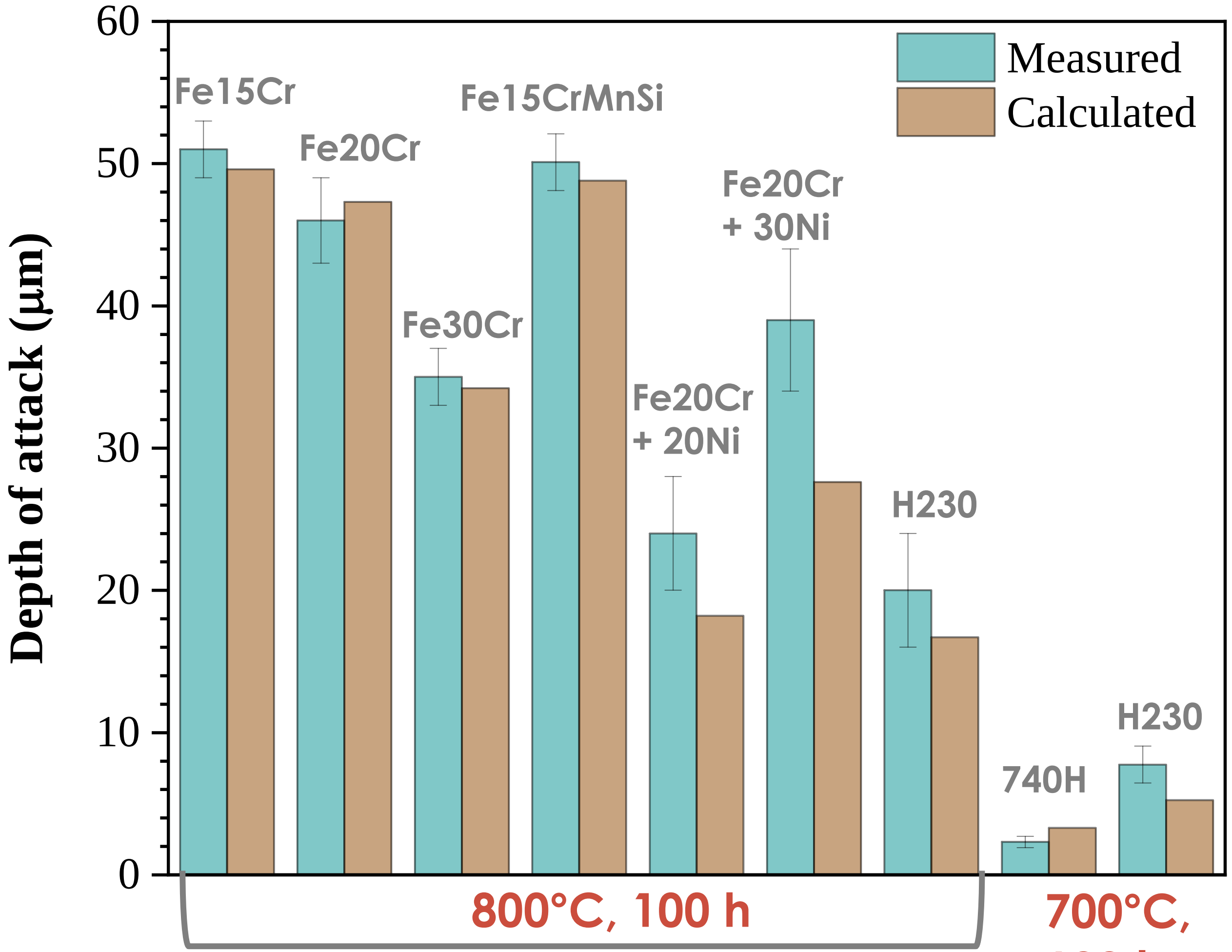




Model can predict Cr depletion and depth of Cl salt attack across different alloy chemistries at different isothermal temperatures: Need dissolution rates for model

KCl:$MgCl_2$, 800°C, 100h

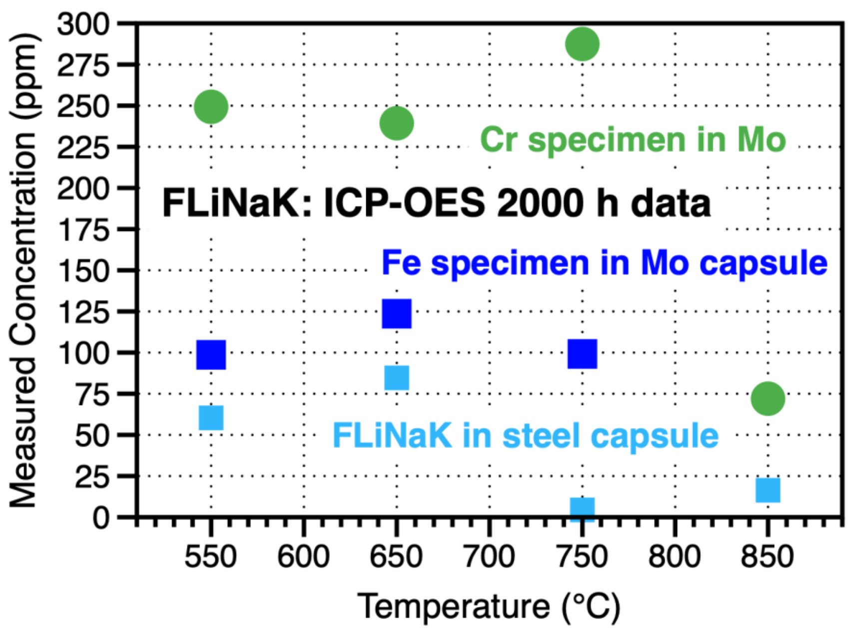


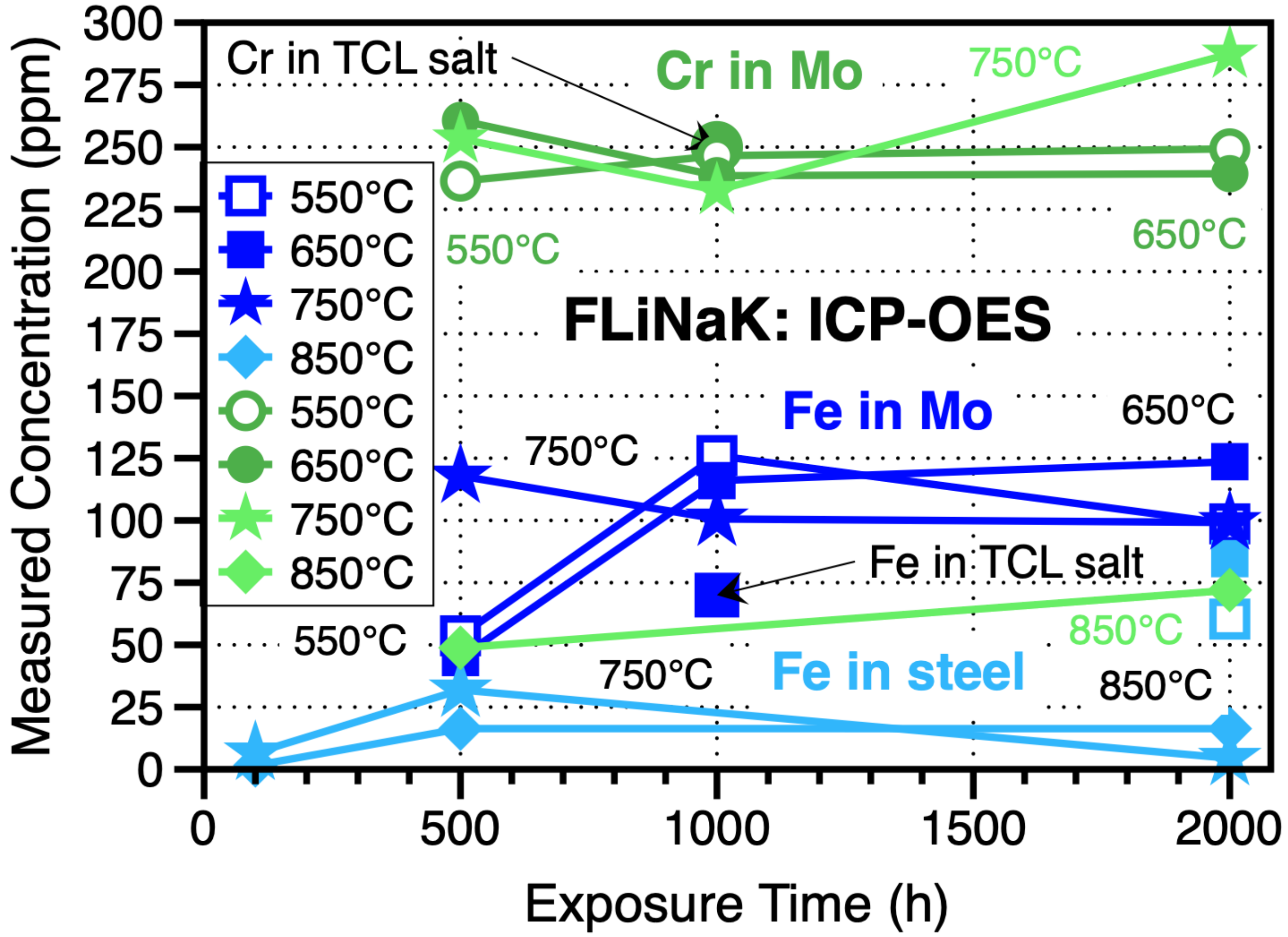


Pillai et al., JNM 2021, Ni-Cr alloys
Pillai et al., **JOM 2023**, Fe-Cr alloys

FLiNaK: curious lack of time effect: saturation?

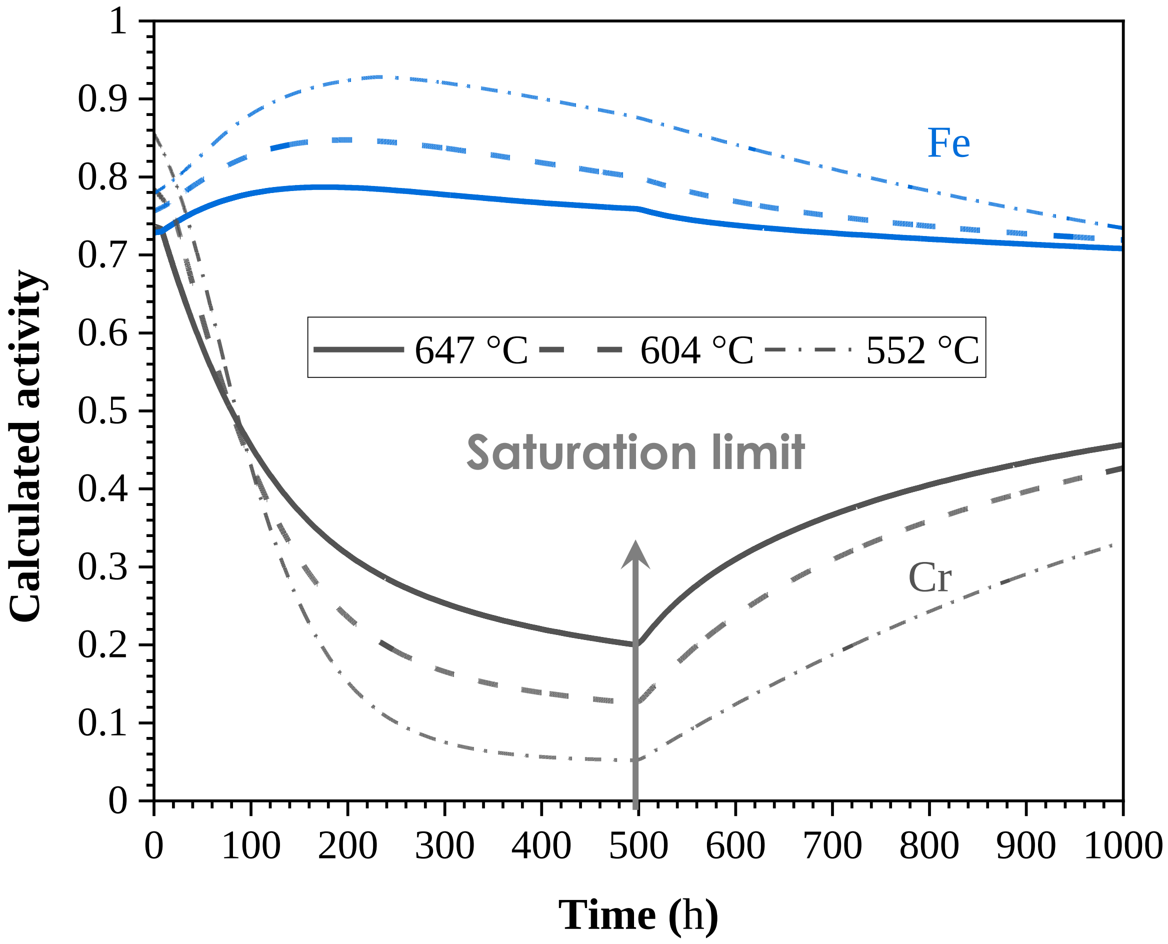
2000 h summary shown before





650°C Cr ppm: capsule = loop!

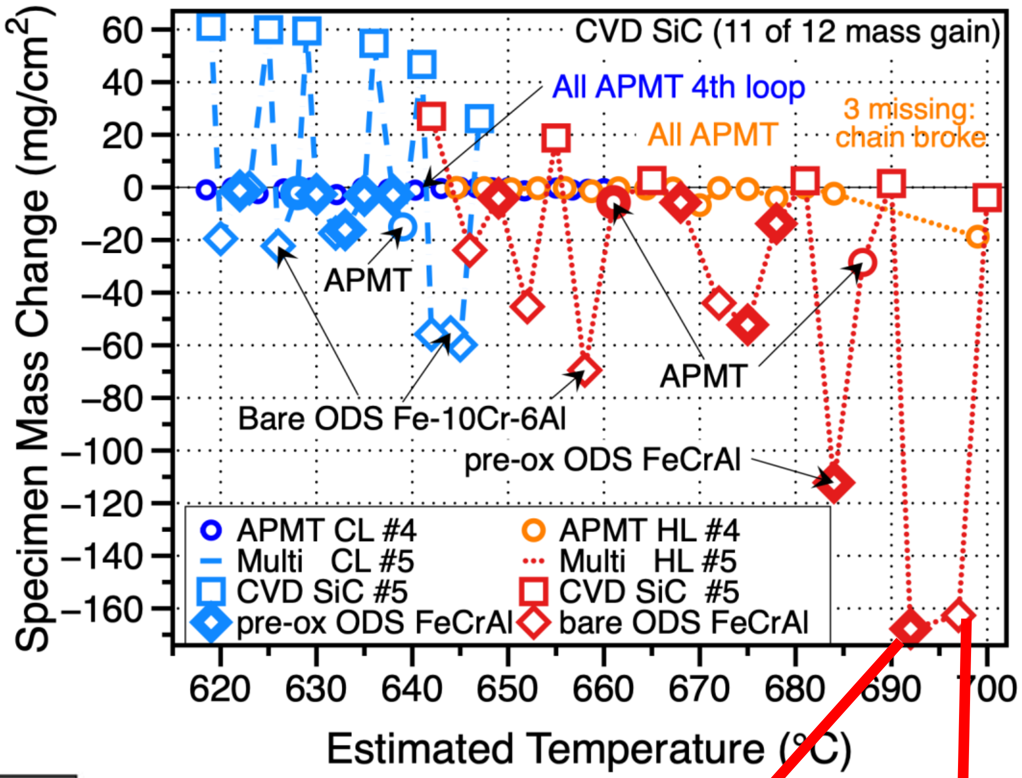
Calculated time evolution of Fe and Cr surface activity shows Fe dissolution begins after Cr is saturated in the salt

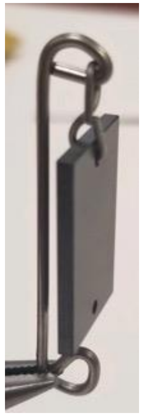


- Saturation limit (~280 ppm) was measured in FLiNaK dissolution tests
  - **~250 ppm in TCL**
  - **Assume Cr stops dissolving and Fe starts dissolving**
- Much slower Fe dissolution rate was derived from dissolution tests
- Validation needed
  - **Longer times**
  - **What if graphite getters Cr?**

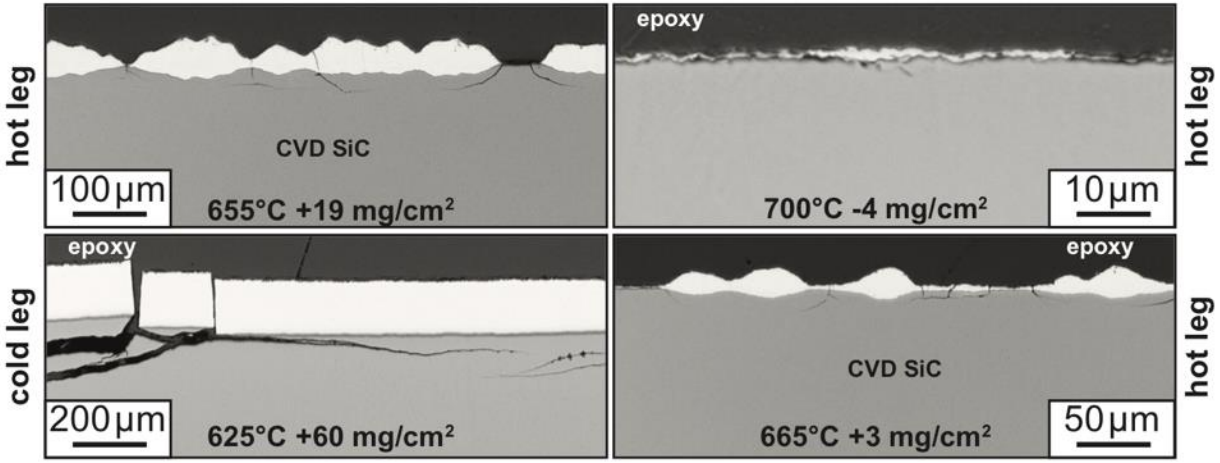
5th PbLi loop: 'Dissimilar material interaction' between SiC & ODS FeCrAl

- High mass changes in Pb-Li
  - CVD SiC gained mass in cold leg
    - Non-uniform (Fe,Cr) carbides + silicides
    - Reaction with Fe and Cr in Pb-Li
  - Large FeCrAl mass losses
    - Acceleration: Fe/Cr removed from Pb
    - Mistake to not-pre-oxidize all specimens
- Conclusion: 700°C is too high!

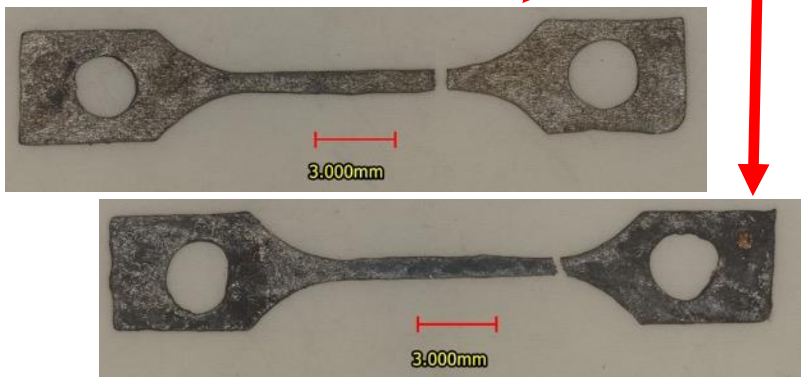




Cross-sections of SiC coupons:

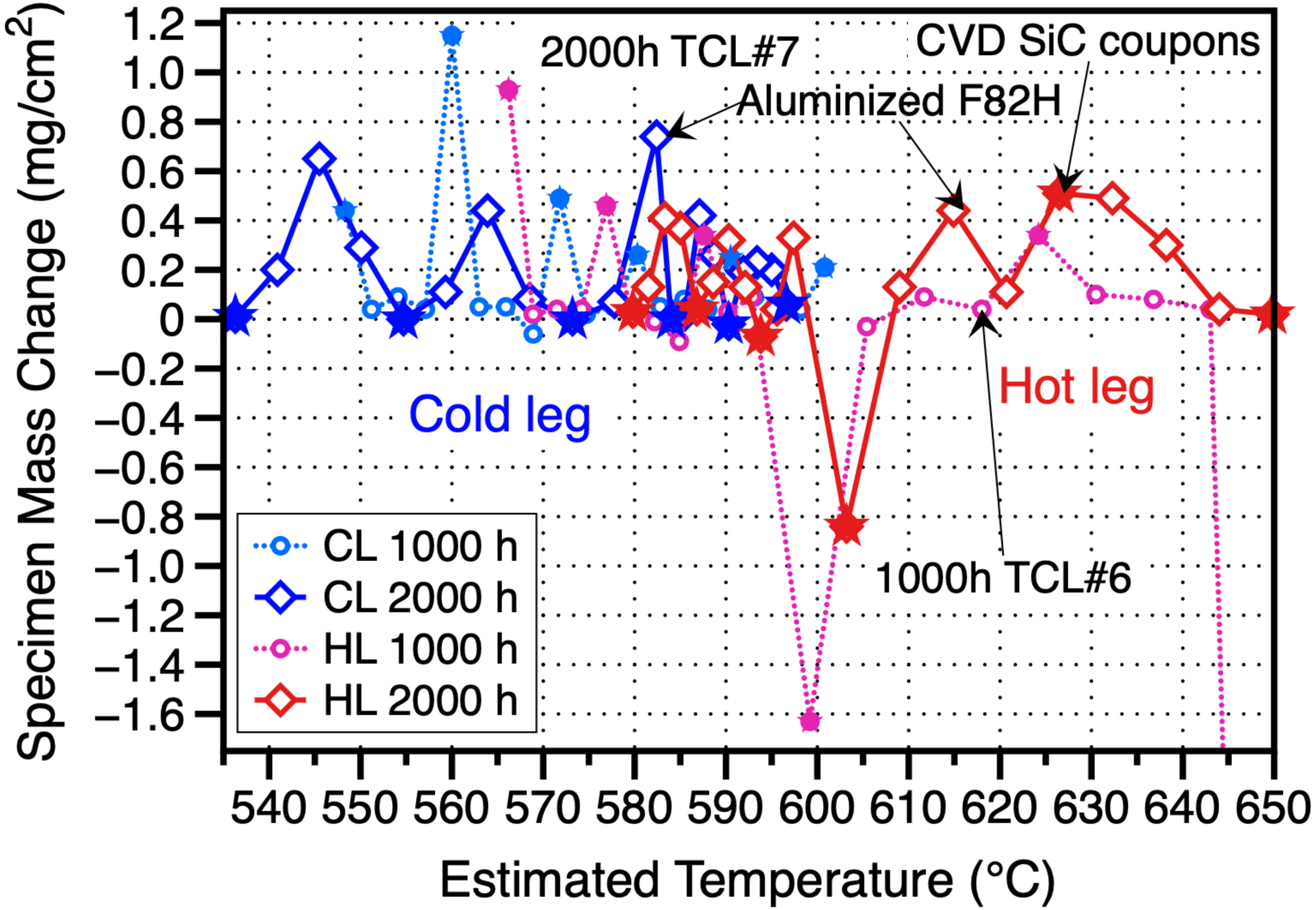


Pre-oxidized ODS FeCrAl

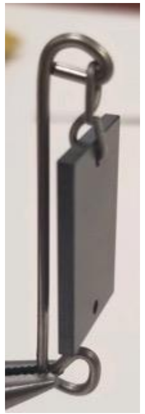


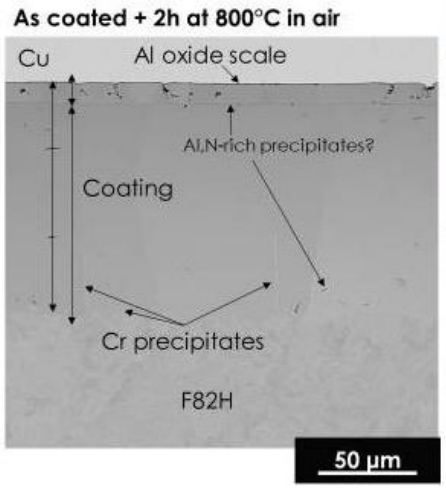
Bare ODS Fe-10Cr-6Al

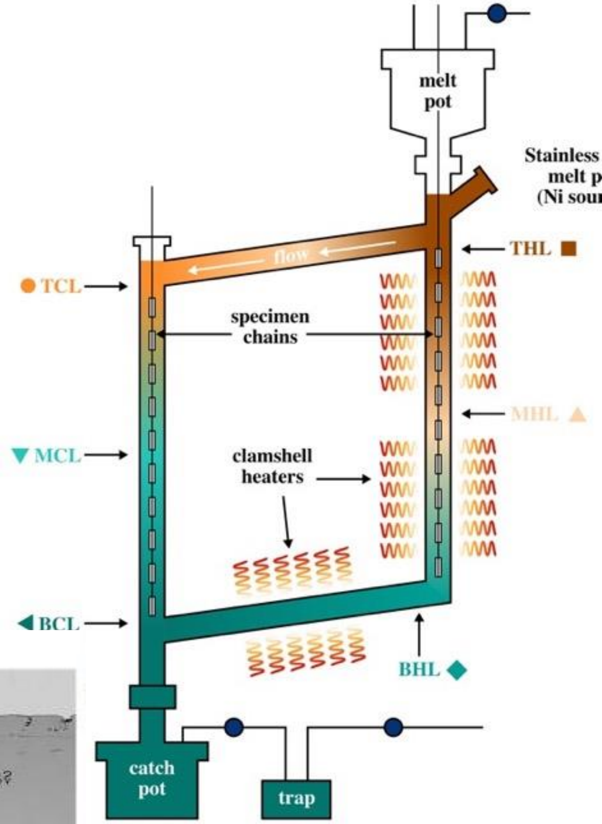
#6 & #7 PbLi TCL results: lowering peak temperature to 650°C (and pre-oxidizing all metal) greatly reduced attack



CVD SiC







Pack aluminized F82H (Fe-8Cr-2W)

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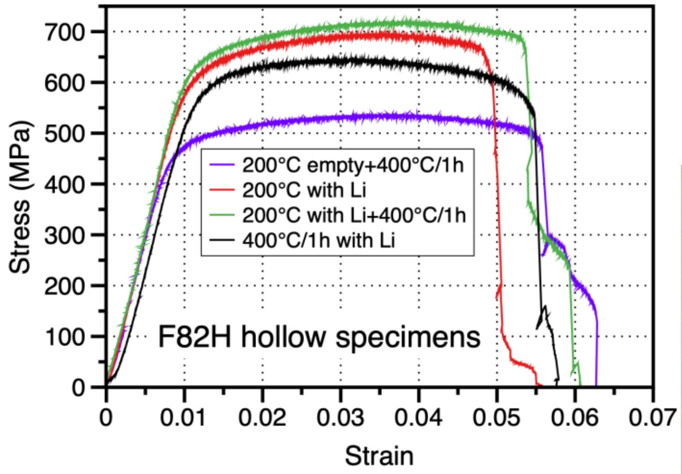
Four different fusion liquid compatibility tasks in progress at ORNL

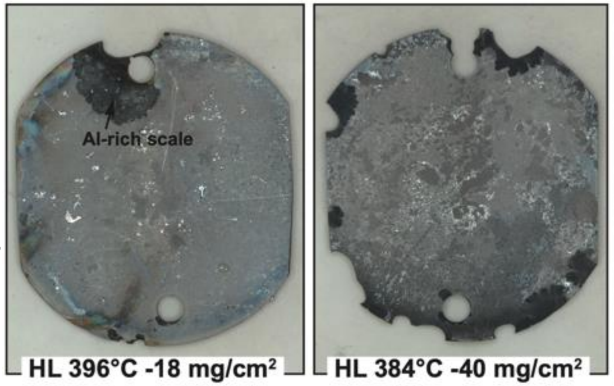
Plasma Facing Comp. (Li)

- Verified LME in hollow specimens with 4340 steel specimen
- No significant LME observed for F82H
  - 200°C tensile/400°C wetting
  - 500°C/500 h anneal



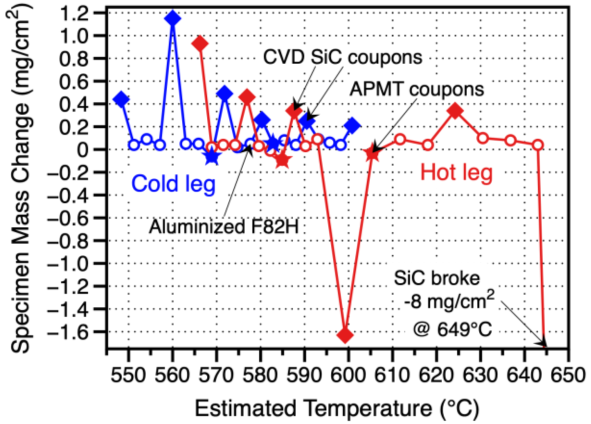
Sn: FRONTIER Task 3

- Flowing Sn loop showed attack
  - Massive FeCrAl dissolution unlike static tests
  - High hot leg loss
    - Al_2O_3 not protective
  - **FeCrAl/Sn not viable**
- Complete HFIR irradiation PIE



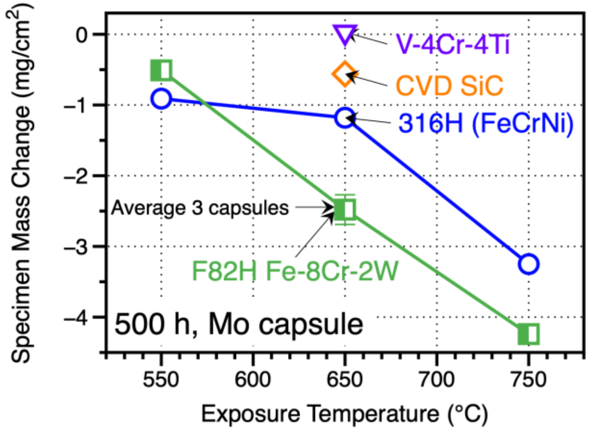
Blanket (PbLi)

- PbLi loop #5: >675°C massive SiC-FeCrAl interaction
- PbLi loop #6: reduced interaction CVD SiC-aluminize F82H: 650°C
- PbLi loop #7 done:
  - 2000 h, less attack than #6

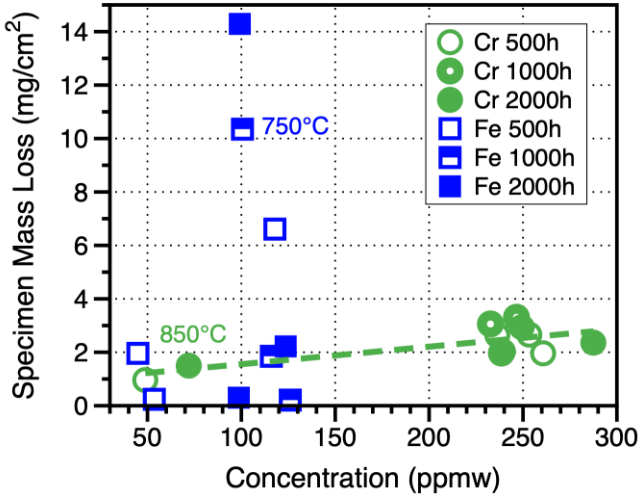


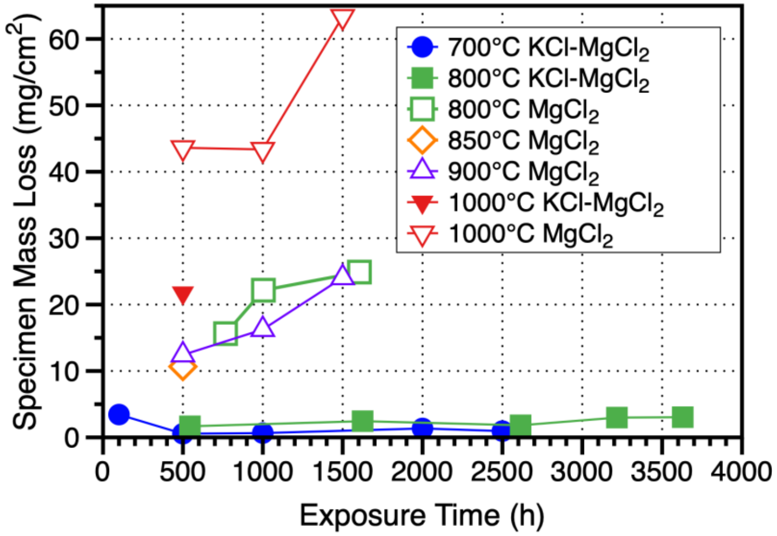
Blanket (FLiBe)

- Limited FLiBe data for fusion-relevant alloys
  - Fe-Cr-W steels
  - SiC composites
  - V-4Cr-4Ti alloys
- Initial static data in Mo capsules
  - Characterization in progress



Clean. **Reliable. Nuclear.**





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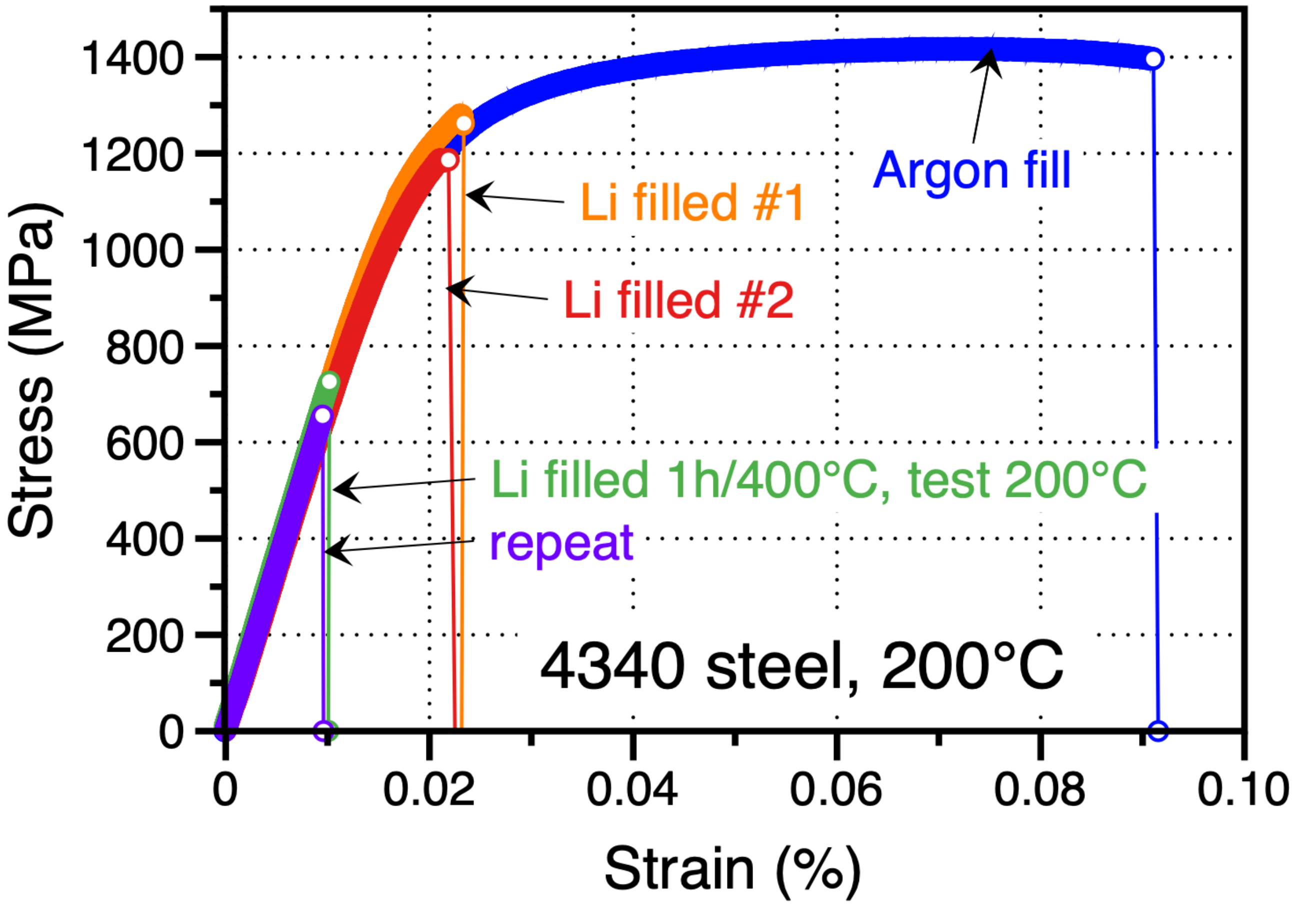
4340 steel: demonstrated hollow specimen methodology

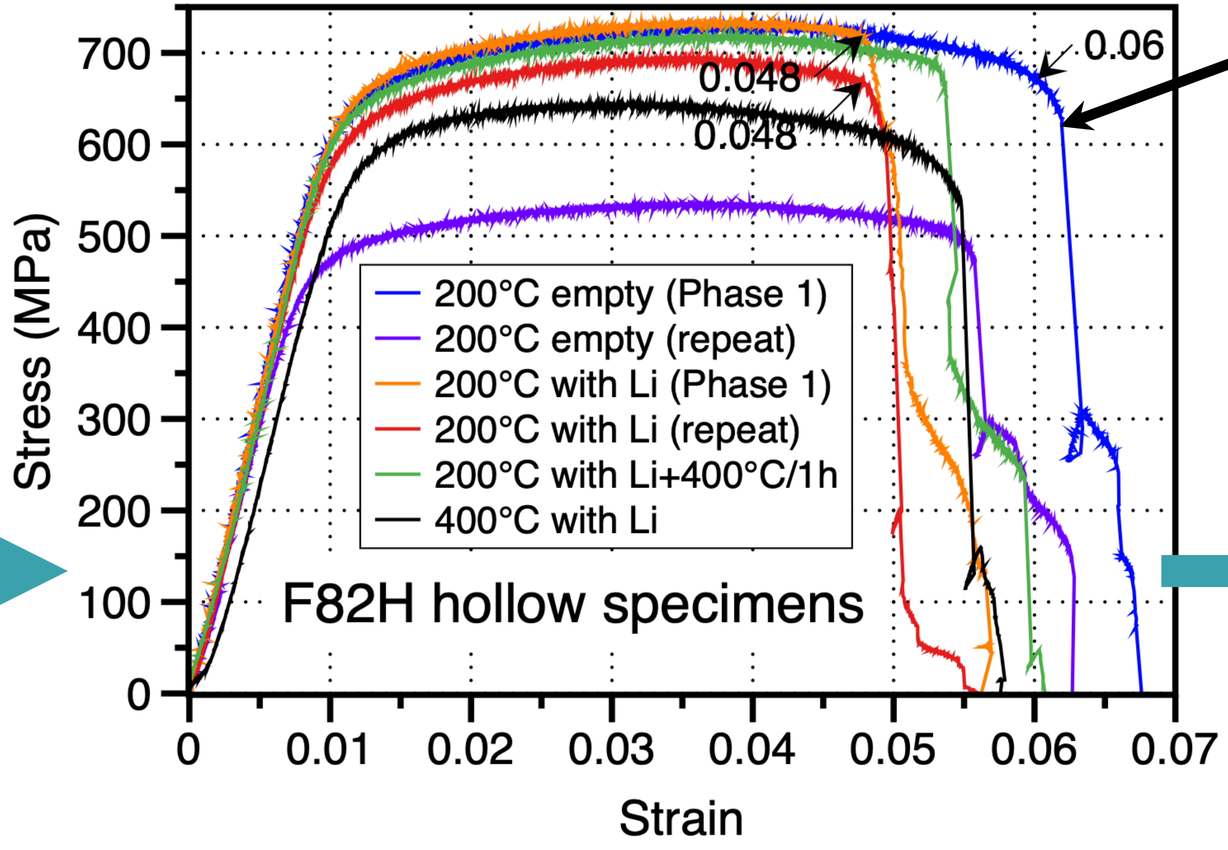


- All 200°C tensile tests, 0.005/mm strain rate
- Plus 400°C/1h anneal for wetting
- Reproducible results

Hollow F82H tensile specimens: no indication of Li embrittlement

Tensile test at 200°C or 400°C: 0.005/min strain rate per ASTM E21

Li-filled F82H: Fe-8Cr-2W tensile specimens

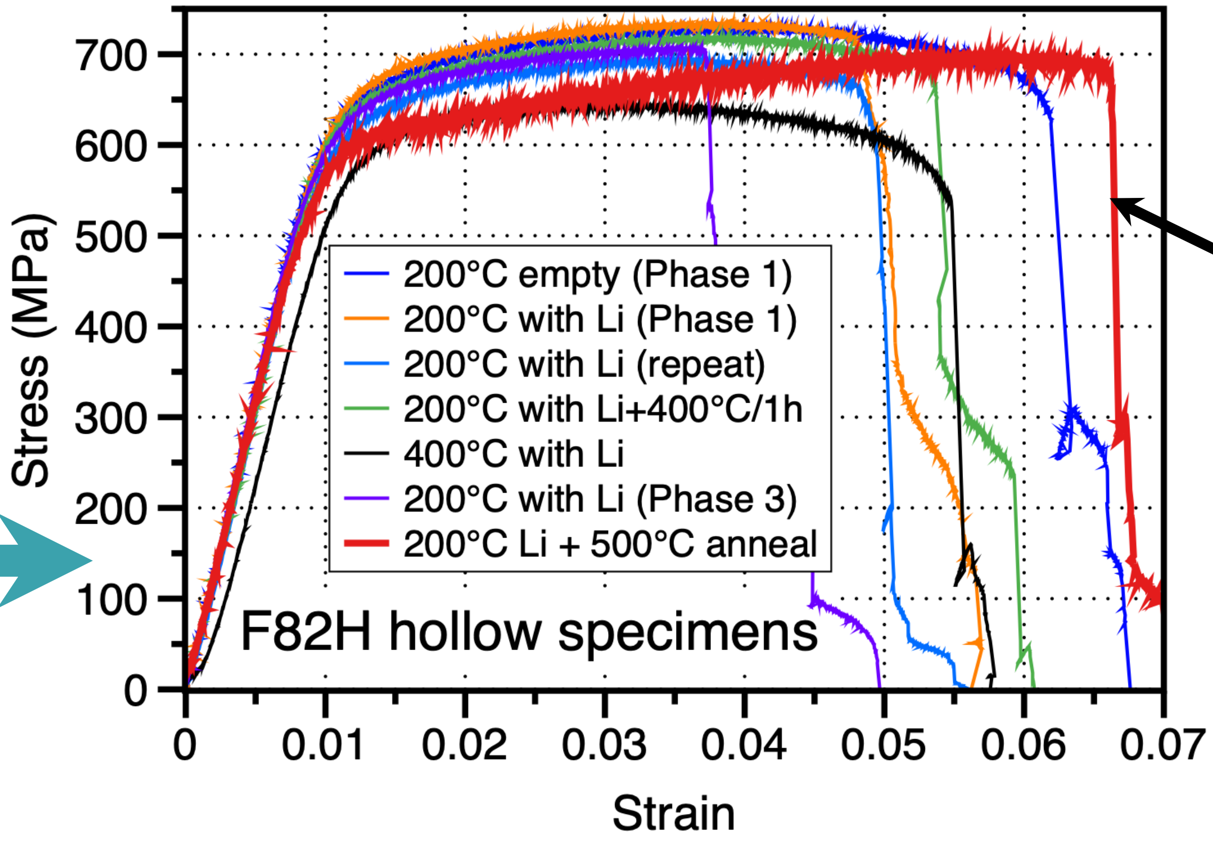


One empty specimen (no Li)

Hollow F82H tensile specimens: no indication of Li embrittlement

Tensile test at 200°C or 400°C: 0.005/min strain rate per ASTM E21

Li-filled F82H: Fe-8Cr-2W tensile specimens



Specimen annealed 500°C/500h

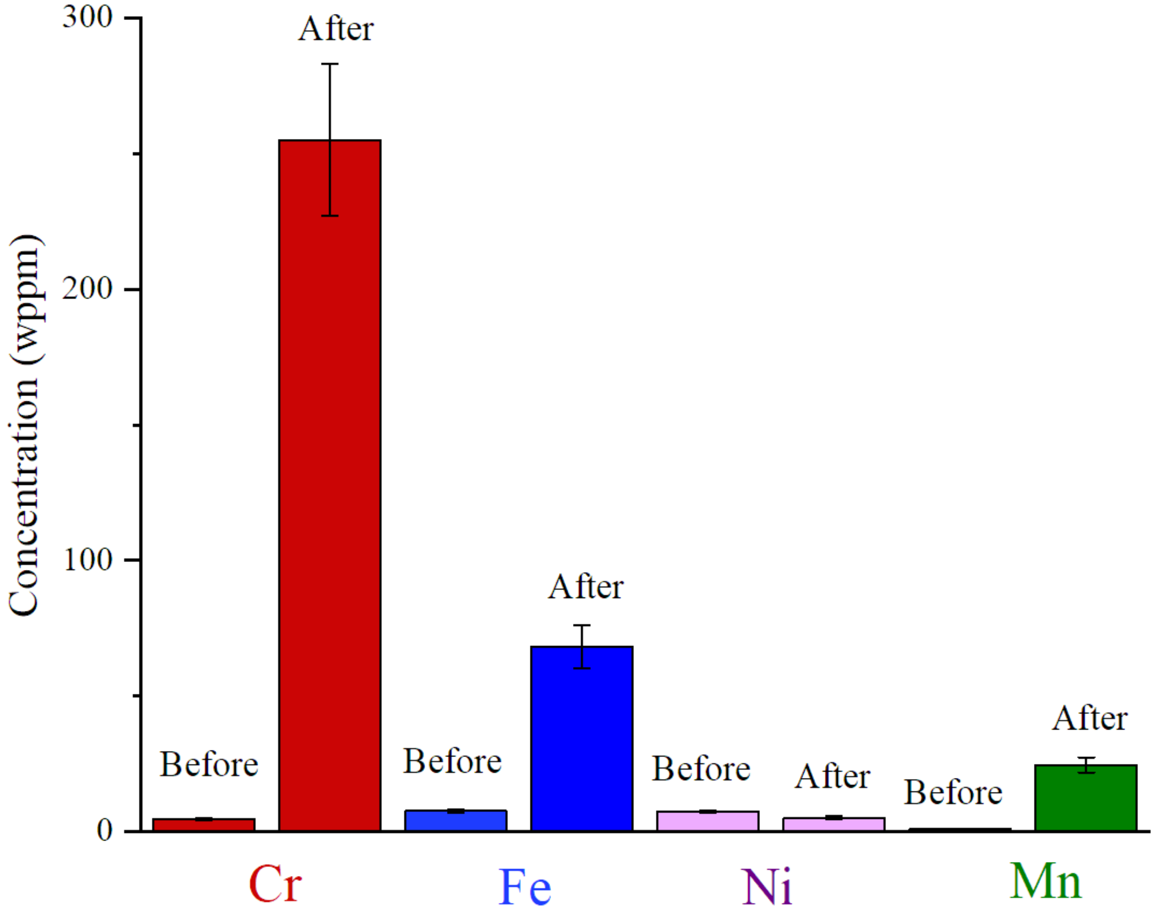
Manuscript submitted October 2023:
Romedenne et al., Corrosion Science

Recent FLiNaK salt leak on 316H TCL

Flowing FLiNaK 316H loop (540°-650°C): ICP-OES after 1000 h
Increased Cr, Fe and Mn after loop run

Inductively coupled plasma-optical emission spectroscopy

316H: 68wt.%Fe-16.5Cr-10.4Ni-1.9Mo-1.5Mn-0.3Si-0.4Cu



Raiman et al. *JNM 2022*

Furnaces + Insulation

Thermal convection loop

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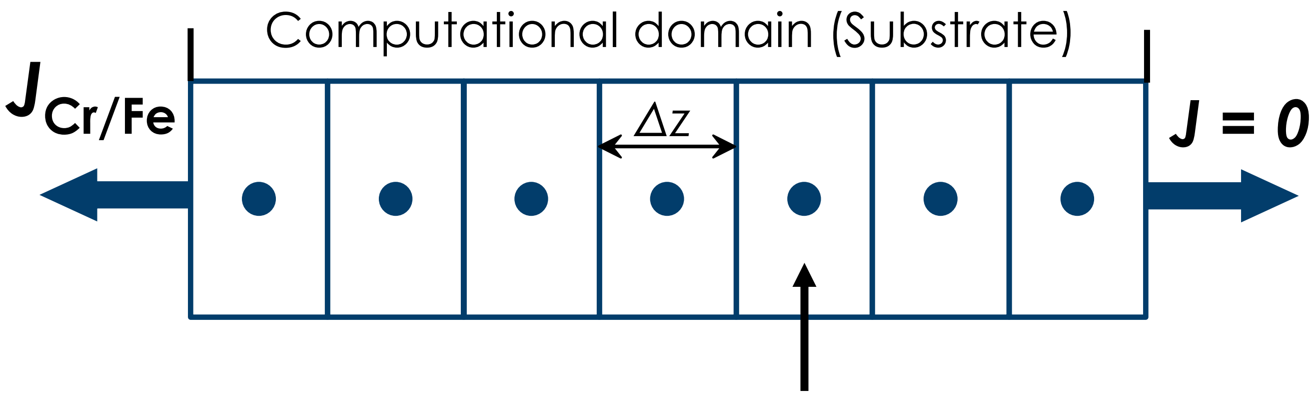
<u>Hypothesis</u>: Corrosion of alloying constituents is primarily governed by their chemical activity (thermodynamics) and mobility (kinetics) in the alloys

Coupled thermodynamic-kinetic modeling approach

$$J_{\mathrm{Cr/Fe,alloy}} \propto N_{\mathrm{Cr/Fe,pure}} * a_{\mathrm{Cr}/Fe,\mathrm{alloy}}$$

Dissolution rate of alloying elements in multicomponent alloys is directly proportional to their dissolution rate in pure form and chemical activity in the alloy



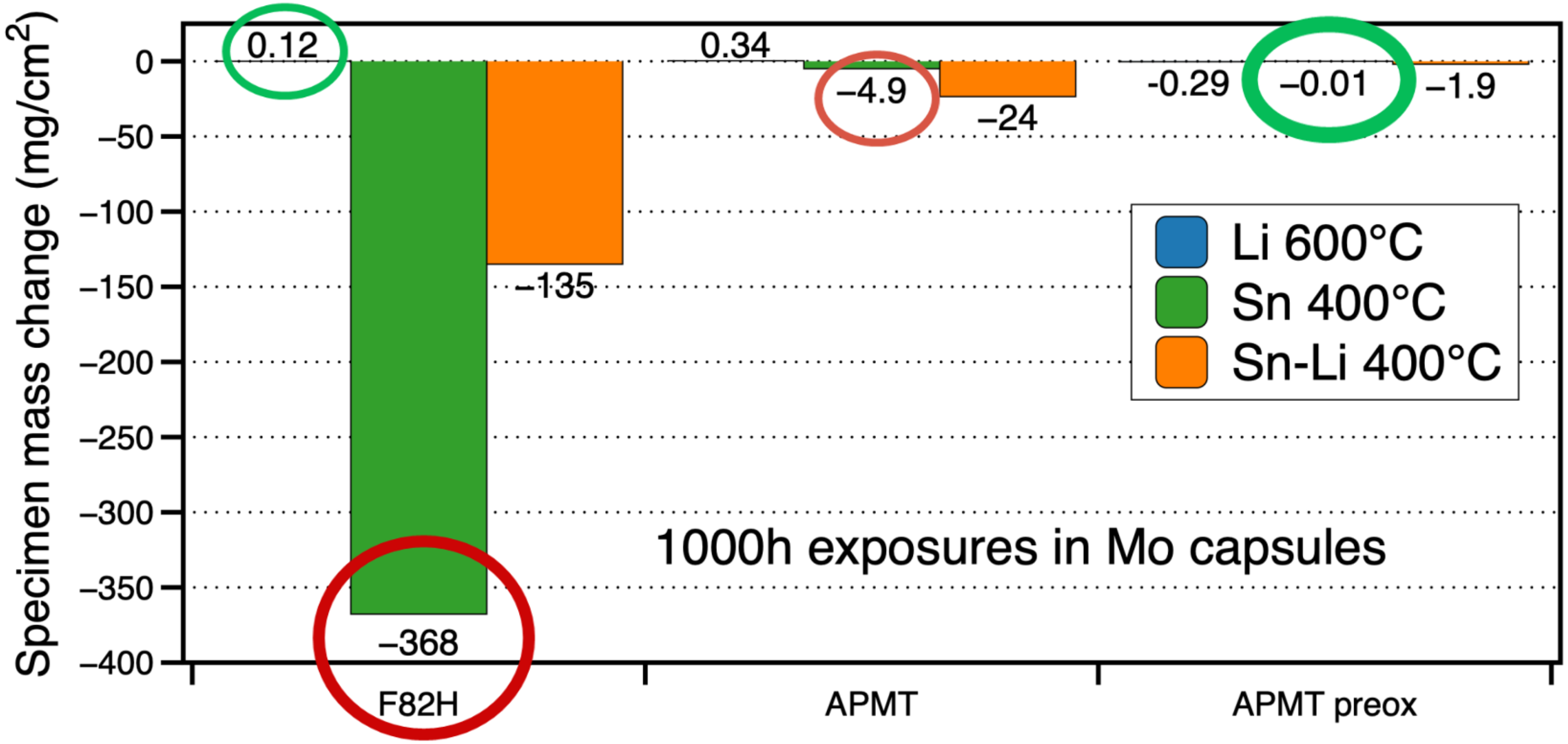
- *Calculation of element fluxes (chemical potential gradients)*
- *Calculation of phase equilibria*

– **Calculate diffusion in the alloy**
  - **Using measured Cr and Fe concentrations after exposure of pure Cr and Fe in purified FLiNaK**
  - **Use of independent thermodynamic-kinetic data -TCNI/MOBNI (Thermo-Calc)**
  - **Consideration of relevant elements & phases in commercial high temperature alloys and coating systems**
  - **Mesh adaption accounts for surface recession (predictions for metal loss)**
  - **Thermodynamic calculations on multiple cores**

** Pillai et al., JOM, 2023*

Sn: bad for F82H at 400°C, good for pre-oxidized FeCrAl

Mass change after 1000h in Mo capsule **+ Li cleaning**



F82H: Fe-8Cr-2W
APMT: Fe-20Cr-5Al-3Mo+Y,Zr,Hf,Ti,O
Preox = pre-oxidation for 2h/1000°C

Static capsule testing:

#1 F82H: not compatible with Sn
#2 Sn-Li mass loss for all: no further work
#3 Need flowing test for pre-ox FeCrAl in Sn