Materials compatibility update

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Let's start with recent accomplishments:

- LECO combustion analysis has been validated as a technique for measuring oxygen and hydrogen content of fluoride salt
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- Excellent progress in modeling salt compatibility (NEAMS)
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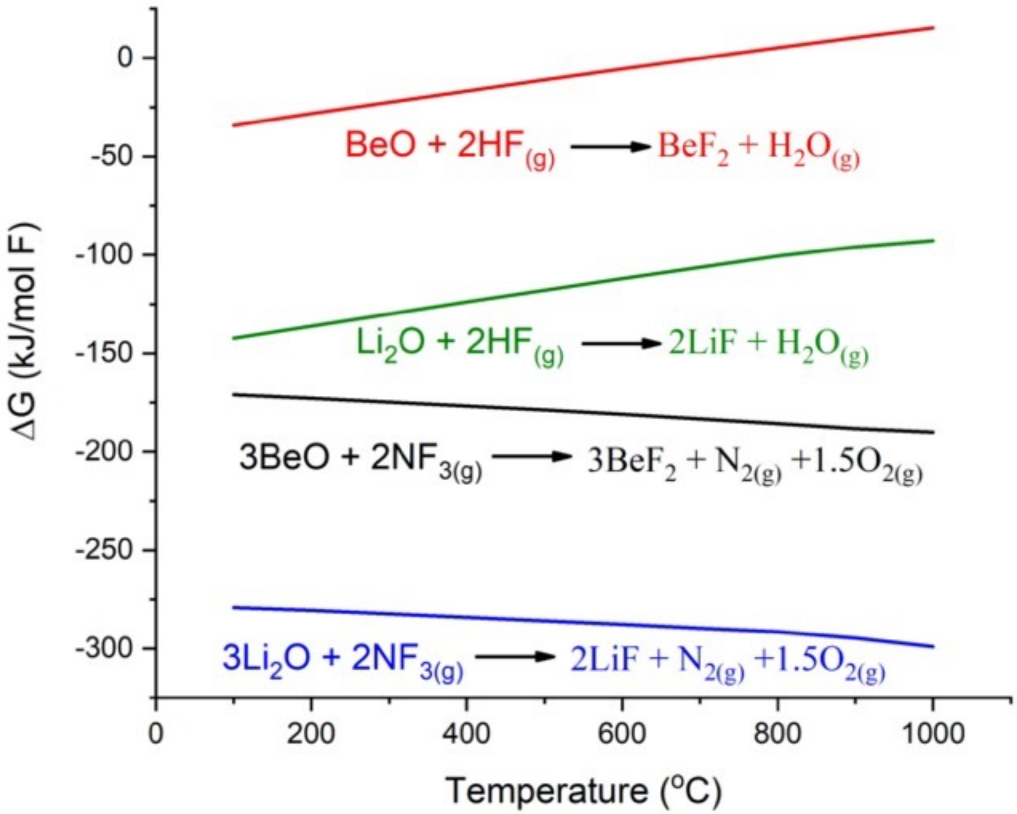
- FY20 built new infrastructure to handle FLiBe (glovebox + walk-in hood)
  - Previous work on Cl salt (FY18) and FLiNaK (FY19)
  - Alignment with industry interest

ORNL FY21 materials tasks have clear objectives

- Salt preparation: explore cheaper/safer methods to purify FLiBe
  - Smaller F salt production line being assembled in FY21
  - Compare reaction kinetics of HF and NF_3 purification routes
  - Quantify differences in corrosion (capsule) experiments and study impurities as a function of purification parameters
    - Using impurity quantification methods developed in FY20
- Salt compatibility: develop baseline for 316H in FLiBe
  - FY20 worked stopped as no salt was available for tests due to COVID
    - Salt obtained from Kairos in March 2021
  - Capsules completed May 31 and first thermal convection loop (TCL) under vacuum and awaiting salt and specimen loading
    - Initial flowing salt experiments will establish a baseline for 316H in FLiBe salt and provide a comparison to FY19 results in FLiNaK
  - In future, need to develop understanding of how salt purity & additives impact corrosion rates so that operating standards can be developed

Fluorination by NF_3 thermodynamics are more favorable compared to HF fluorination

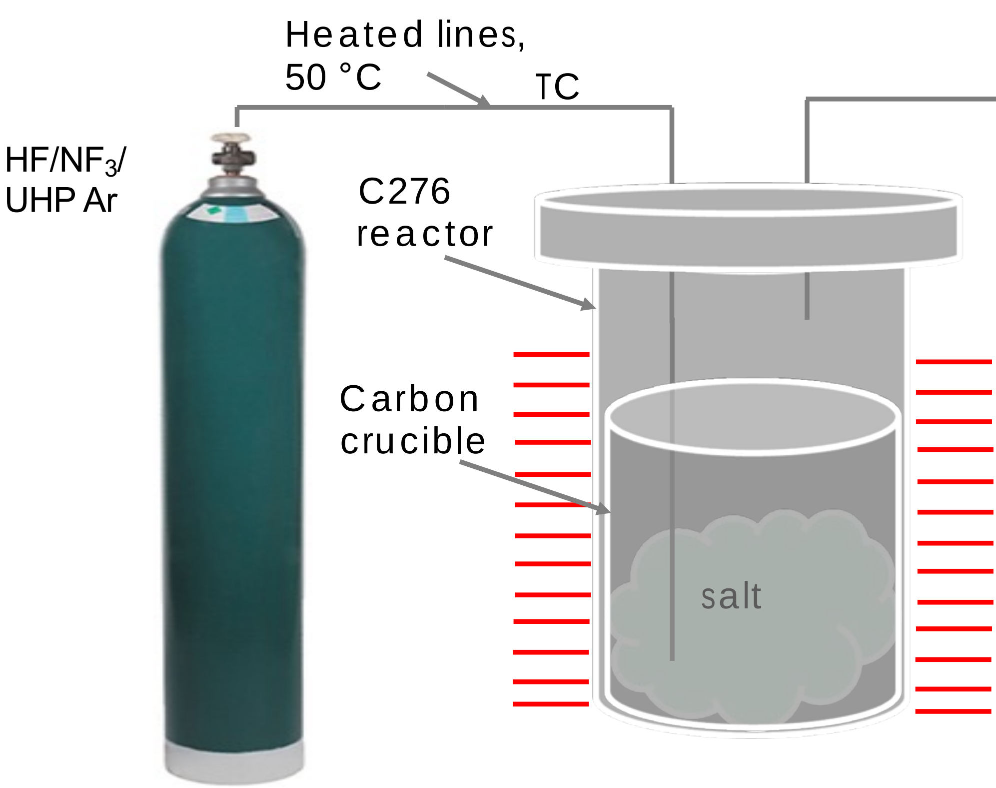


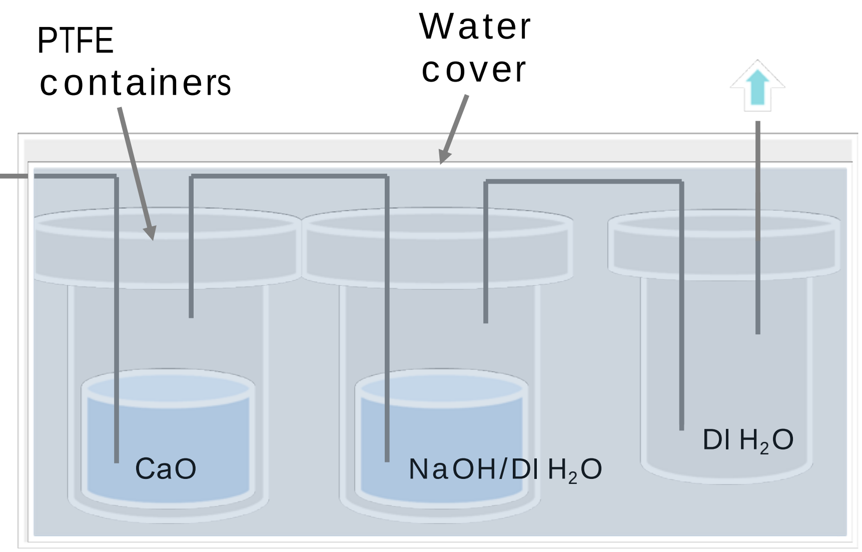
HF

NF_3 – is it too reactive?

Or will it enable faster, lower T purification?

Fluoride Salts Purification Setup: under construction





$$CaO + 2HF \rightarrow CaF_2 + H_2O$$
$$NaOH + HF \rightarrow NaF + H_2O$$

$$3CaO + 2NF_3 \rightarrow 3CaF_2 + N_2 + \frac{1}{2}O_2$$
$$12NaOH + 4NF_3 \rightarrow 12NaF + 2N_2 + 3O_2 + 6H_2O$$

Waste generation: CaF_2, NaF

FY21 Milestones

- Purification
  - M3AT-21OR0702022: Compare the impurity contents in two FLiBe batches
    - Would like to demonstrate that we can make FLiBe faster and cheaper using NF_3
    - Dino Sulejmanovic is the lead on this project (PhD chemist, joined ORNL in 2018)
    - Building new purification rig has been challenging in FY21 (final assembly in progress)
- Compatibility
  - M3AT-21OR0704012: Complete FY20 FLiBe Capsule testing (delayed)
    - Capsule testing before flowing (loop) experiment
    - Capsules completed 5/31: complete characterization in 3-4 weeks
  - M3AT-21OR0704013: Complete FY20 FLiBe Loop Exposure (delayed)
    - Salt loading soon, should start operation week of June 21
  - M4AT-21OR0704011: Complete exposure in flowing FLiBe
    - Ideally, use new salt from purification task in 2nd loop
    - At this time, the source salt for this experiment is not clear

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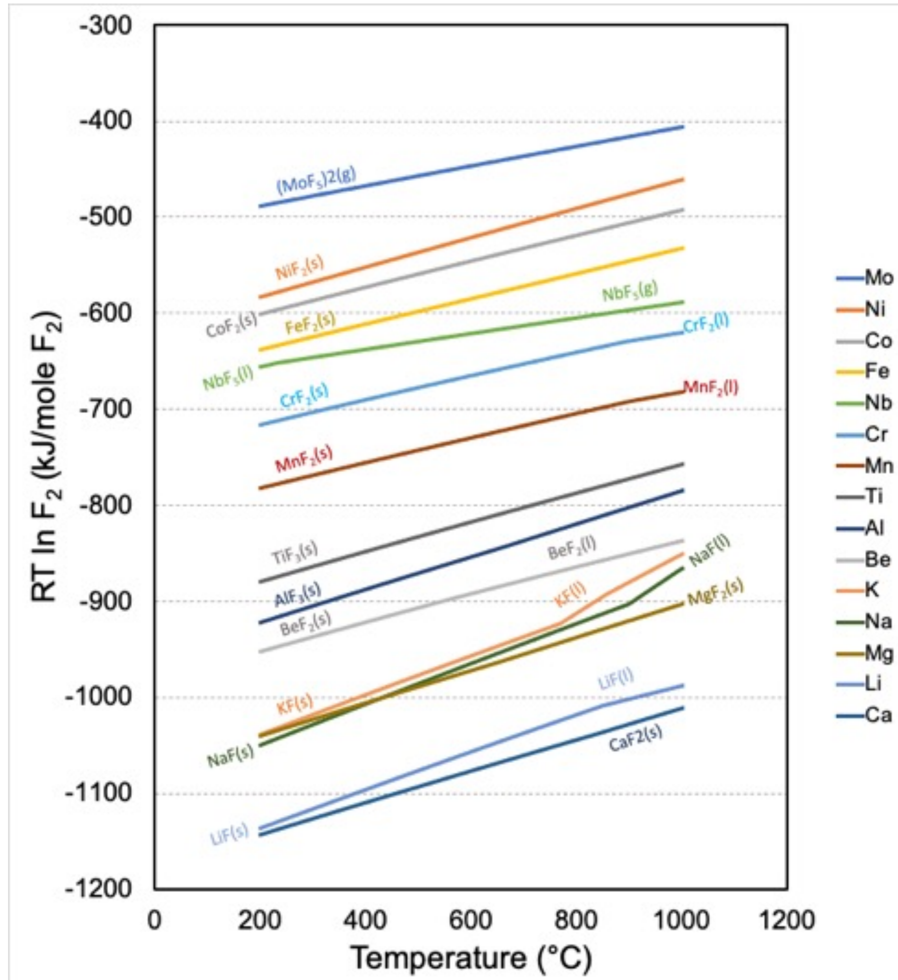
F salt thermodynamics are frequently shown

- Mo and Ni have low stability
  – Use Mo for capsules
- Salts have highest stability
  – Li, Na, K, Be
- Some alloy components more stable than Cr:
  – Mn, Ti, Al



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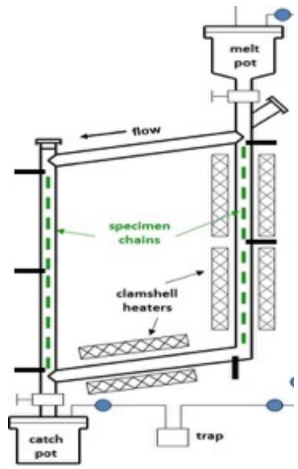
Salt corrosion concern for solar + nuclear
How do we assess compatibility?

- 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 loop
  - Most realistic conditions for flow: necessary, prototypic experiments
  - Historically, similar qualitative results as TCL at 10-20X cost



Source: Pawel JNM 2017

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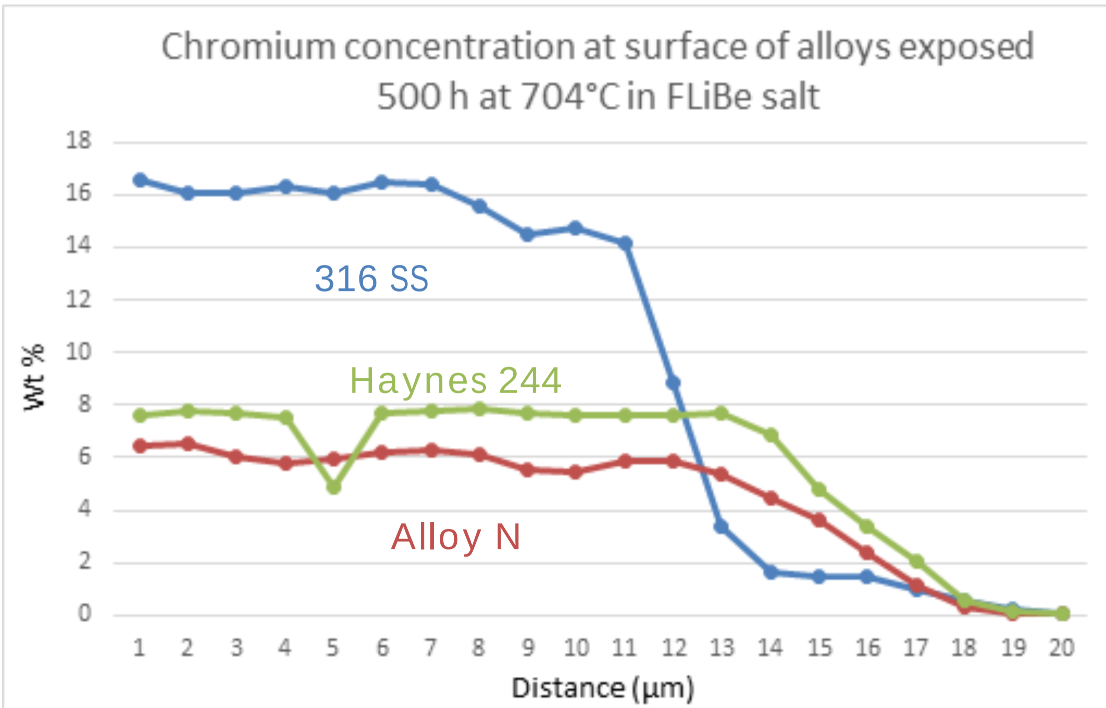
Industry wants ASME code-approved available alloys But far less data available for type 316H stainless steel

Fe-base

Ni-base



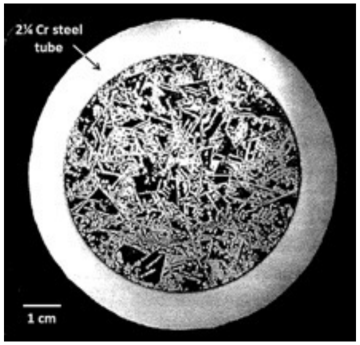
Higher starting Cr in 316SS and more severe Cr loss

Hastelloy N used in ORNL Molten Salt Reactor Experiment: Ni-7Cr-16Mo-5Fe

(unpublished J. R. Keiser 2018)

Liquid degradation modes: what are we afraid of?

- Historical observations of liquid metal and molten salt compatibility
  - Traditional protective scales can dissolve, particularly in halide salts
- Alloying between liquid and structural alloy (showstopper for Sn in contact with Fe)
- Wetting: required for reactions to occur
- Segregation
  - Embrittle alloy grain boundaries
- **Dissolution (and precipitation on cooling)**
  - Temperature limit not set by metal loss but by **threat of plugging flow**
  - **Drop in solubility with temperature** can result in precipitation
  - Liquid metals: elements with high solubility (e.g. Ni in Pb)
  - Molten salts: selective attack of most stable fluoride or chloride
  - Dissimilar material interactions
    - Dissolved element from one alloy could be gettered by another material



Steel tube plugged
by precipitation

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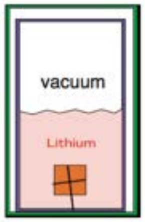
Why is a flowing test with a temperature gradient needed?



- Well-established compatibility evaluation progression
  - Thermodynamic assessment
  - Isothermal capsule testing (typically 500-1000 h in sealed capsule) $5K/capsule
  - Thermal convection loop testing (T gradient, low velocity) $100K/loop + salt
  - Pumped loop testing (higher velocity) $2000K to build

- Dissolution flux of element X: $J_X \propto k(C^o - C_X)$ where k = const.
  - C^o = solubility limit of X in liquid; C_X = actual concentration in liquid
- Static (capsule) test $C_X = f(t)$; as saturation occurs, J_X -> 0
- Dynamic test $C^o = f(T)$, C_X = const. (due to precipitation in cold leg)

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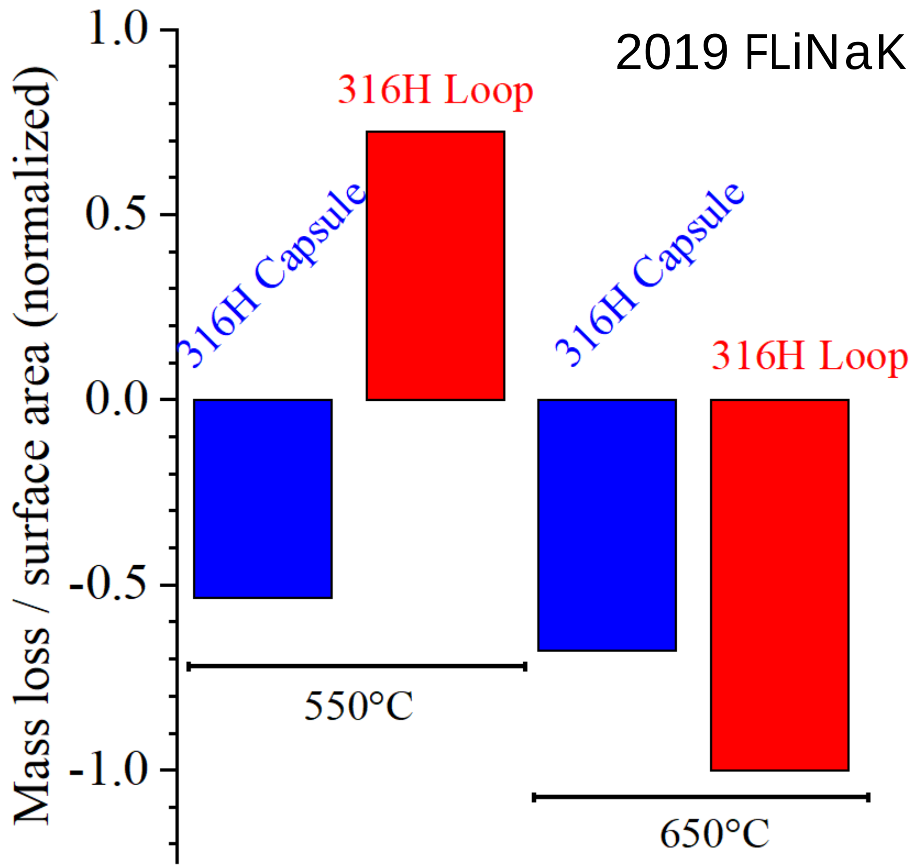
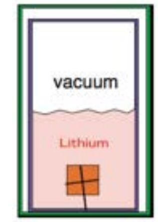


2019 FLiNaK study



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- Dissolution flux c :onst.
  - C^o = solubility lin ıuid
- Static (capsule) t 0
- Dynamic test C^o in cold leg)

Because you don't get the same result!

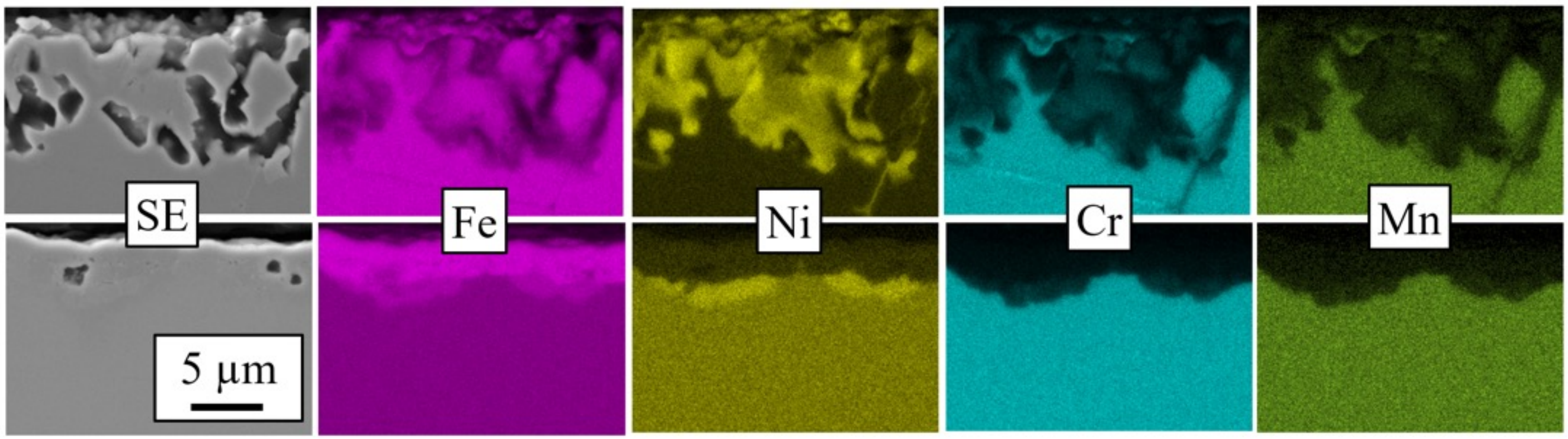
316H specimens exposed to flowing FLiNaK for 1000 h: Clear evidence of mass transfer of Fe to the cold leg

Surface voids

Cr/Mn dissolved from surface

Hot leg: 647°C

Cold leg: ~552°C



SEM secondary electron images

Fe-rich deposited layer

Ni rich areas: Cr diffuses into outer ferrite layer

Cr/Mn absent at surface because Fe-rich deposit layer

These results need to be incorporated into future modeling work

Raiman et al., submitted to JNM

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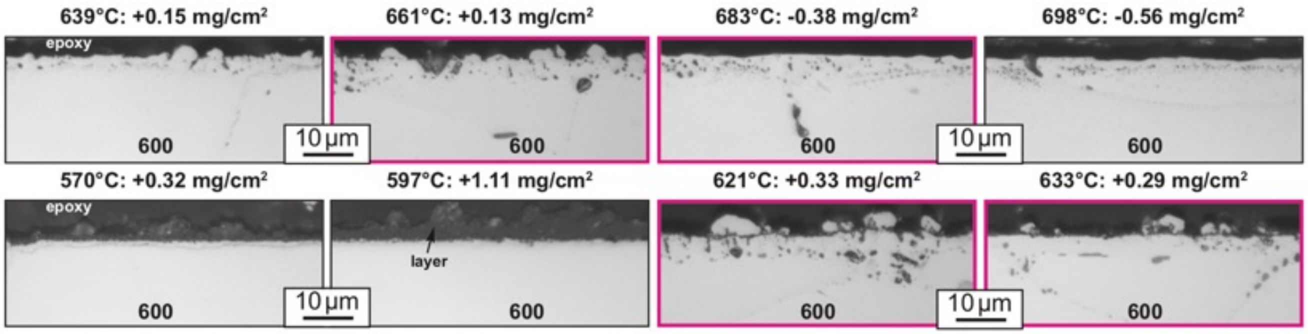
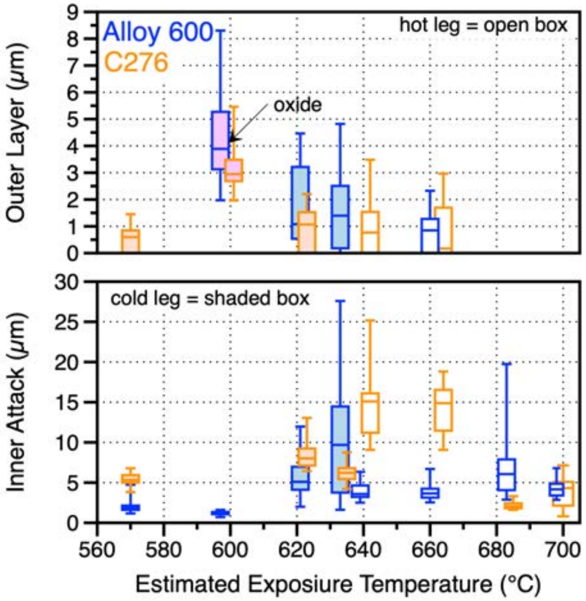
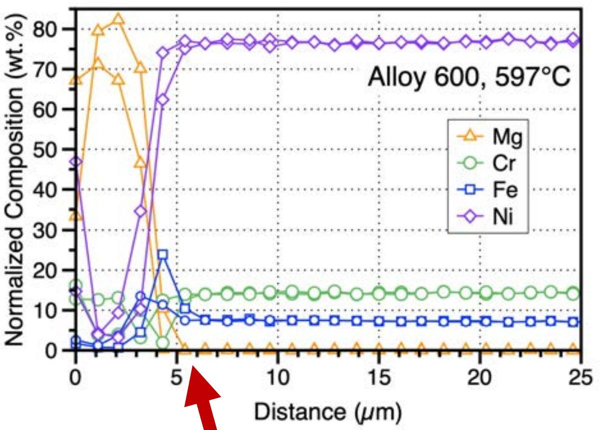
Fe transfer also observed in Cl salt loop (SETO): 700°C peak

Alloy 600 loop: Ni-14Cr-7Fe



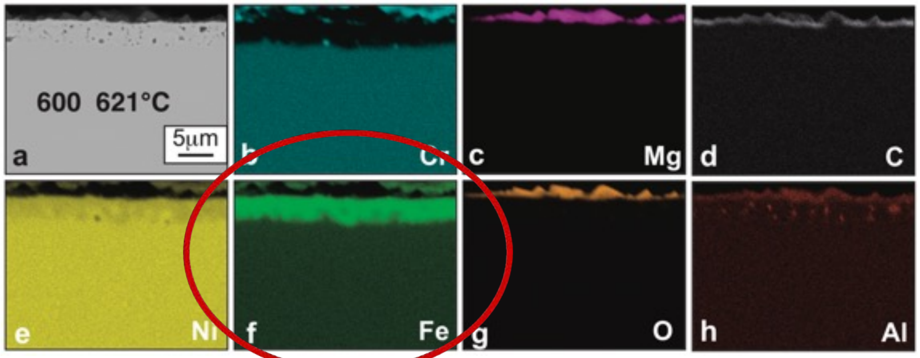


Mg deposited on specimen surface at 597°C



Fe peak

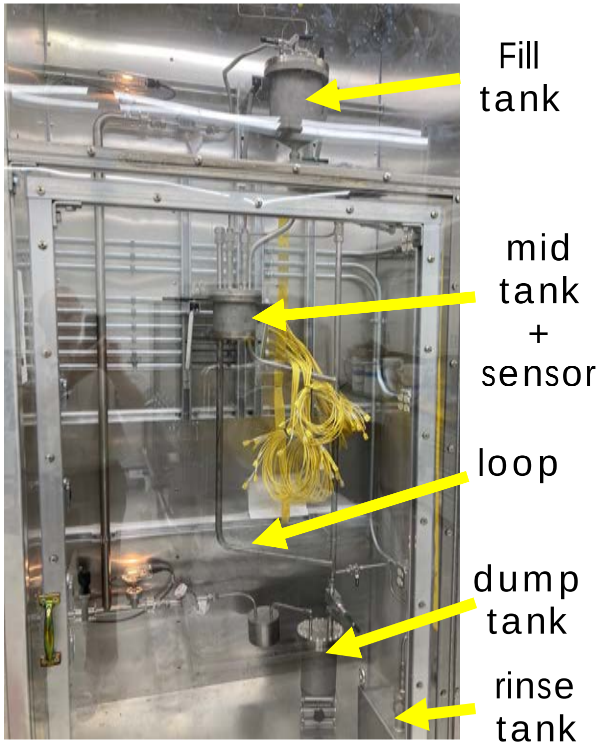
EDX maps: Fe enrichment + Mg-rich oxide. (cold leg)



FLibe loop almost ready to begin first experiment

Approved FLiBe loop design

FLiBe-dedicated glove box is operational



Loop in enclosure for flowing FLiBe experiment

Remaining issue is salt for 2nd FY21 TCL experiment

Future objectives are being finalized

- FY22
  - What happens at higher temperature/accident scenarios?
    - Industry identified need
    - Loop testing at 700°C or higher peak temperature
  - Continue to develop lifetime model
- Future topics
  - Compatibility effect of impurities/additives
  - Further development of corrosion sensors
  - Risk reduction for replacing 316H with higher strength 709 (20Cr-25Ni)
  - Similar studies for Cl salts

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