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Materials: Focus on Salt Compatibility

MSR Campaign Review Meeting

26 & 27 April 2022

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Oak Ridge National Laboratory

Molten Salt Reactor PROGRAM

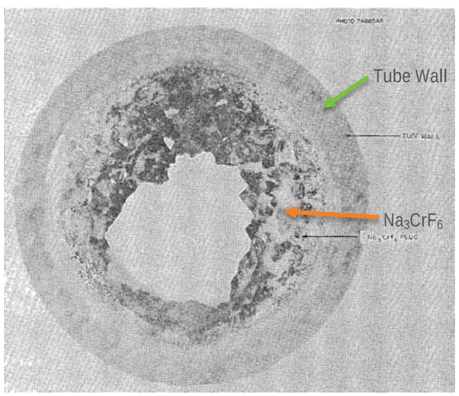
Acknowledgments

- Funding: DOE Office of Nuclear Energy, Molten Salt Reactor Campaign
- ORNL team
  - Dino Sulejmanovic: salt purification, handling and characterization
  - Rishi Pillai: modeling
  - Cory Parker (leaving for NRC): experiments and characterization
  - Adam Willoughby: thermal convection loops
  - Yi-Feng Su and Michael Lance: characterization
  - Kevin Robb: salt purification
  - Stephen Raiman (Texas A&M since 2020): former project lead
  - Jim Keiser, David Holcomb, Lou Qualls: consulting
- Kairos Power: salt (A. Kruizenga) and feedback (G. Young)

Molten salt compatibility: what is our motivation?

What are we afraid of?

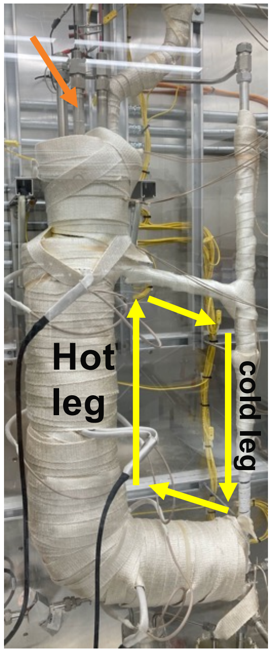
- Inconsequential: Cr surface depletion
- **Mass transfer**
  – Block flow in channel!



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

How do we study it?

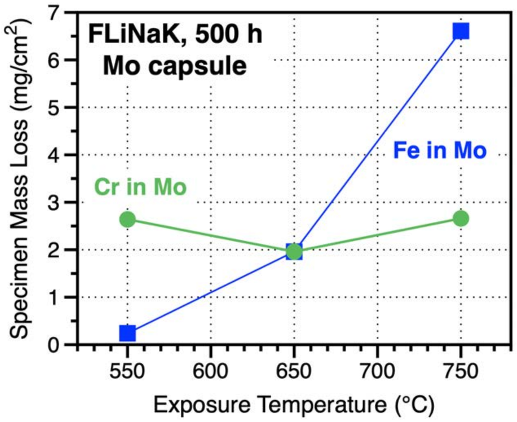
- Flowing salt experiments
  – Forced convection loop
  – Thermal convection loop



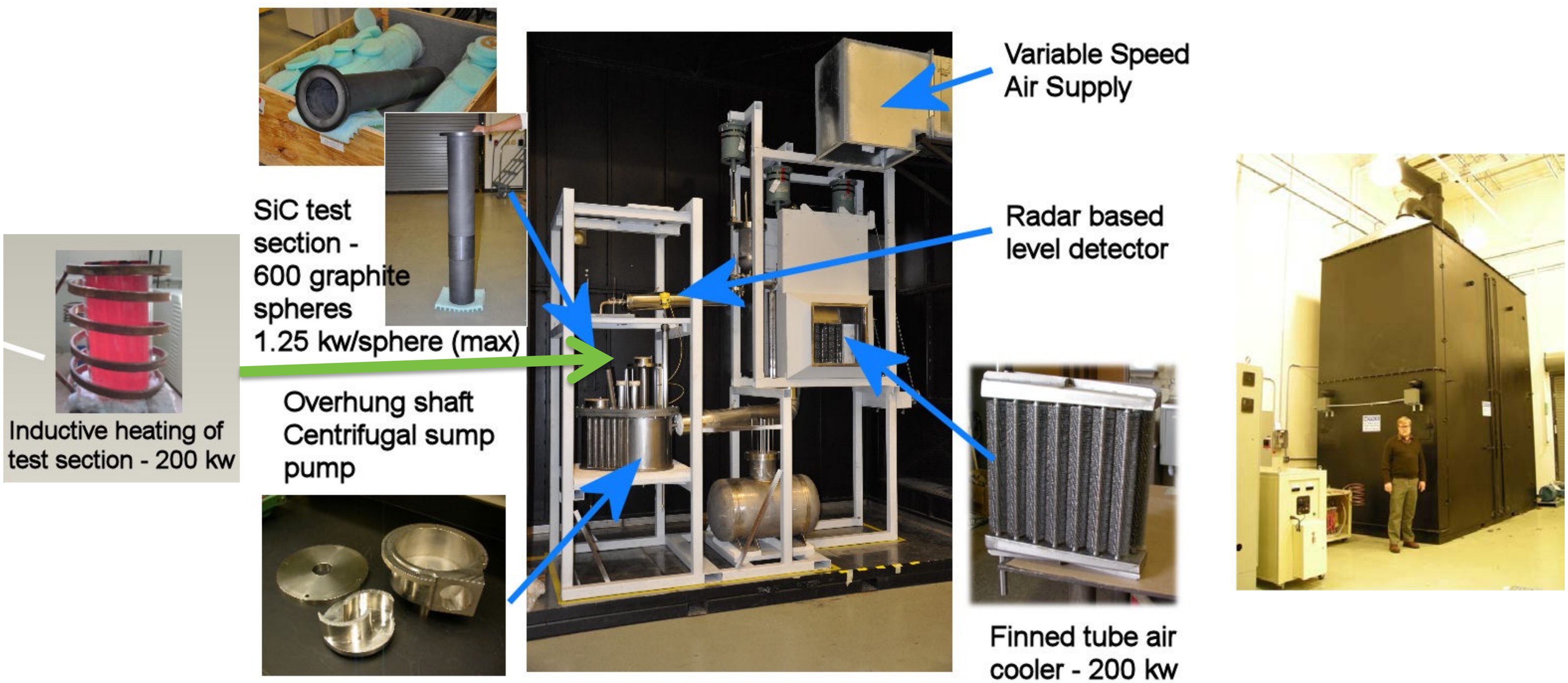
2021 ORNL FLiBe TCL

How do we understand it?

- Dissolution experiments
  – Compare Cr and Fe in isothermal salt
  – Experiments in FLiNaK and FLiBe in progress
    - 550°-750°C



ORNL FLiNaK pumped loop: learn first on inexpensive TCL



FCL: more prototypic conditions and more versatile

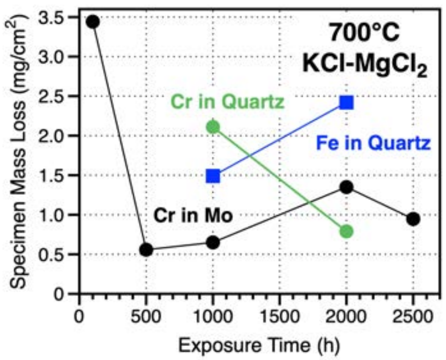
ORNL molten salt tasks now focused on FLiBe compatibility

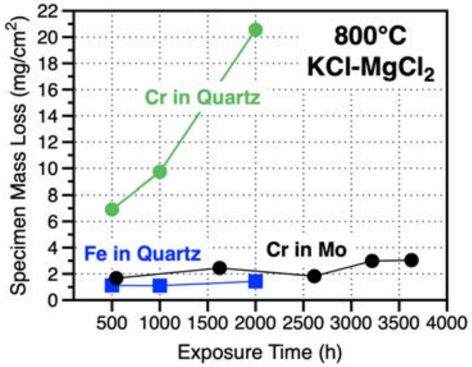
- FY2018: restart chloride and fluoride salt studies
  - Some existing facilities available (added TIG welding in glove box)
  - Joint funding from DOE Solar Energy on chloride salts
  - Produced new FLiBe salt (reestablished capability)
- FY2019: prepared FLiNaK thermal convection loop + operation
  - 1000 h capsule experiments as safety check before flowing experiment
  - 1000 h thermal convection loop using legacy FLiNaK salt
- FY2020-22: transition to FLiBe (vs. COVID)
  - New FLiBe-only glovebox (with TIG welding)
  - New FLiBe-only TCL hood/enclosure
  - New F salt production capability
    - Initial goal to replace HF purification with NF_3
      - Expected operation in May 2022

Salt and Materials Interactions: R&D Goals

- FY22 goals
  - Cr and Fe dissolution experiments in FLiNaK and FLiBe (Mo capsules)
    - Three temperatures: 550°, 650°, 750°C
    - Three times: 500-2000+ h
  - Continue to develop lifetime model (Pillai et al., JNM 2021)
- Future topics
  - FLiBe/316H interaction: higher temperatures/accident scenario TCLs
    - Feedback from MSR developer
  - Compatibility effect of impurities/additives (salt purity standards)
  - Further development of corrosion sensors/electrochemistry aspects
  - Similar studies for Cl salts
- FY25 goal
  - De-risk the transition from 316H to higher performance alloy 709
    - Focus on higher temperature operation and lifetime modeling

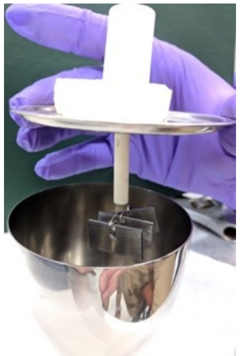
Unexpected temperature effect:





Quartz was cheap, but not a good choice

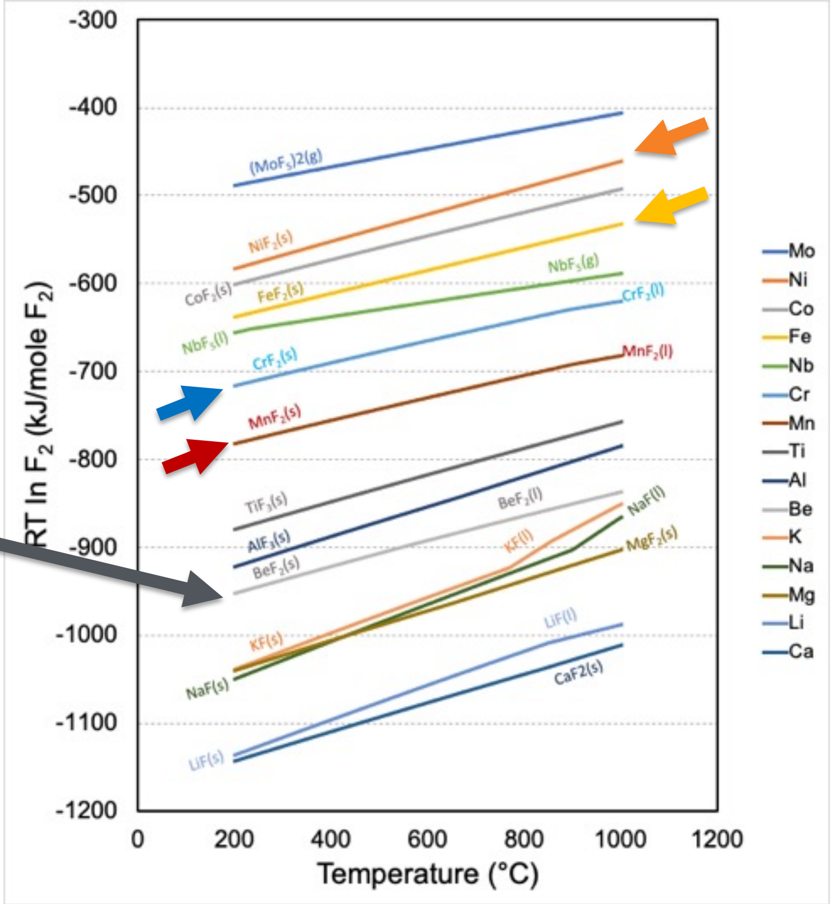
How do we assess compatibility?



- Thermodynamics
  - First screening tool but data is not always available
- Capsule/crucible (screening test)
  - 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
- 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
- Pumped or forced convection loop (FCL)
  - Most realistic conditions for flow
  - Historically, similar qualitative results as TCL at 10+X cost
  - Thermal hydraulics and other objectives

1st step: Thermodynamics are relatively well-known

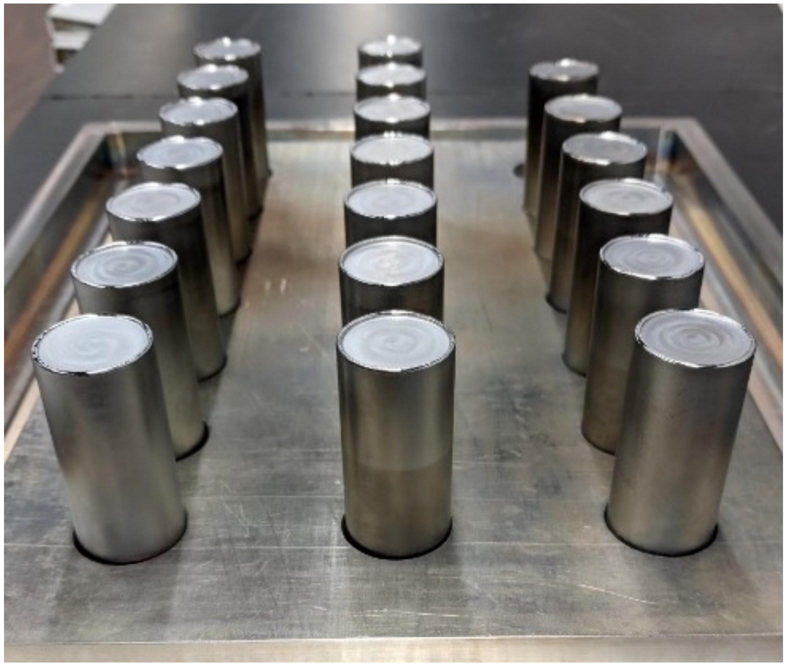
- Mo and Ni have low stability
  - Use Mo for capsules
- Salts have highest stability
  - Li, Na, K, Be
- For 316 steel (Fe-17Cr-13Ni-2Mn)
  - Expect Mn and Cr selective attack
- Be to lower F potential in FLiBe
  - Or K/Na to FLiNaK
- Impurities in salt
  - $2HF + Cr(s) \Rightarrow CrF_2 + H_2$
  - $NiF_2 + Cr(s) \Rightarrow CrF_2 + Ni(s)$

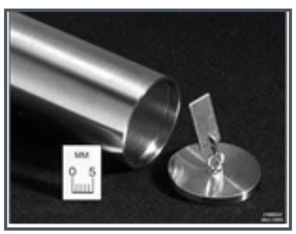


Summary of recent/planned ORNL thermal convection loops

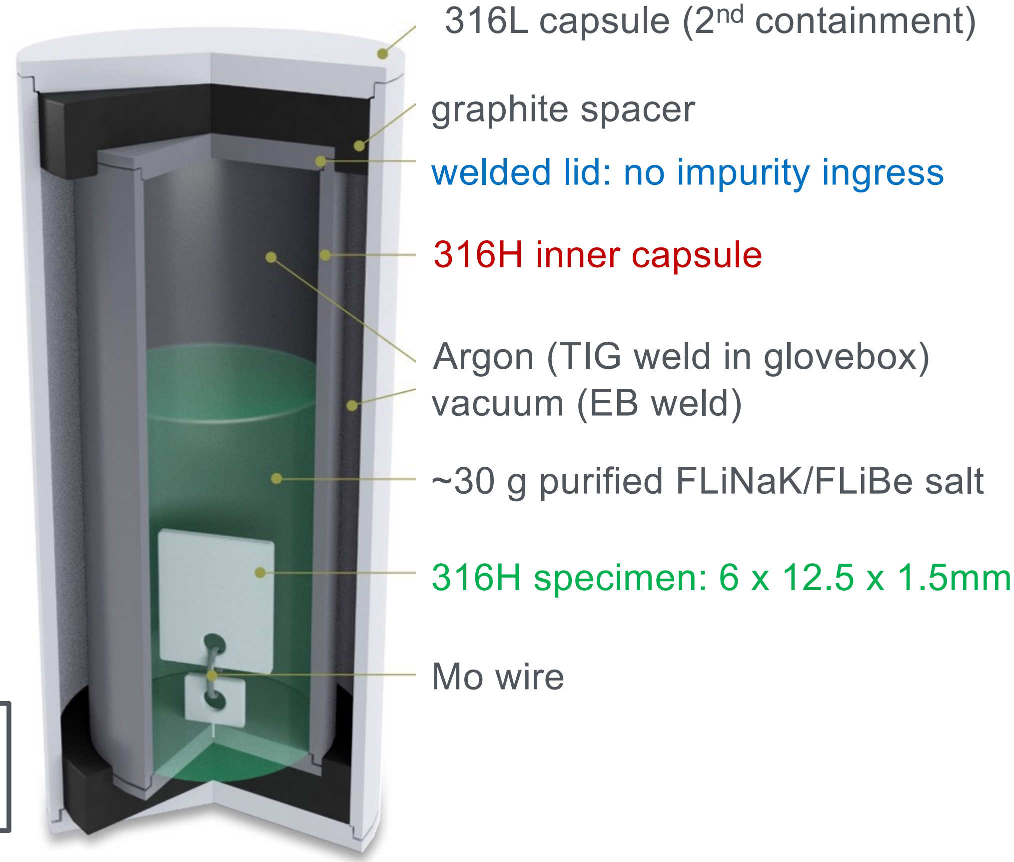
Sponsor	Material Loop: specimens	Salt	Temperature	Time	Note
DOE TP/SO	??	??	??	500h	Issue with 316 fitting leak
SETO CSP	600: 600	Purified KMgCl	700°C	1000h	
SETO CSP	600: 600+C276	Purified KMgCl	750°C	110h	Furnace failure
SETO CSP	600: 600+C276	Dried KMgNaCl	700°C	1000h	Mg in salt + Gasket leaked
MSR	**316H: 316H**	**FLiNaK(Zr)**	**650°C**	**1000h**	**2022 JNM paper**
SETO SBIR	C276: 740H/coat C276/600	Dried KMgNaCl	750°C	1000h	Coated 740H coupon study
MSR	**316H: 316H**	**Kairos FLiBe**	**650°C**	**1000h**	**Reporting in progress**
MSR	316H: 316H	?? FLiBe	750°C	1000h	Planned FY22
NE SBIR	600: 600	Dried KMgNaCl	650°C	?	Planned sensor test FY23
NE SBIR	316H: 316H	?? FLiNaK	750°C	1000h	Planned coating test FY22?

Capsule testing performed to check salt before loop

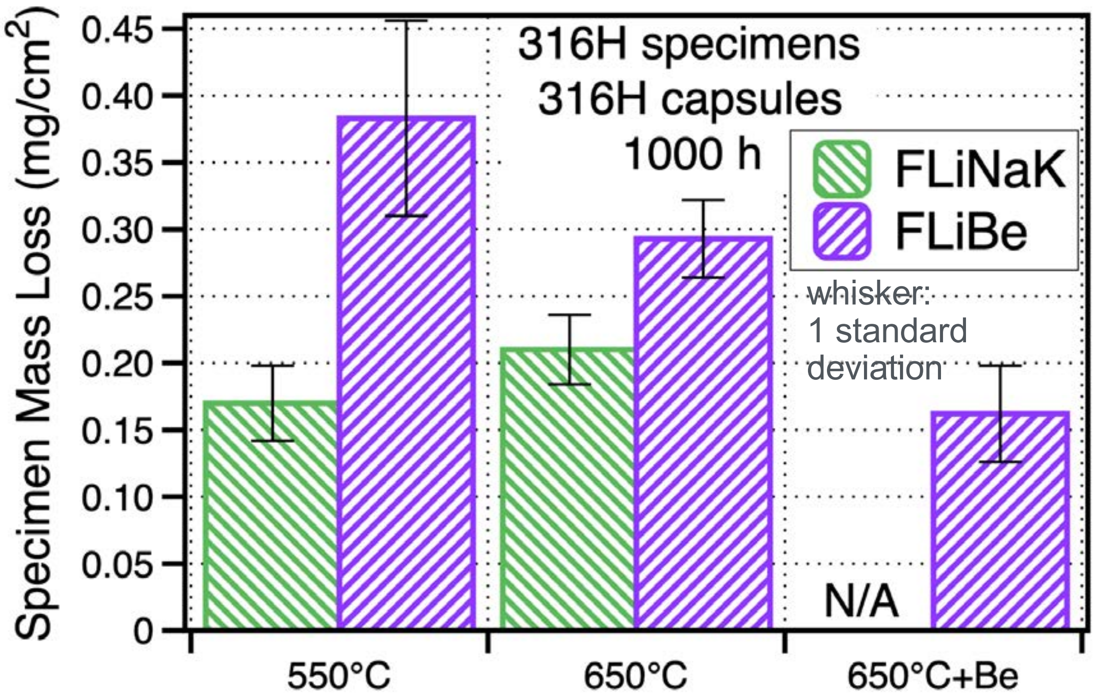




1000h in box furnace
Flip at the end for removal



#1 mass change: all small mass losses (good!)



Required pre-experiment for loop

550°-650°C: temperature range of loop

~50 ppm Be: expected to reduce attack

Average 3 capsules

FLiNaK
- Purified
- 400ppm Zr

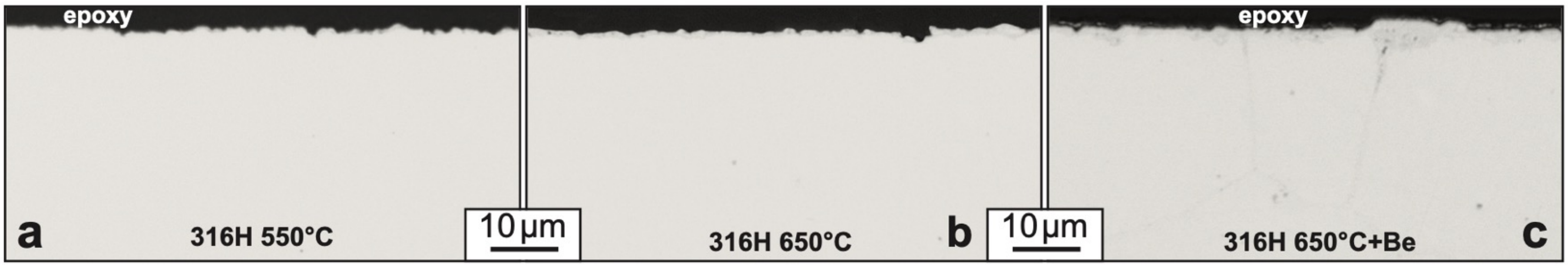
FLiBe
- Purified
- Commercial
- High C content

316H capsule

ORNL Capsule test

#2 light microscopy: not much change in 316H

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



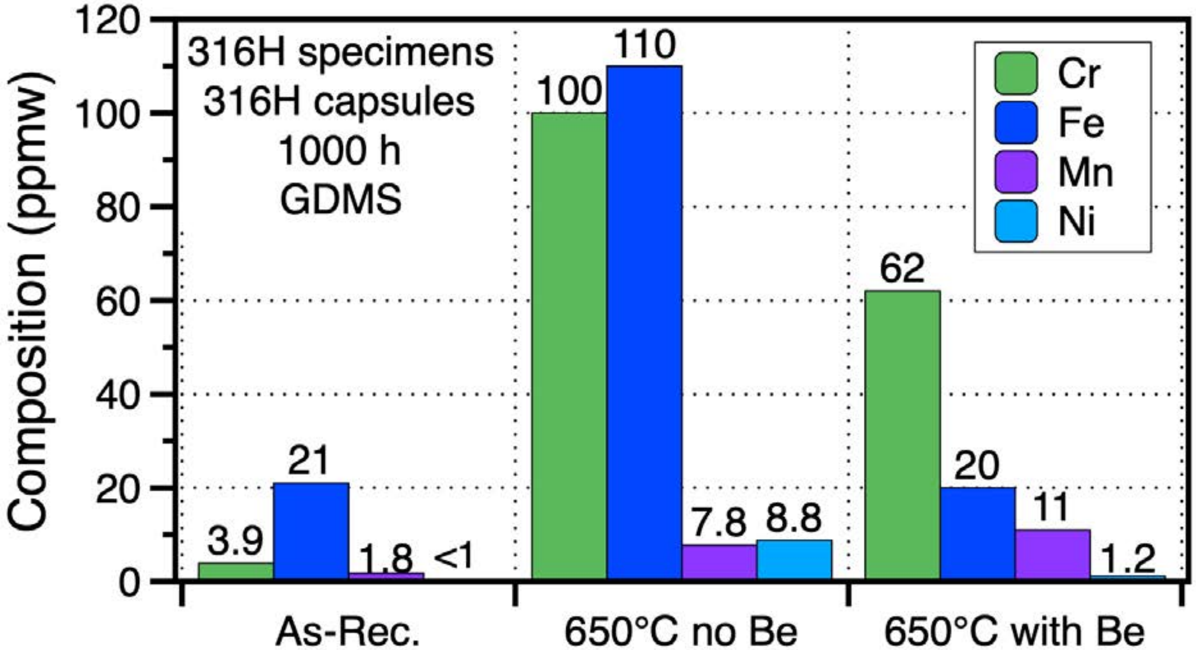
No Be rich phase observed with ~50 ppm Be

Ni-Be observed after 500 h at 750˚C in FLiBe with 150-550 ppm Be additions

J. Keiser, et al., JNM, in press

#3 post-test salt characterization: interesting!

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



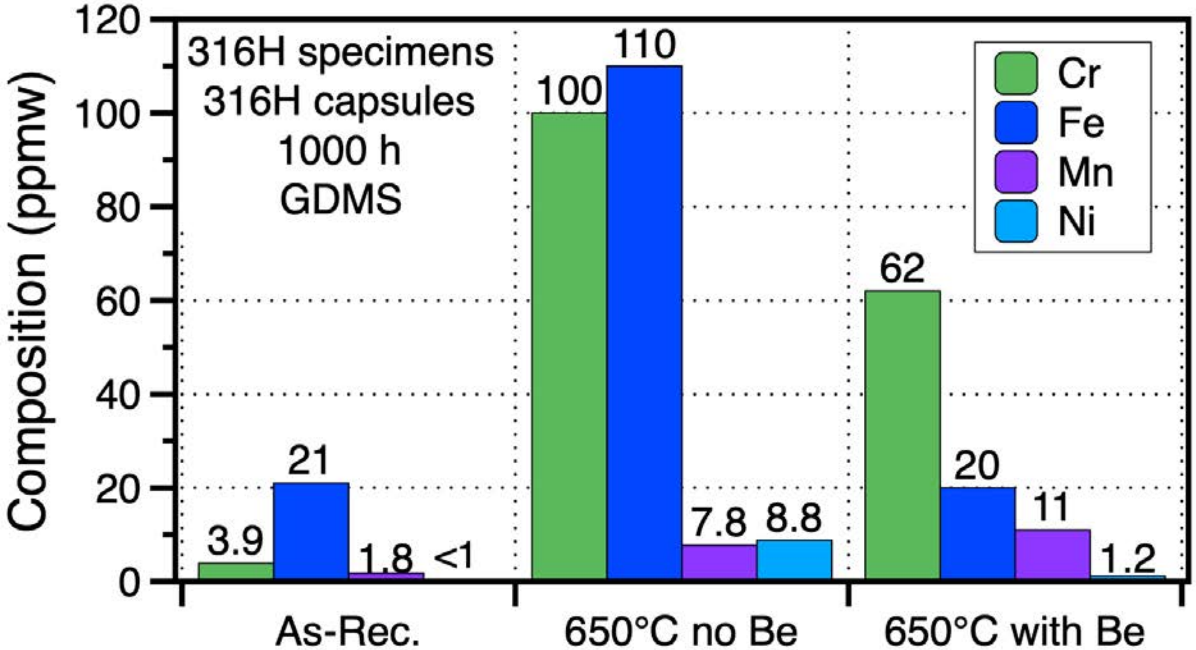
FLiBe: low initial impurities

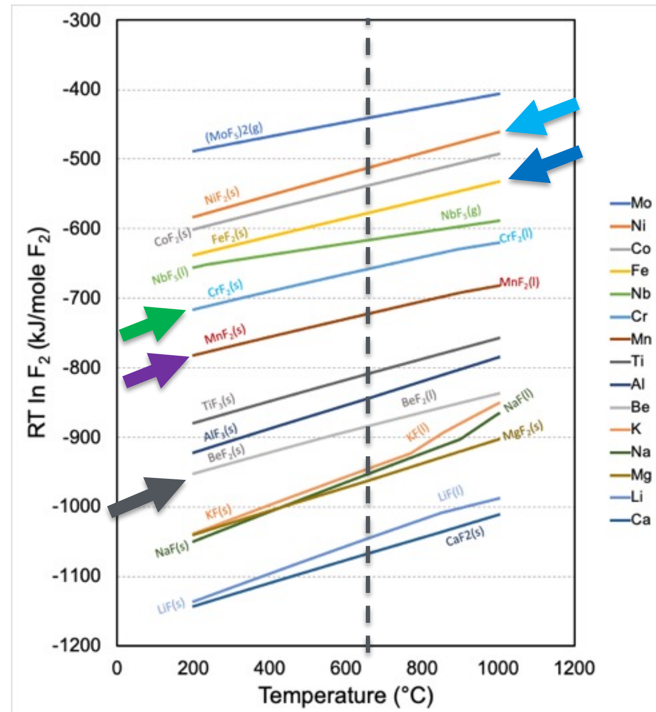
No Be: Cr and Fe increase ≥90 ppm, Ni increase

With Be: Cr and Mn increase (~45% less mass loss)

#3 post-test salt characterization: interesting!

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





FLiBe: low initial impurities

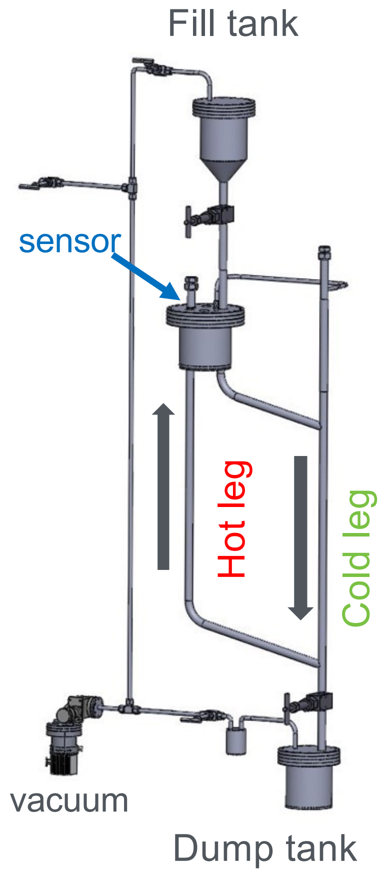
No Be: Cr and Fe increase ≥90 ppm, Ni increase

With Be: Cr and Mn increase (~45% less mass loss)

Current (2019) thermal convection loop design used

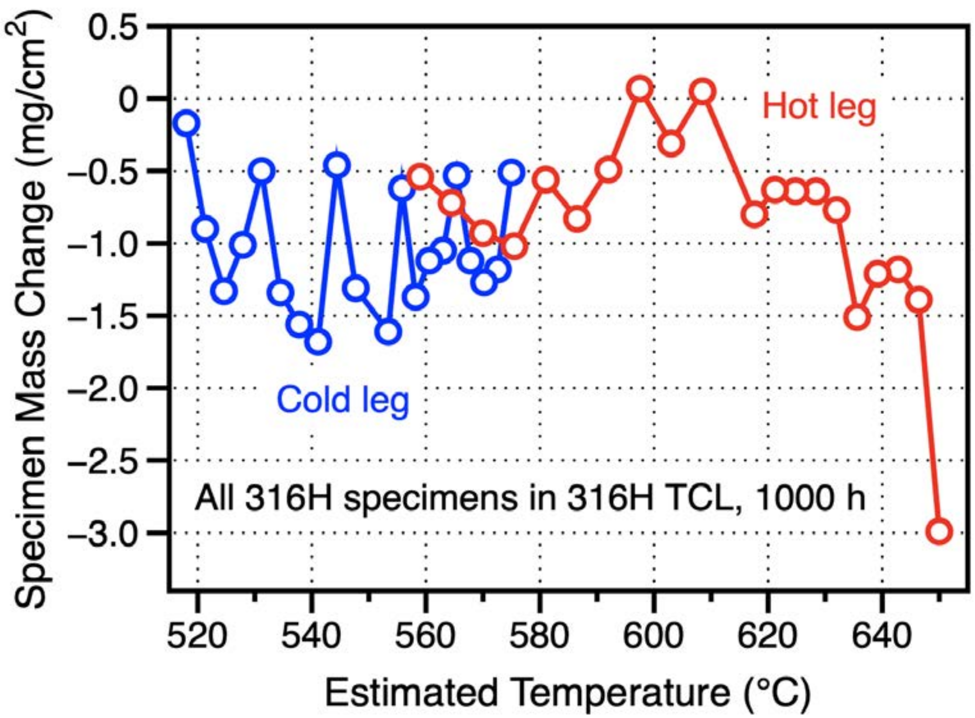
- 316H loop: 27mm OD pipe
- Chains of 316H specimens in hot and cold legs
- Salt is introduced at top
- Flow is driven by thermal gradient (Δ density)
- 1000 h operation
- Temperatures measured at 6 thermowells
  - Controlled at top of hot leg
- 520°-650°C gradient
- 1-2 cm/s velocity
- Salt dumped at end
- Specimens cleaned with water

Specimen chains

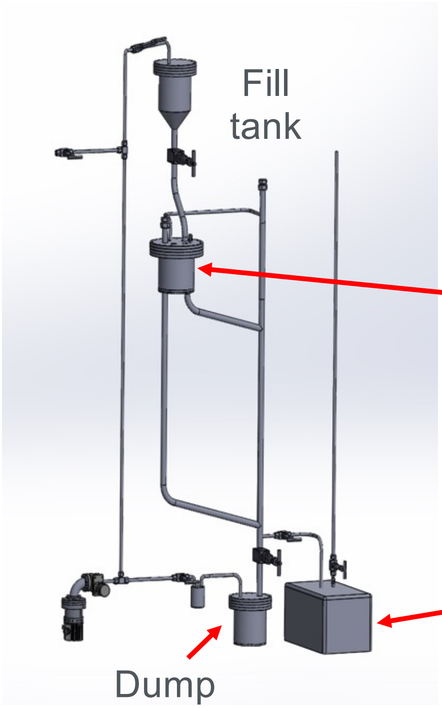


Furnaces + Insulation

#1 mass change: 1,000 h FLiBe TCL = small mass changes!

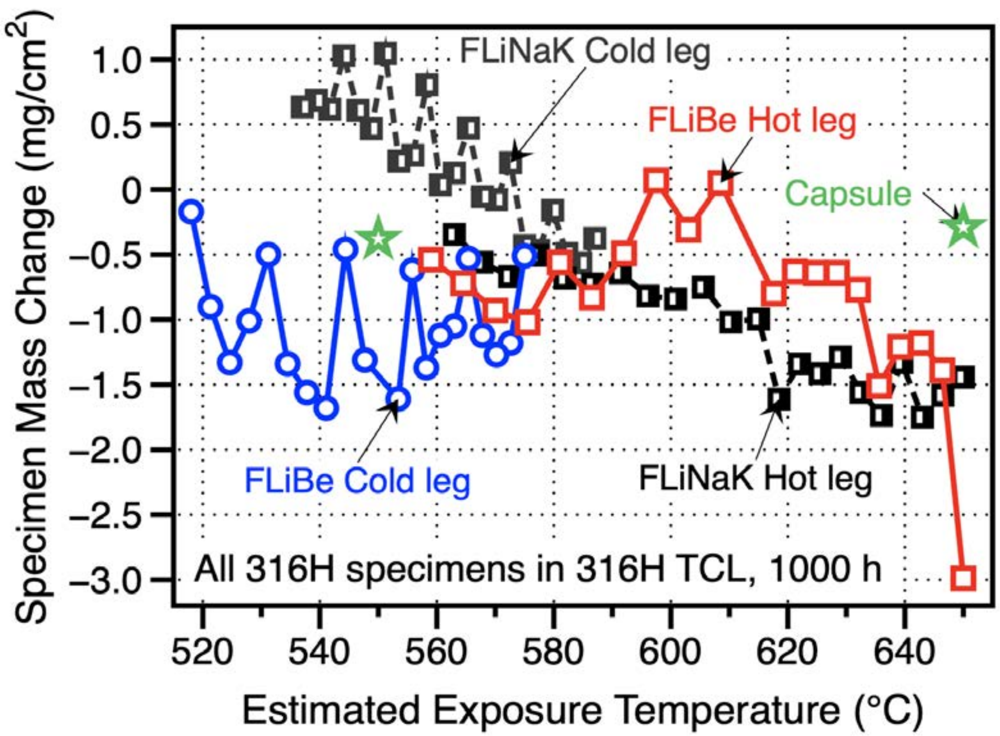


Specimen chains

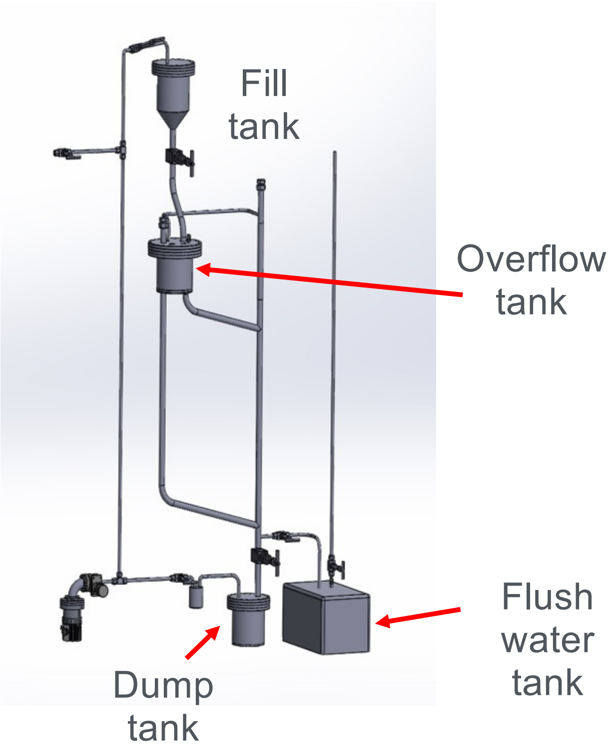


- FLiBe salt from Kairos Power
- Every specimen at a different temperature
- Mass losses in most cases: no obvious mass transfer

#1 mass change: 1,000 h FLiBe TCL = small mass changes!

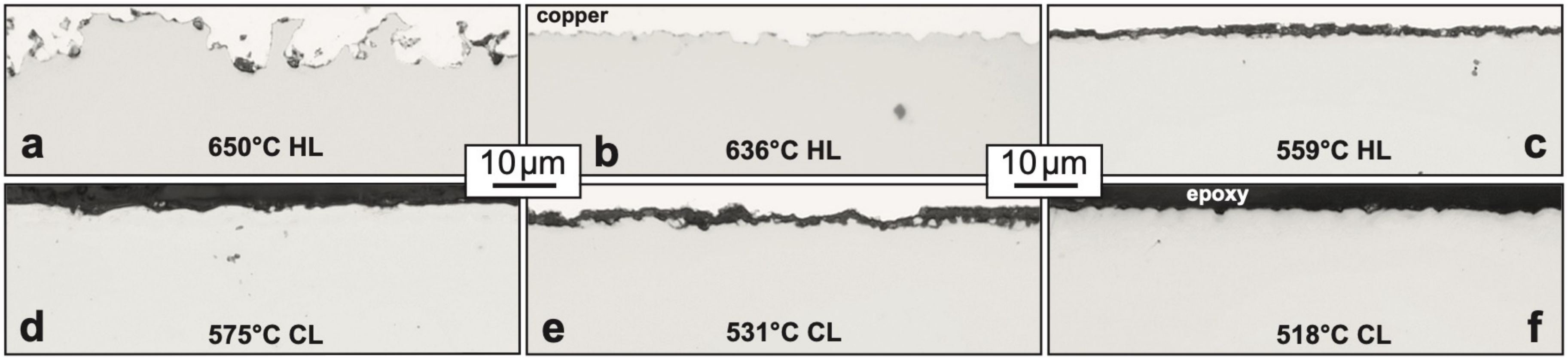


Specimen chains

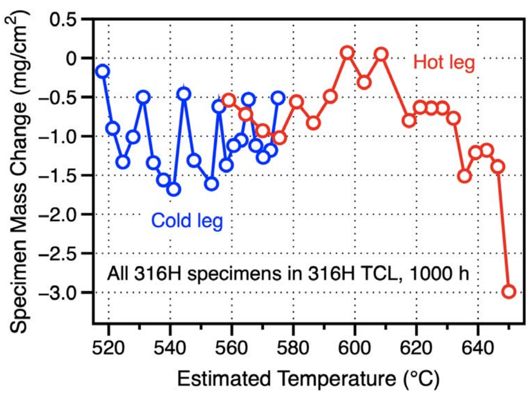


- FLiNaK: mass gains in cold leg
- FLiBe capsules: less mass loss at 650˚C

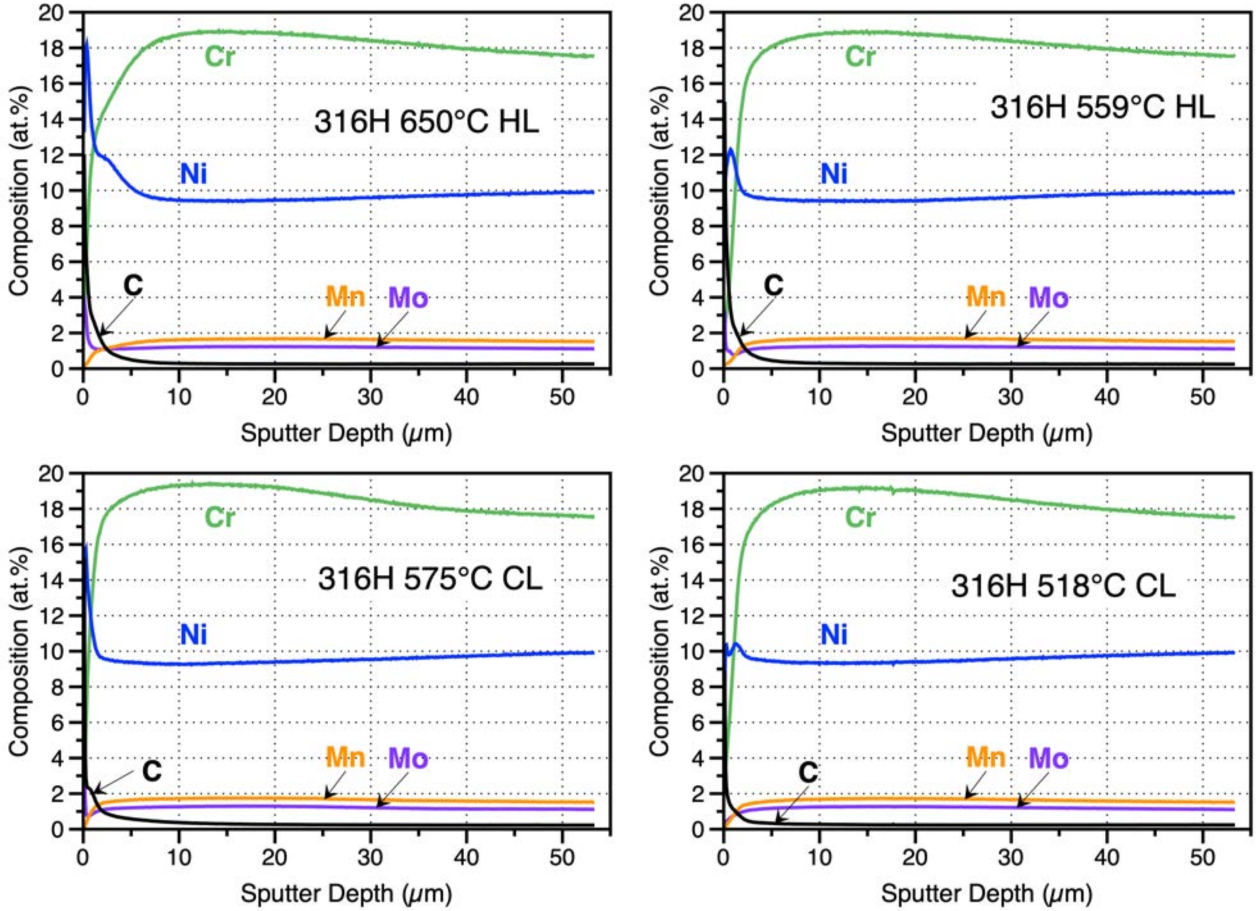
#2 316H characterization (in progress): light microscopy



- HL surface attack: consistent with mass loss
- CL: oxide(?) on surface
  - Issue during cleaning:
  - Bottom valve clogged
  - Rinse water in TCL for >24h may have oxidized surface



#2 316H characterization (in progress): GDOES

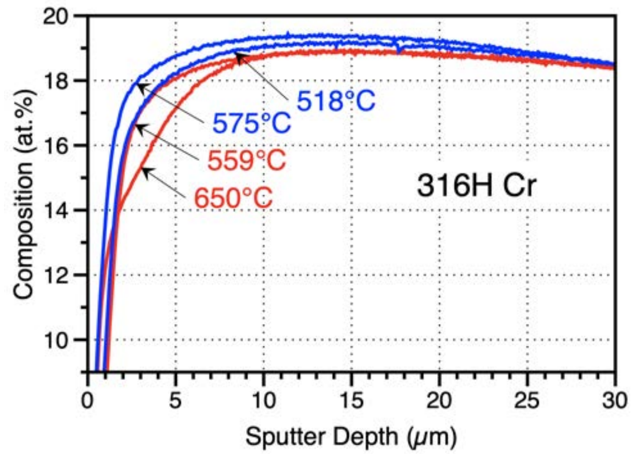


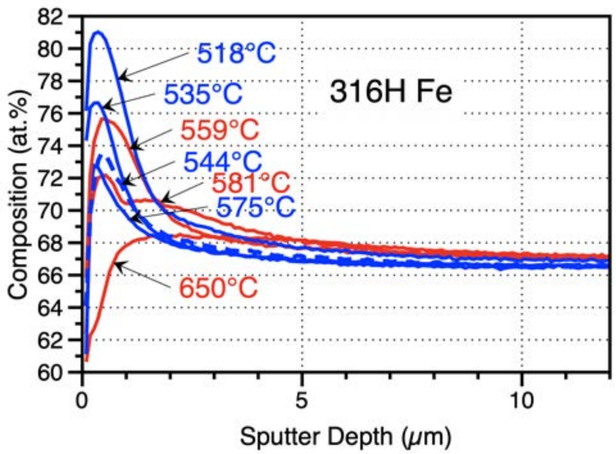
Glow discharge optical emission spectroscopy:

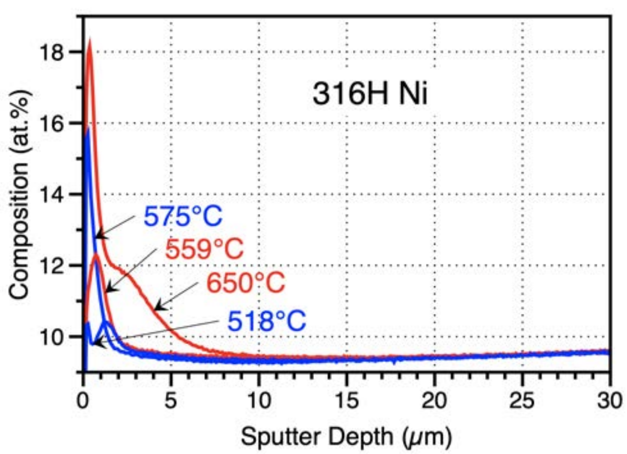
- Sputter depth profiles
- Depth from crater depth
- Composition based on unexposed specimen

#2 316H characterization (in progress): GDOES

- Surface Cr depletion similar in all cases
- Most Fe enrichment at bottom of CL
  - Depleted at top of HL (where Ni enriched)
  - Some indication of Fe transport



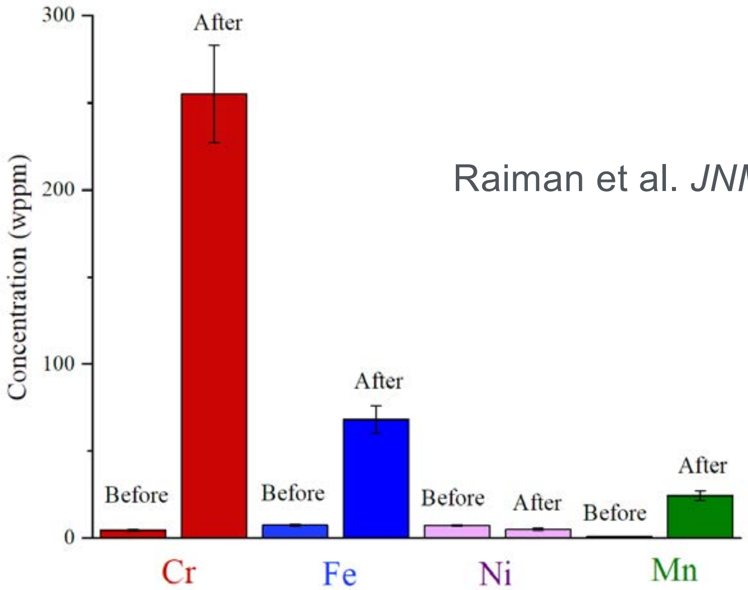




GDOES: Glow discharge optical emission spectroscopy

ICP-OES of FLiNaK: Increased Cr, Fe & Mn after 1,000h TCL

Inductively coupled plasma-optical emission spectroscopy



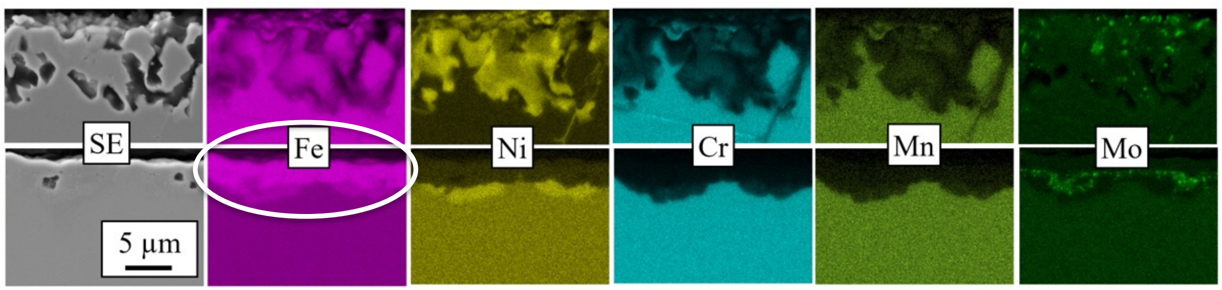
Raiman et al. *JNM 2022*

- FLiNaK contained 400ppm Zr
- Higher Cr in salt after TCL
- Evidence of Fe deposition in CL

- Waiting for ICP data for FLiBe TCL

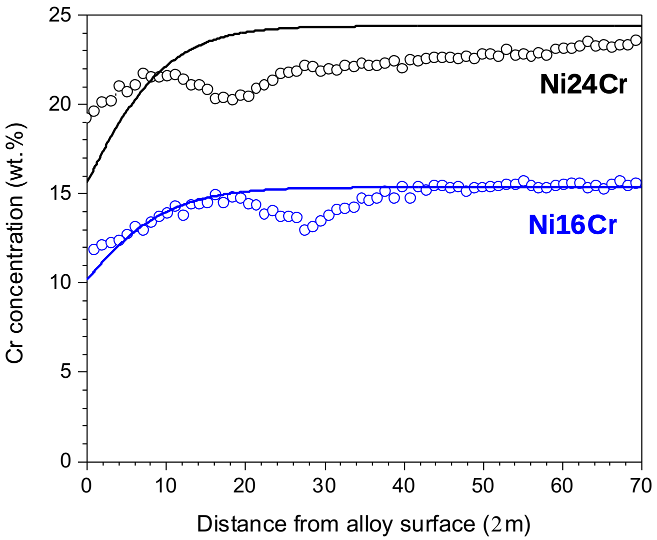
650°C hot leg

550°C cold leg



Model development needs relevant data

Data for model Ni-Cr alloys exposed for 2614 h at 800˚C to $KCl\text{-}MgCl_2$



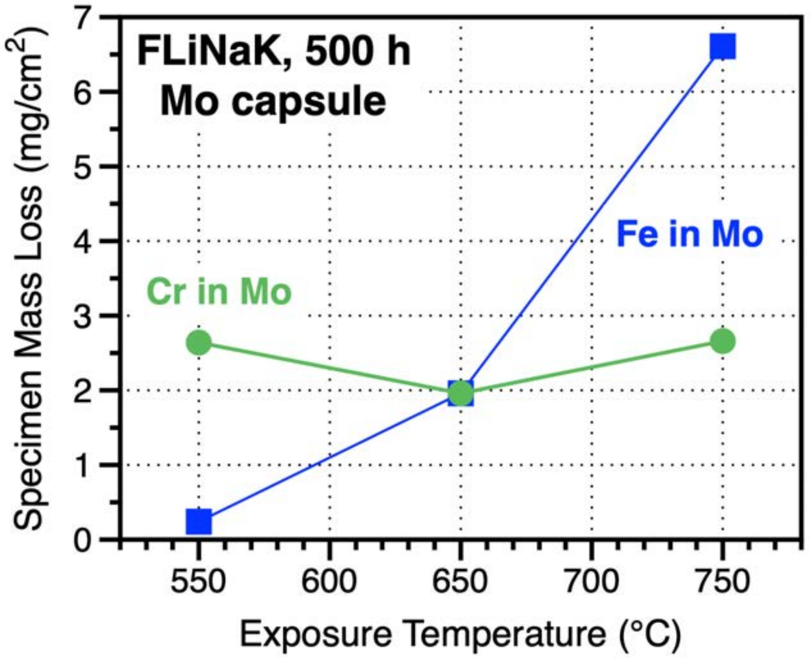
- Proposed model used data for Ni-Cr alloys and Cl salt. (Pillai et al., JNM 2021)
- Need similar data for Fe and Cr in FLiNaK/FLiBe (FY22 milestone)
- Proposed FY22 test matrix in progress
  - Same FLiNaK salt from TCL experiment
  - No FLiBe salt yet

Temperature	500 h	1000 h	2000 h	4000 h
550°C	FLiNaK/FLiBe	FLiNaK/FLiBe		FLiNaK/FLiBe
650°C	FLiNaK/FLiBe	FLiNaK/FLiBe	FLiNaK/FLiBe	
750°C	FLiNaK/FLiBe	FLiNaK/FLiBe	FLiNaK/FLiBe	

Dissolution mass losses: 500 h at 550°-750°C

- Mo capsules
  - standard ORNL procedure
- Purified FLiNaK salt (+400ppm Zr)

- Need to measure salt after test
- Verify no reaction with Mo capsule
  - Examine longest exposure time

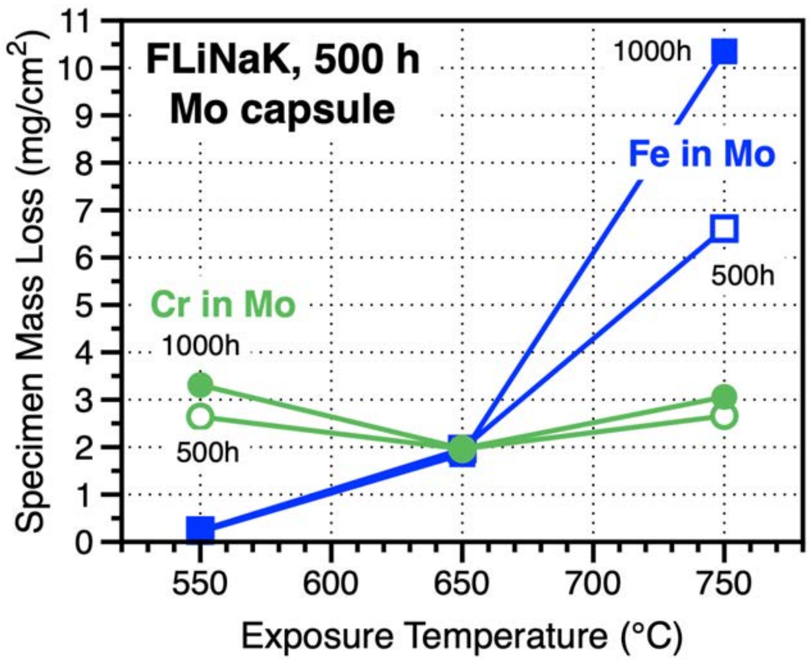


Dissolution mass losses: 1,000 h at 550˚-750˚C

- Mo capsules
  - standard ORNL procedure
- Purified FLiNaK salt (+400ppm Zr)

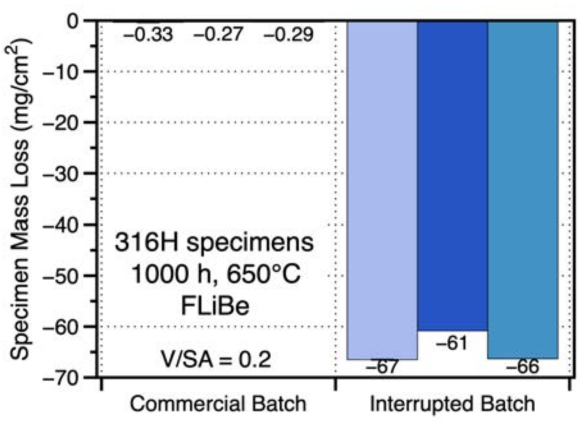
- Need to measure salt after test
- Verify no reaction with Mo capsule
  - Examine longest exposure time

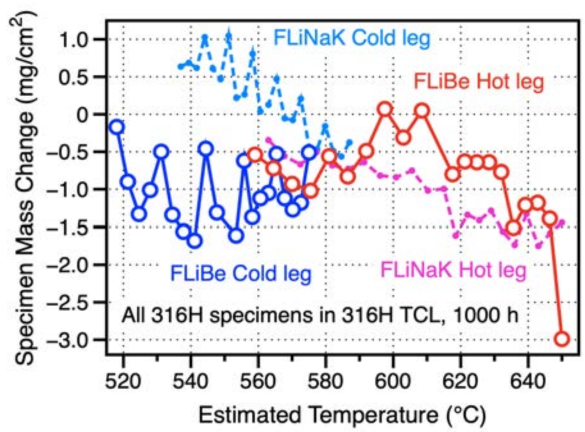
- 2,000 h capsules out in May



Salt and Materials Interactions: FY22 overview

- FY21 Carryover M3AT-22OR0702011: Compare two batches of FLiBe
  - Completed
- FY21 Carryover M4RD-22OR0603034: Complete FLiBe TCL
  - Nearing completion of characterization of FLiBe-exposed 316H specimens
- M3RD-22OR0603031: Measure Cr/Fe solubility in FLiNaK and FLiBe
  - Three temperatures (550˚, 650˚, 750˚C) and three times (500-2000+ h)
  - Waiting for FLiBe salt to start other 50% of capsules

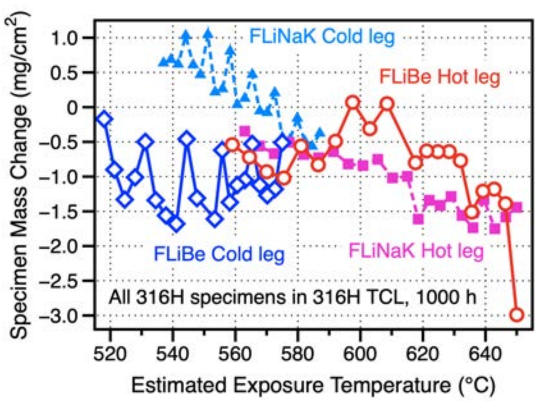




Initial results for 316H in FLiNaK and FLiBe at ~550˚-650˚C

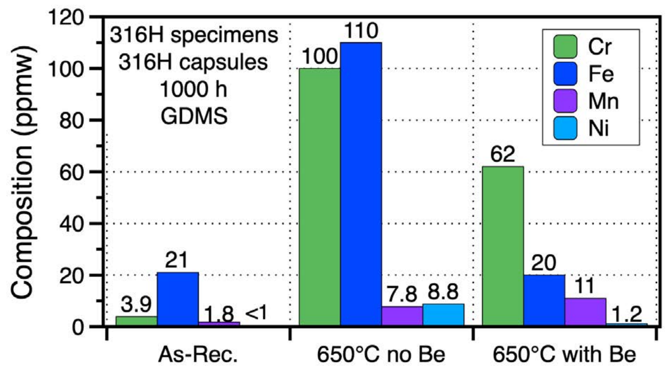
Reasonable compatibility

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



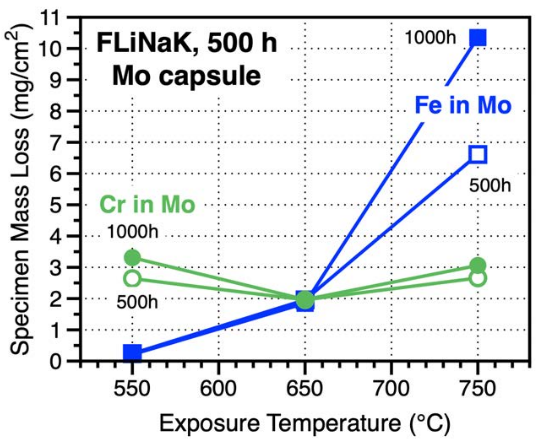
Fe and Cr both dissolving

- Fe dissolves after Cr depleted
- Evidence for Fe dissolution in FLiBe capsule experiments
- Evidence for mass transfer of Fe in FLiNaK TCL
- No Fe enrichment in FLiBe TCL
  - Issue with cleaning salt after exposure



Need modeling

- Dissolution experiments
  - Compare Cr and Fe in isothermal salt
  - Experiments in FLiNaK in progress (FLiBe next)
    - 550°-750°C



Questions

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Molten Salt Reactor
PROGRAM

FLiBe salt chemistry (ICP-OES)

Salt	Cr (ppmw)	Fe (ppmw)	Mn (ppmw)	Ni (ppmw)
Starting commercial FLiBe	3.9	21	1.8	<1
After 650°C/1000 h	100	110	7.8	8.8
650°C+50ppmw Be	62	20	11	1.2
Starting laboratory FLiBe #1	2.4	1.2	1	<1
Starting laboratory FLiBe #2	2.1	1.3	0.5	<1