OAK RIDGE National Laboratory

Corrosion in molten salts: What matters, what doesn't, and what we can do about it.

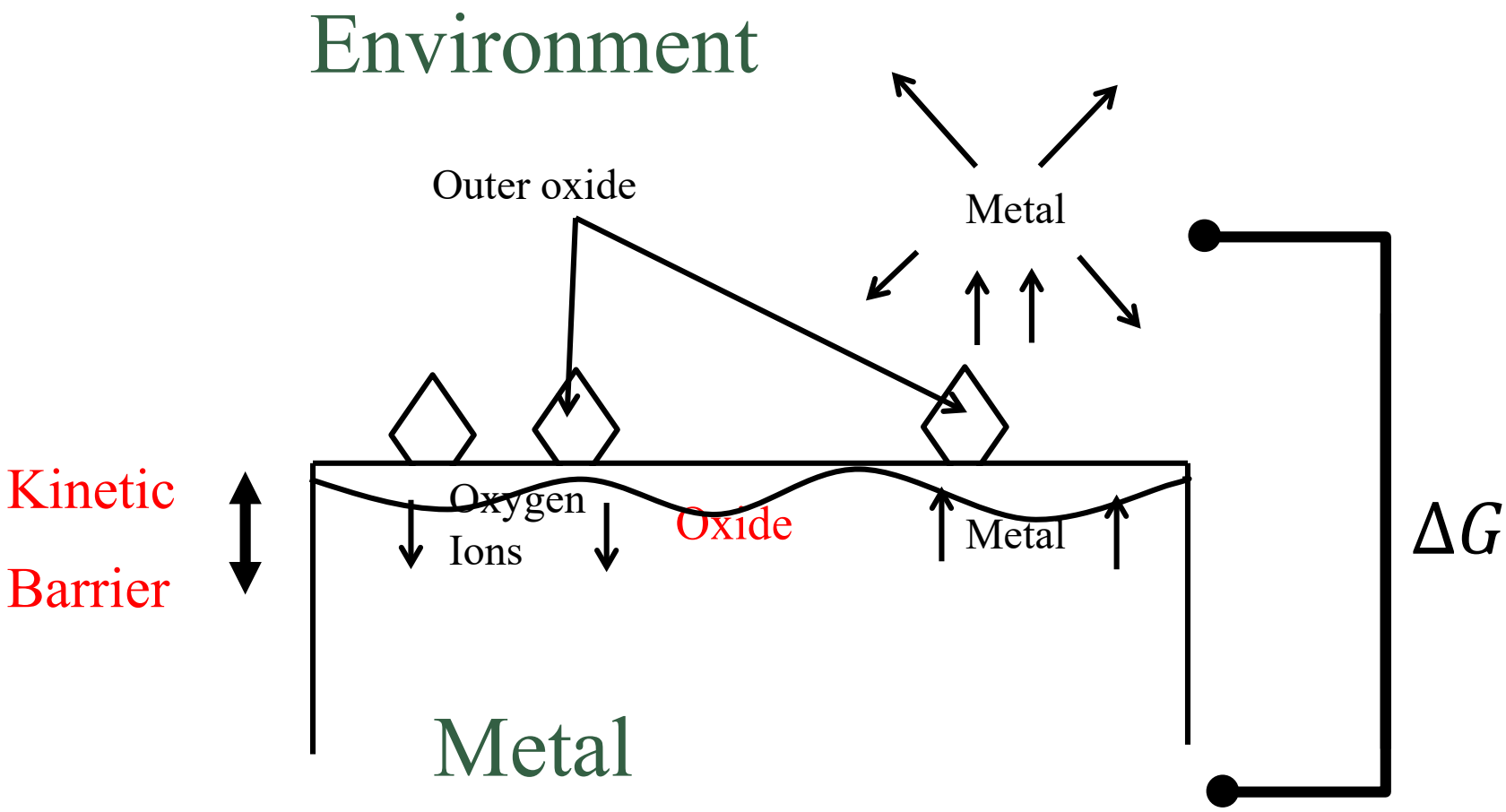
Stephen Raiman
R&D Associate
Materials Science and Technology Division

Supported by:
- DOE Molten Salt Reactor Campaign
- US NRC
- ORNL Laboratory Directed R&D

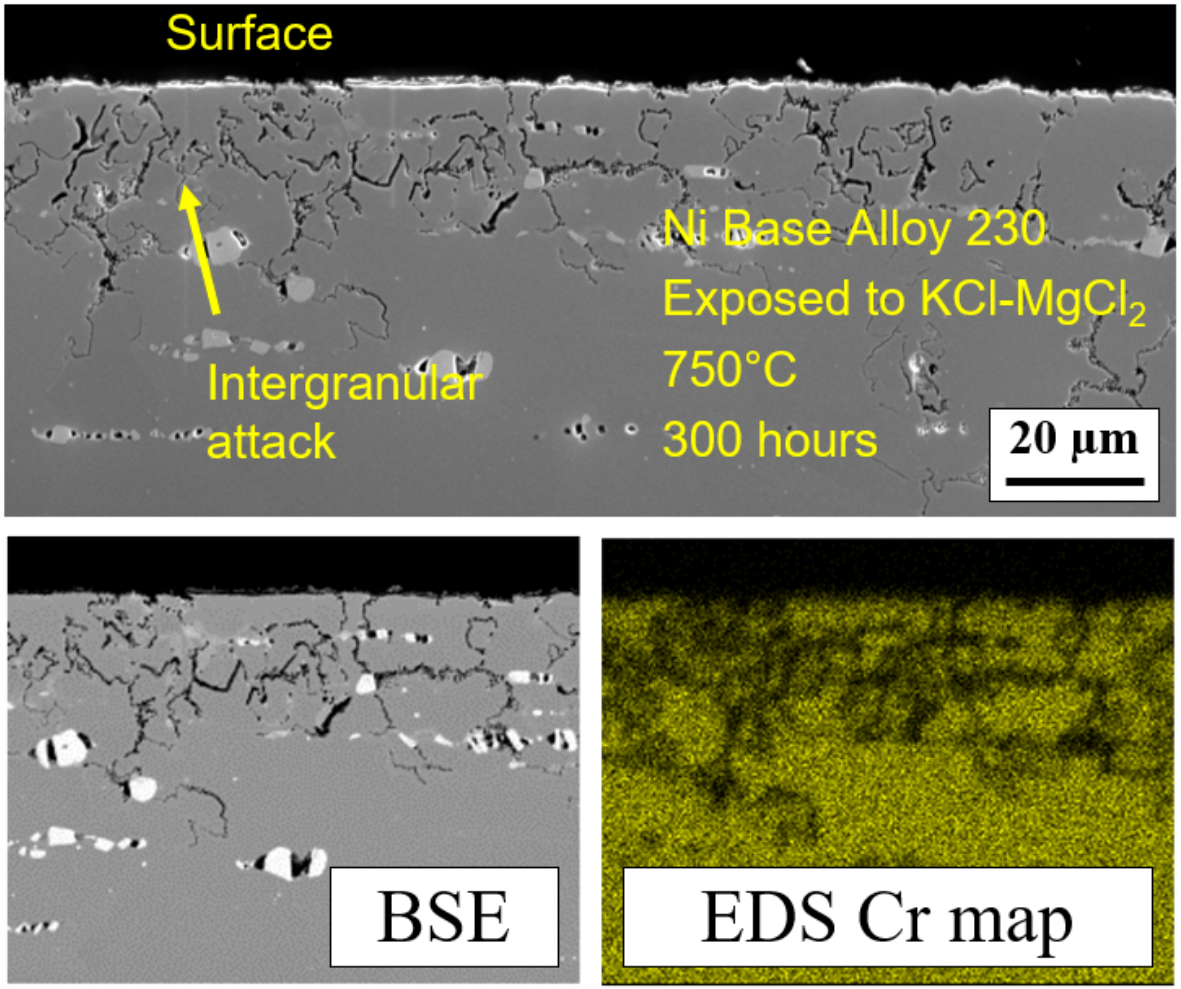
ORNL is managed by UT-Battelle, LLC
for the US Department of Energy

U.S. DEPARTMENT OF ENERGY

This is corrosion (most of the time)

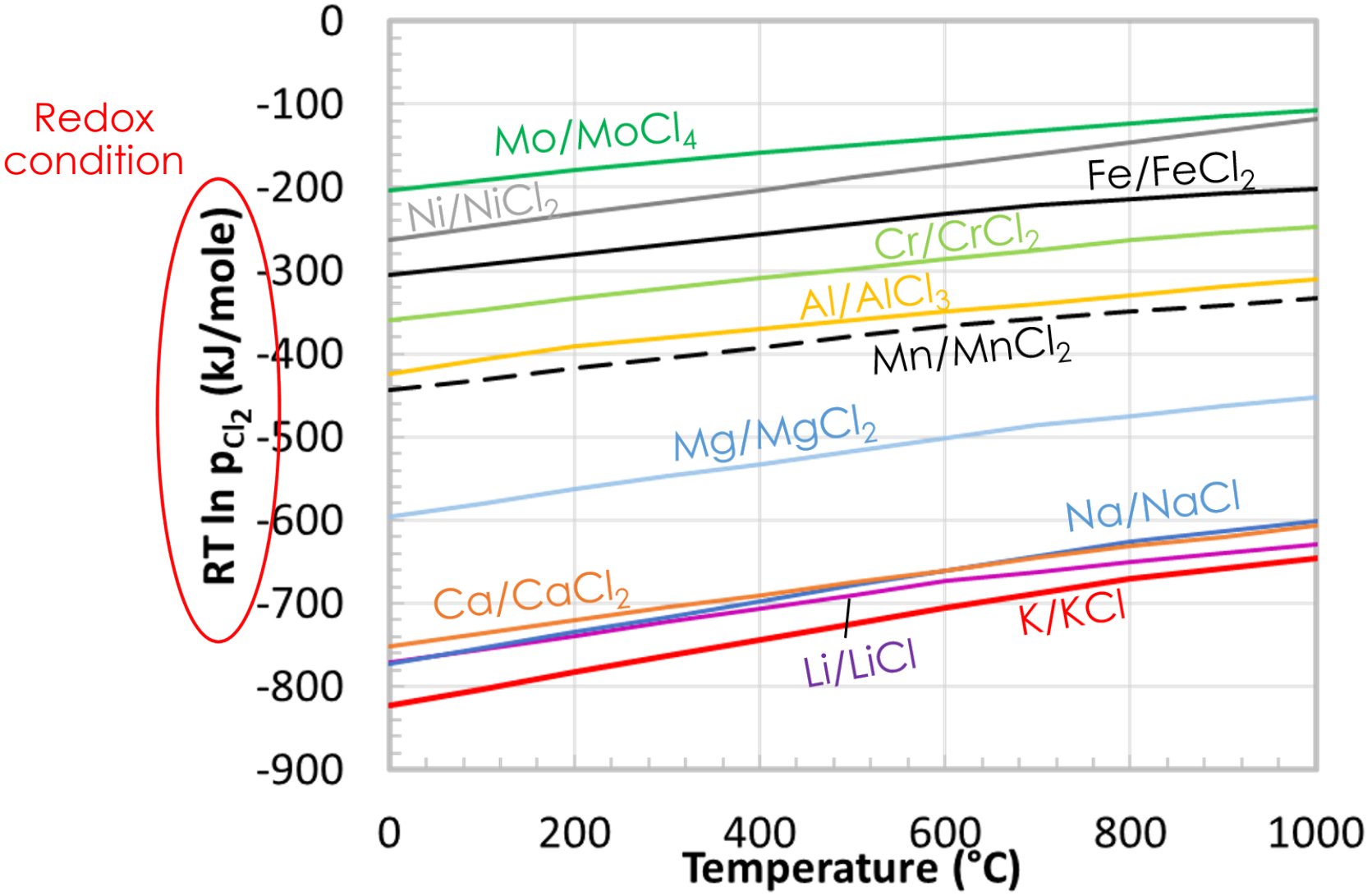


Materials in molten salts degrade by chromium depletion

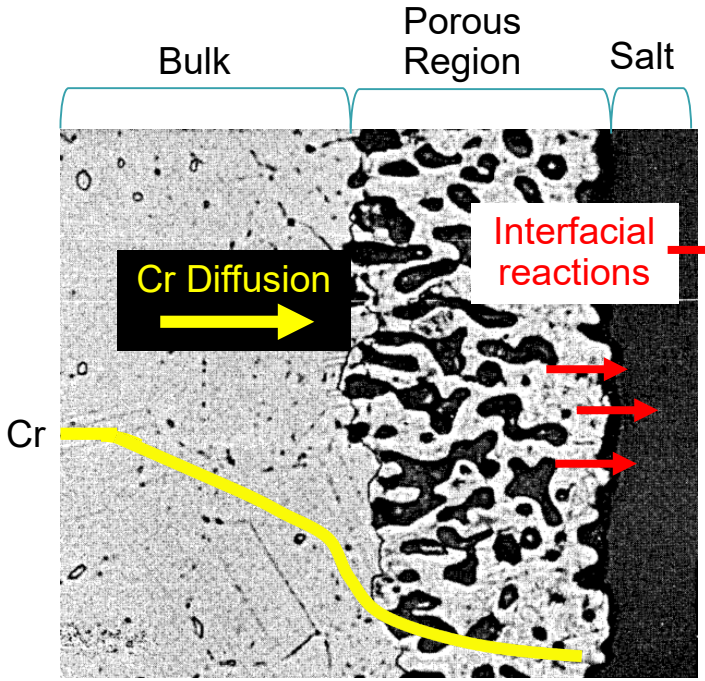


S.S. Raiman, Solar Energy Materials and Solar Cells 201 (2019)

Stability of Metals in Chloride Salts



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



- Salt impurities react with structural alloys

$$2HCl(d) + Cr(s) \rightarrow CrCl_2(d) + H_2(d)$$

- Metallic halides

$$Cr(s) + FeCl_2(d) \rightarrow CrCl_2(d) + Fe(s)$$

- Fuel

$$Cr(s) + 2UCl_4(d) \rightarrow CrCl_2(d) + 2UCl_3(d)$$

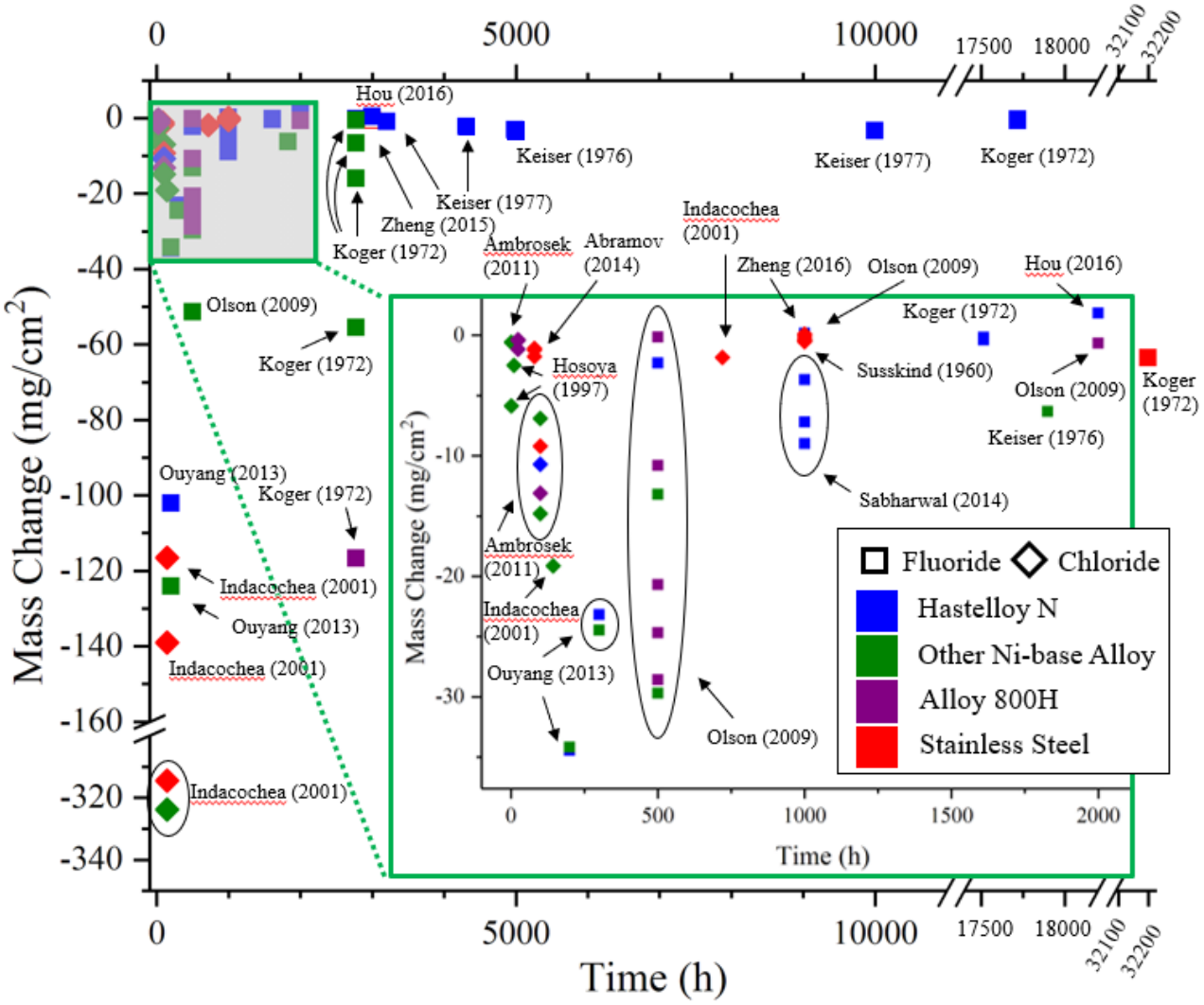
Similar reactions in F salt, just replace Cl with F

Our objective is to understand degradation of structural materials in molten salts, and turn that understanding into actionable engineering knowledge

- Optimized chemistry-material choices
- Accurate models of in-reactor behavior
- Development of advanced materials
- Longer lifetimes & improved economics
- Prudent and informed regulatory decisions

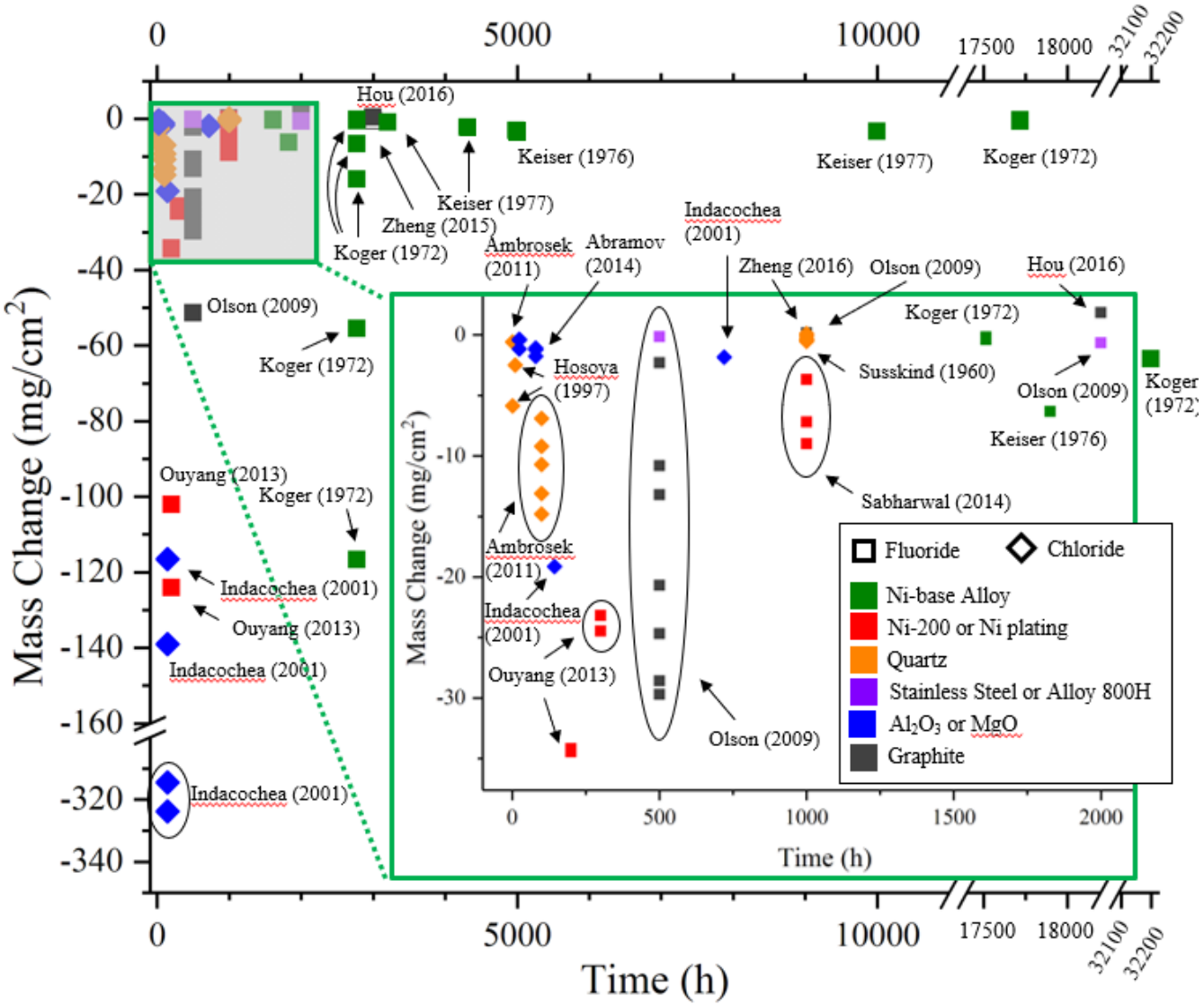
What matters?

This data is a mess



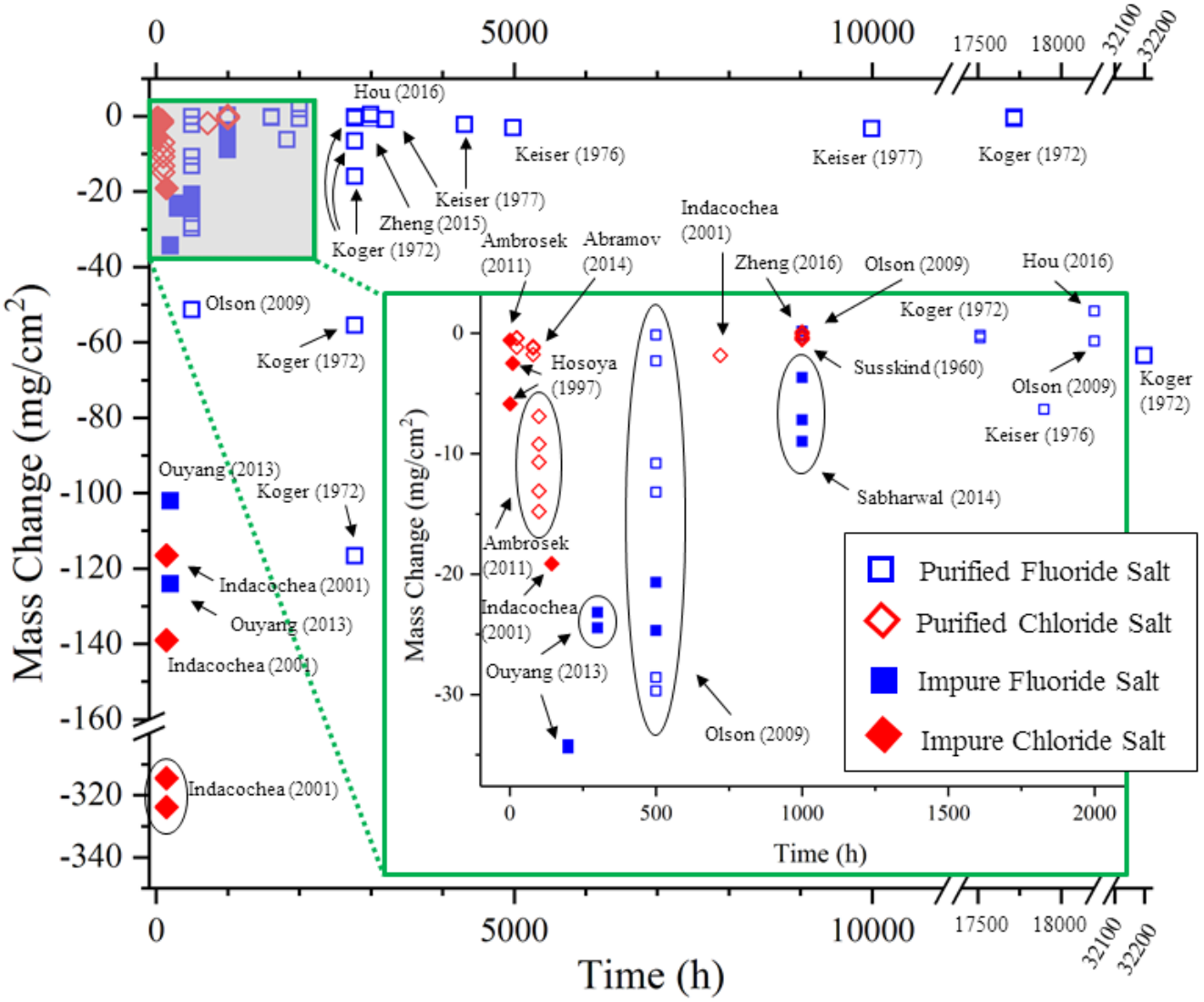
Raiman, Lee, *J. Nucl. Mater. 511 (2018)*

Container material doesn't seem to matter



Raiman, Lee, *J. Nucl. Mater. 511 (2018)*

Salt purity seems to matter

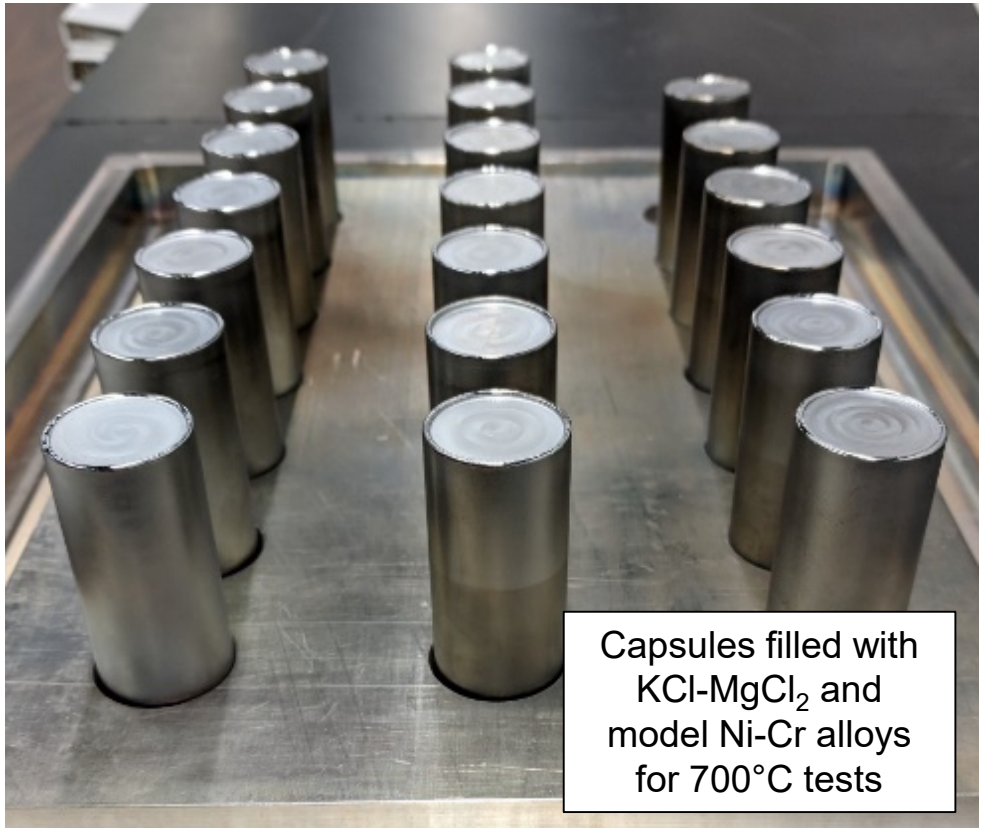


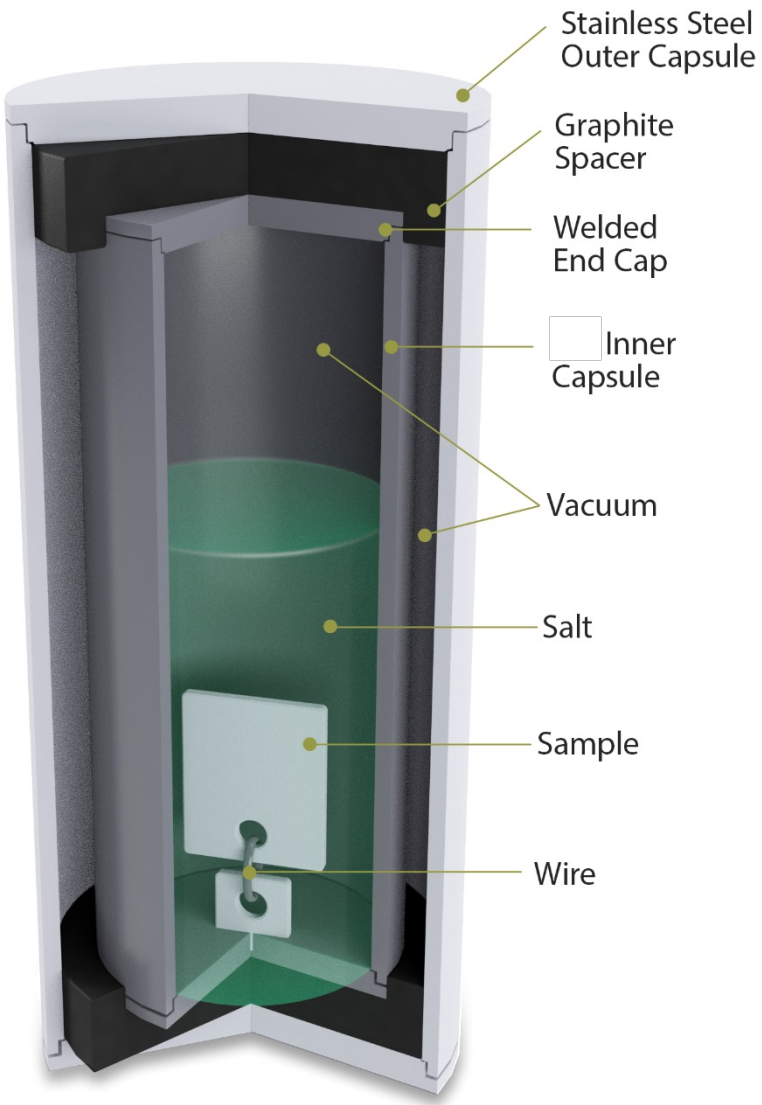
Raiman, Lee, *J. Nucl. Mater. 511 (2018)*

Experimental Techniques

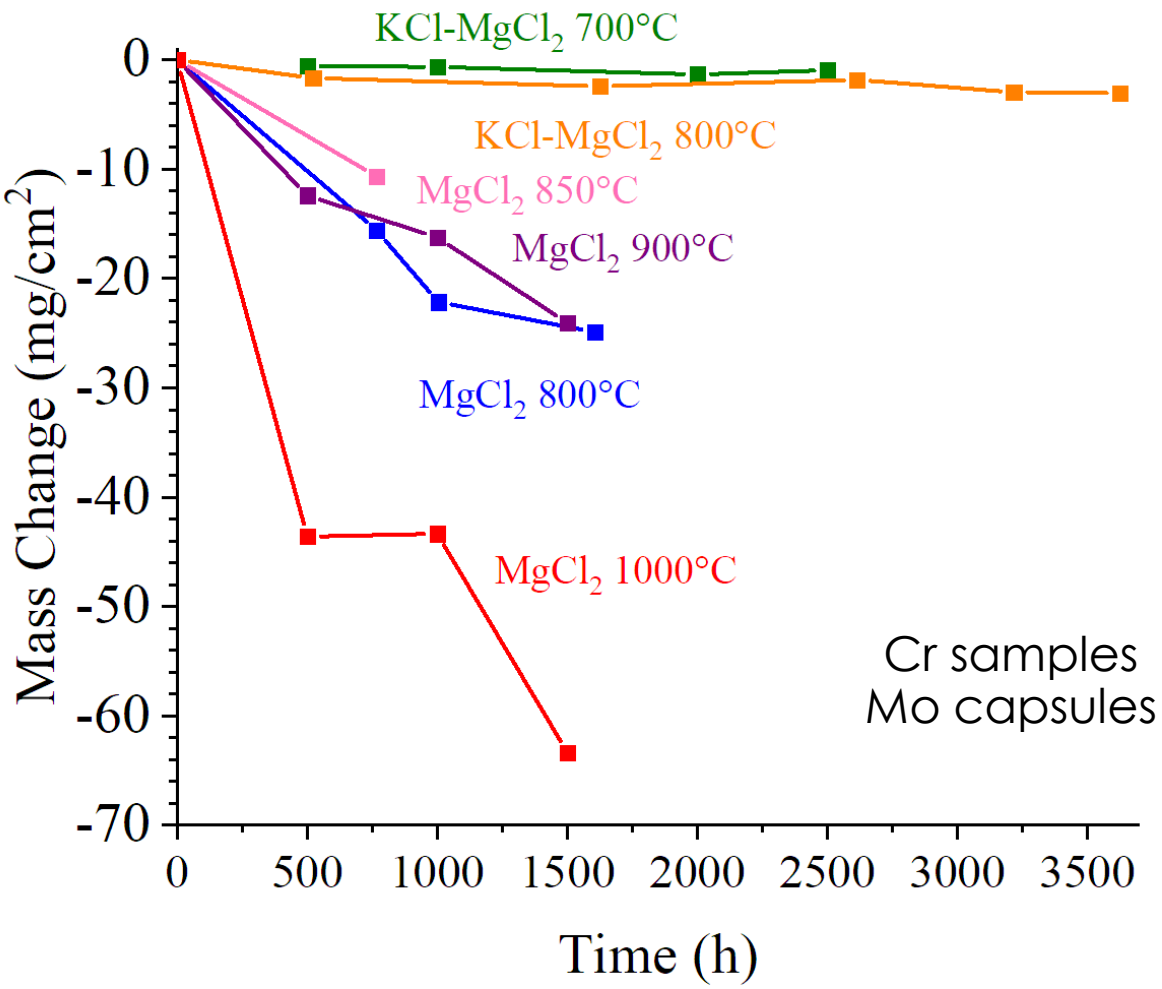
Providing the evidence basis for good decisions

Capsule testing





Mass change in $MgCl_2$ is generally higher than in KCl-$MgCl_2$



Raiman (unpublished)

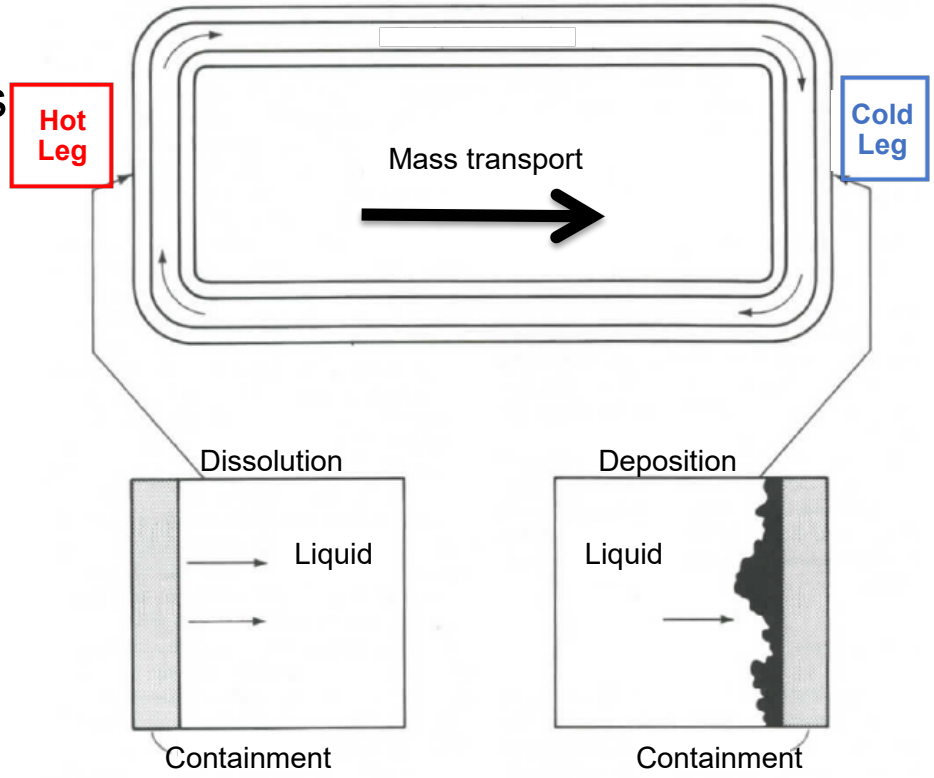
Flowing salt with a thermal gradient is required to accurately reproduce MSR conditions

- Temperature-dependent equilibrium constants drive mass transfer

$$Cr + Cl_2 \leftrightarrow CrCl_2$$

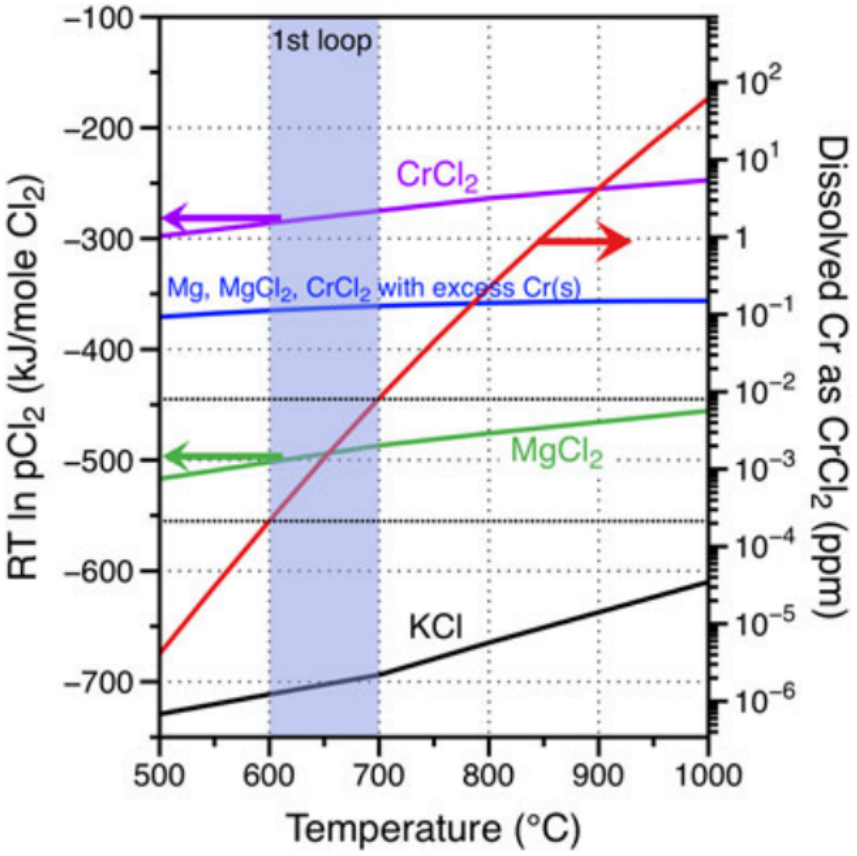
Hot leg: reaction moves to right (depletion)

Cold leg: reaction moves to left (deposition)



Why a thermal gradient matters

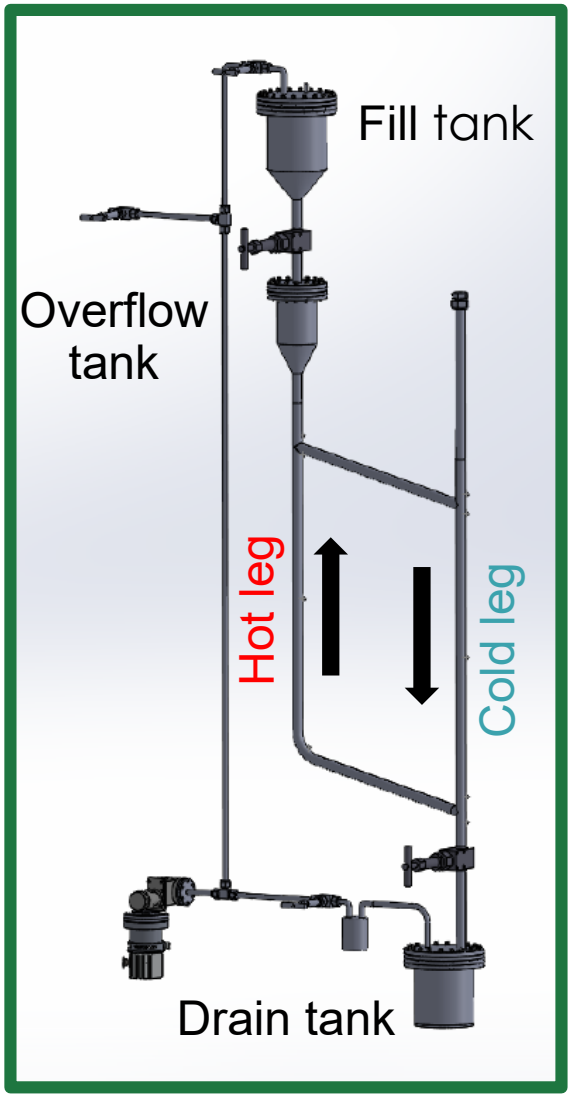
Computed equilibrium concentration of $CrCl_2$ in KCl-$MgCl_2$ based on
Cr + $MgCl_2$ (liq) → $CrCl_2$ (liq) + Mg (liq)



Pint et al. *Mater and Corros* (2018)

Thermal convection loops at ORNL

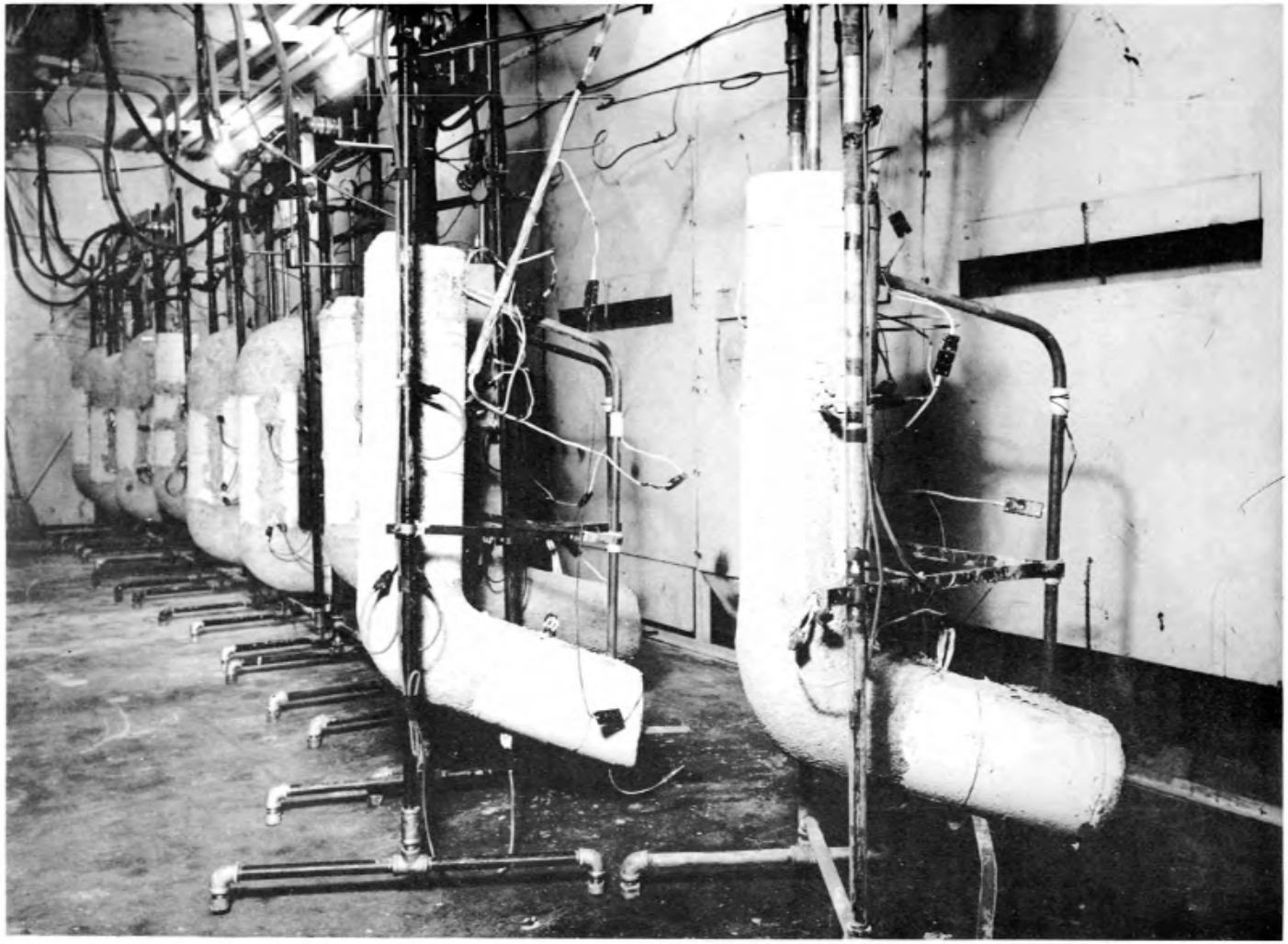
- Salt is introduced at top
- Flow is driven by thermal gradient
- Coupons are hung in both the hot leg and cold leg



Recently completed TCL experiment

- 650°C max temp, 540°C minimum
- FLiNaK salt
- 316 tubing
- 316 samples

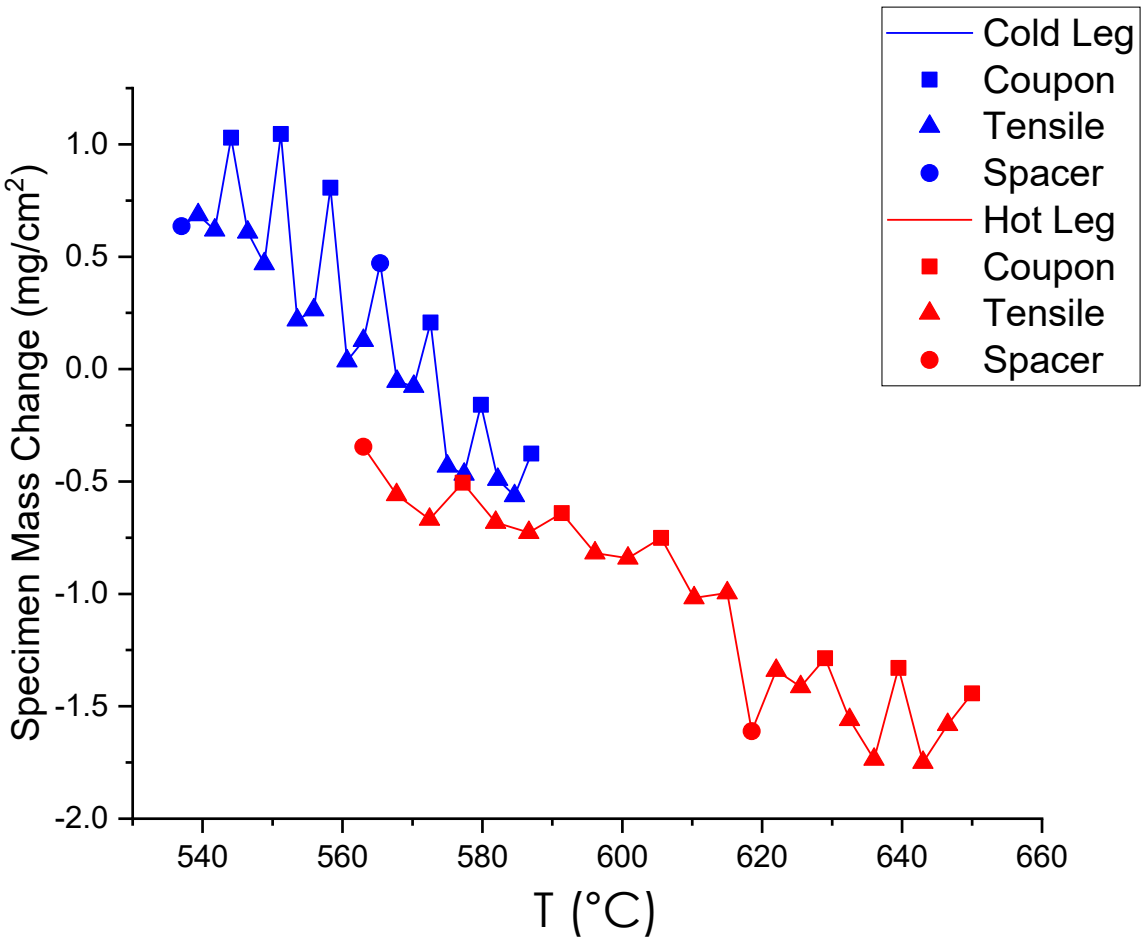
TCLs have been run at Oak Ridge since the Aircraft Reactor Experiment



Manly et al. ORNL-2349 (1957)

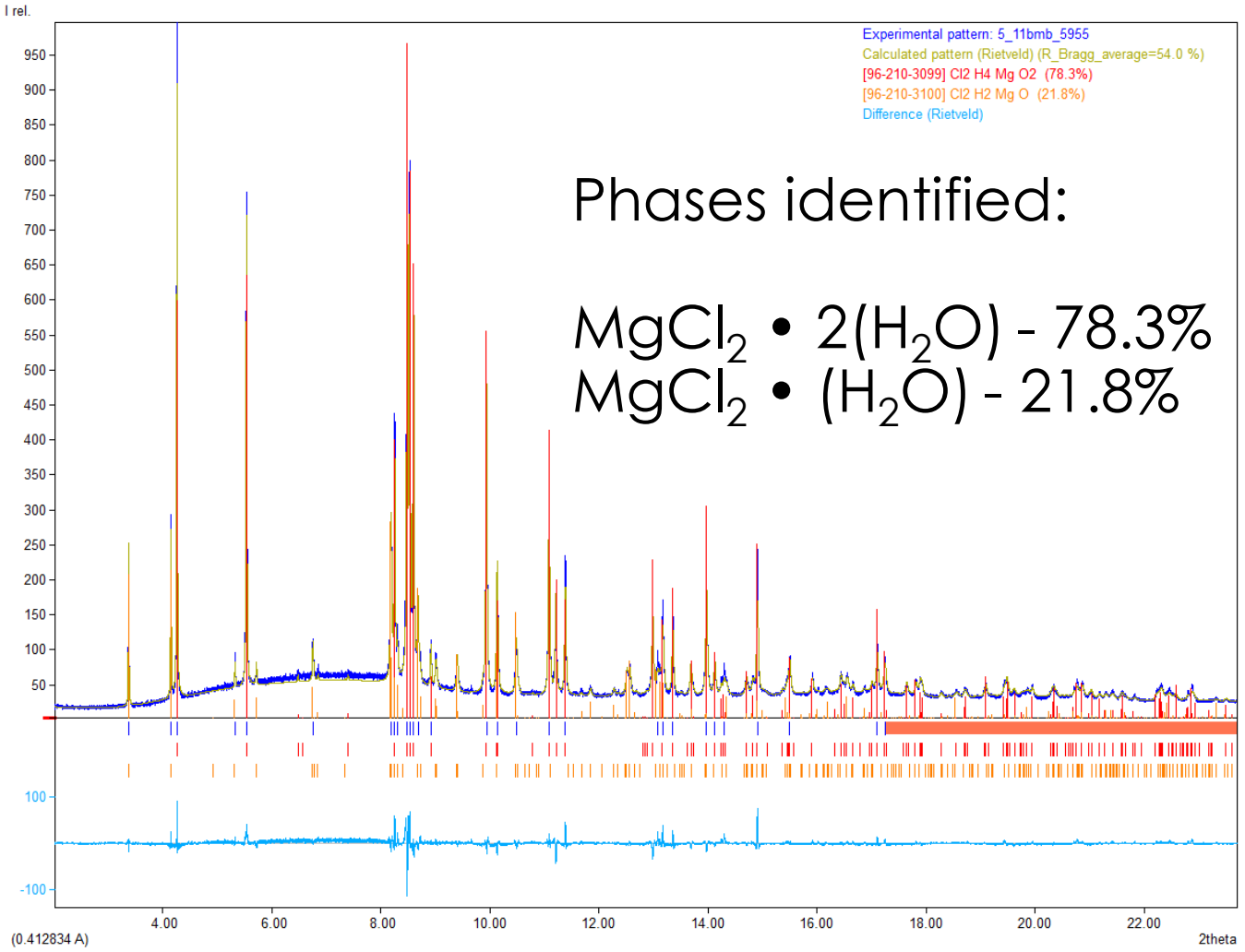
Mass transfer is visible on TCL samples

316 TCL with purified FLiNaK salt



Preparing good salt

As-received 'anhydrous' $MgCl_2$ is a mixture of mono- and di-hydrate

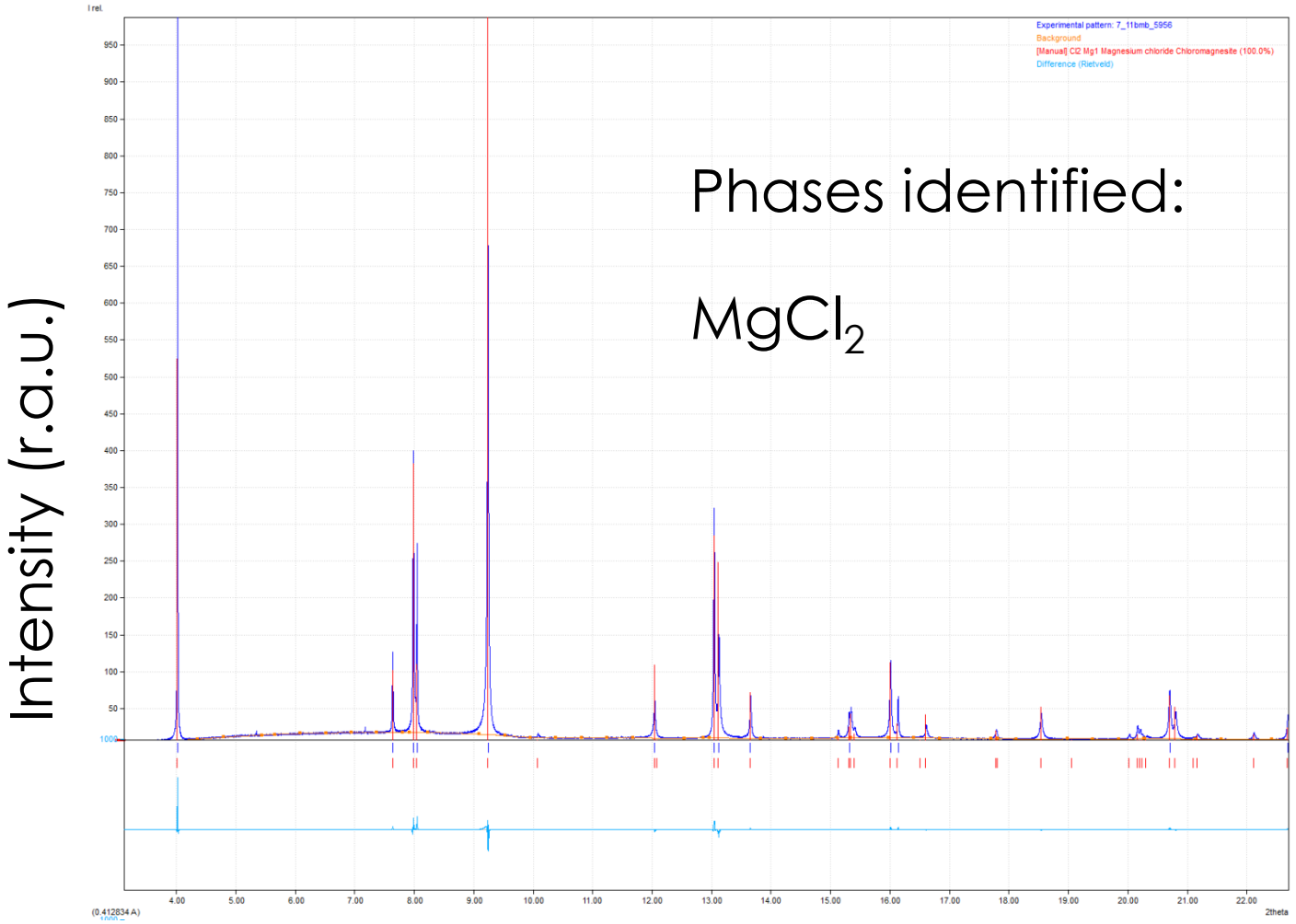


D. Sulejmanovic (unpublished)

This is a big problem

(because salt chemistry matters)

Chemical chlorination successfully dehydrates $MgCl_2$



2θ

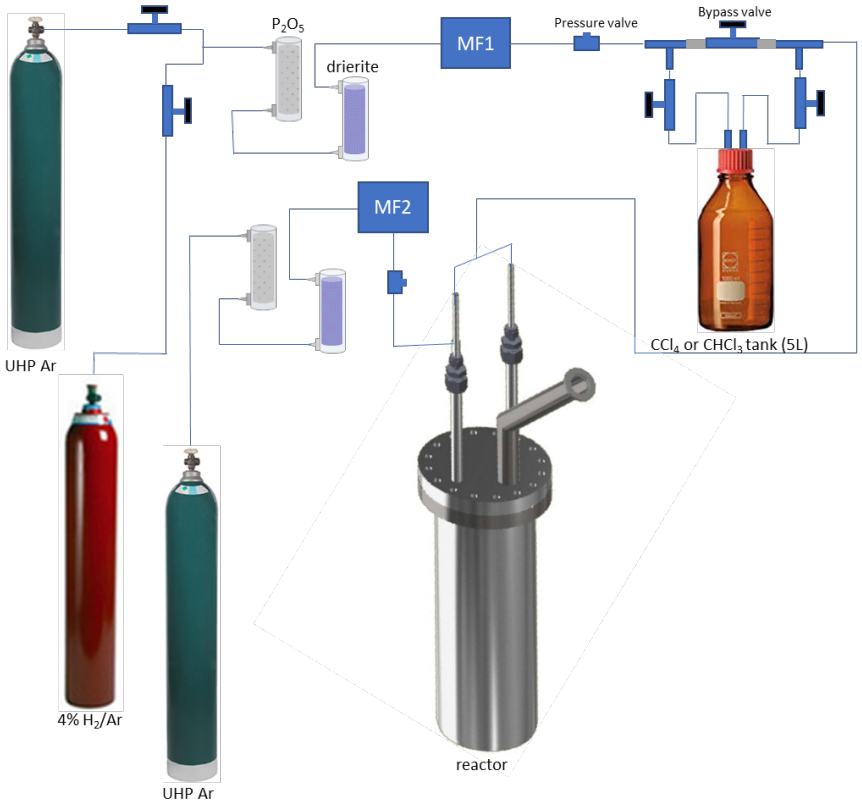
D. Sulejmanovic (unpublished)

Chloride salts purified by chemical dehydration and chemical chlorination

- Dehydration with NH_4Cl:

$$NH_4 \cdot MgCl_2 \xrightarrow{\Delta} MgCl_{2(s)} + NH_4Cl_{(v)}$$

- Chlorination:
- $CHCl_3 + MgO \rightarrow MgCl_2 + \frac{1}{2}CO_2 + HCl + \frac{1}{2}C$
- $\frac{1}{2}CCl_4 + MgO \xrightarrow{\Delta} MgCl_2 + \frac{1}{2}CO_2$



Salt purity must be maintained under all handling and operating conditions

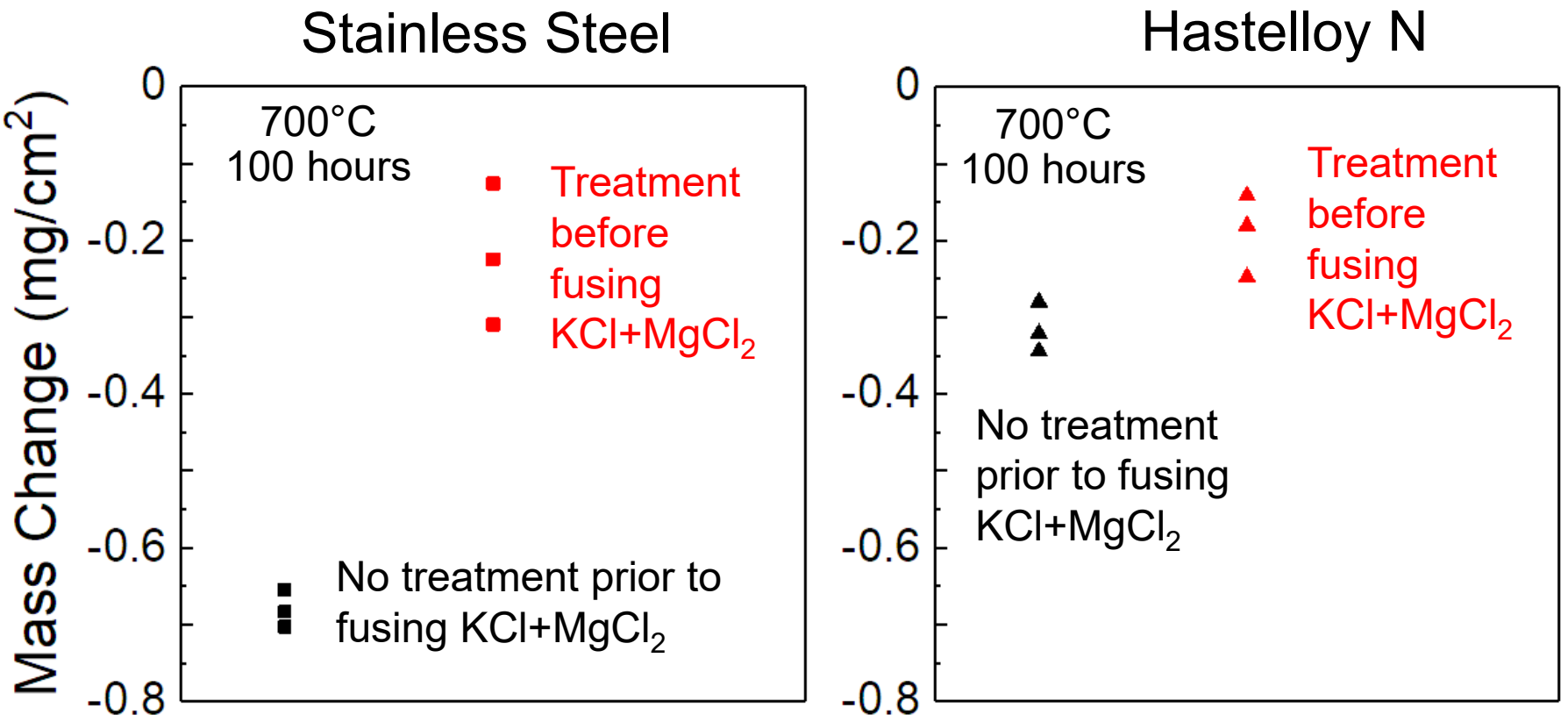
Fluoride salt preparation

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

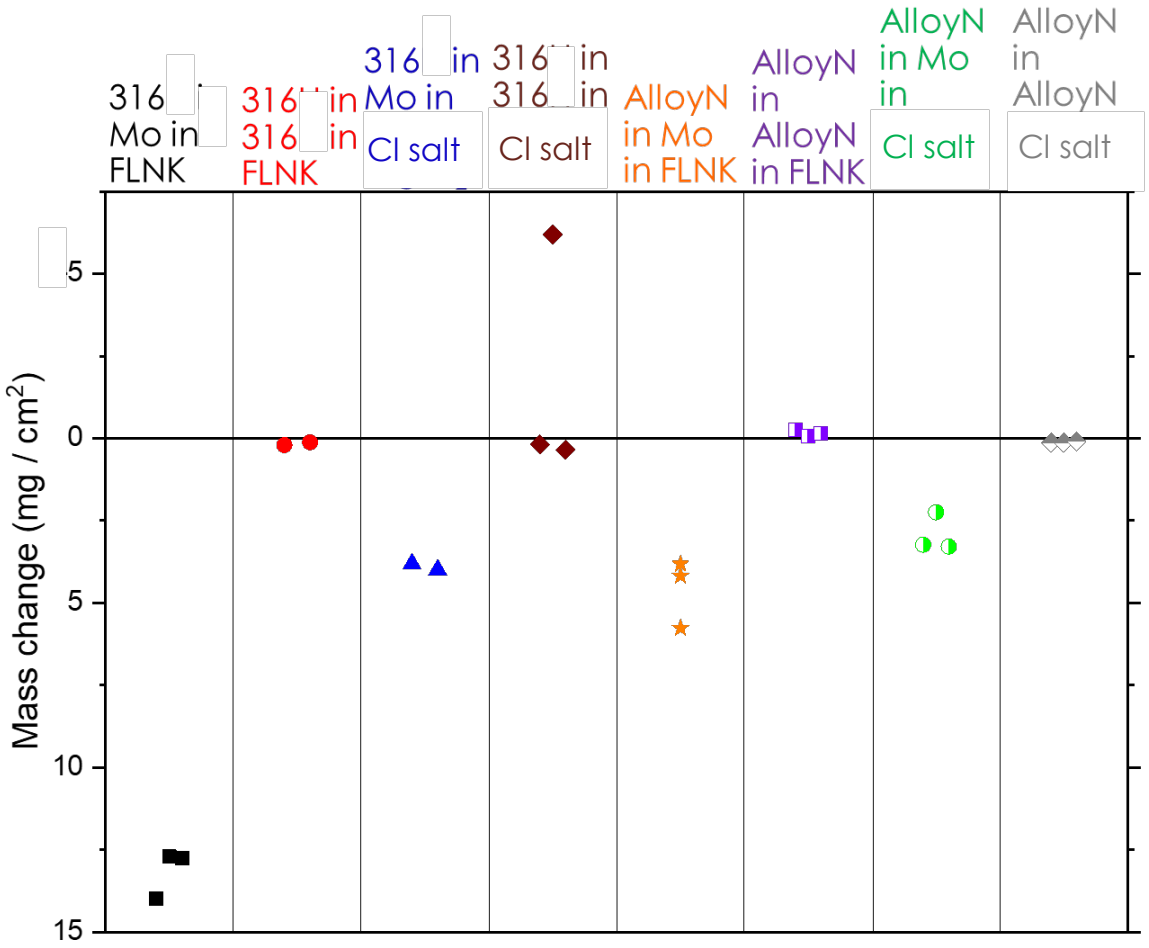
Source: K. Robb

So now that we've got that right

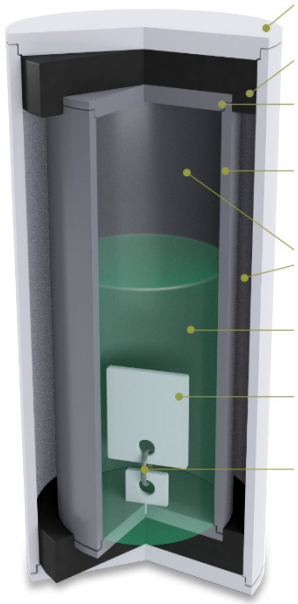
Salt purification matters



Capsule material? Matters

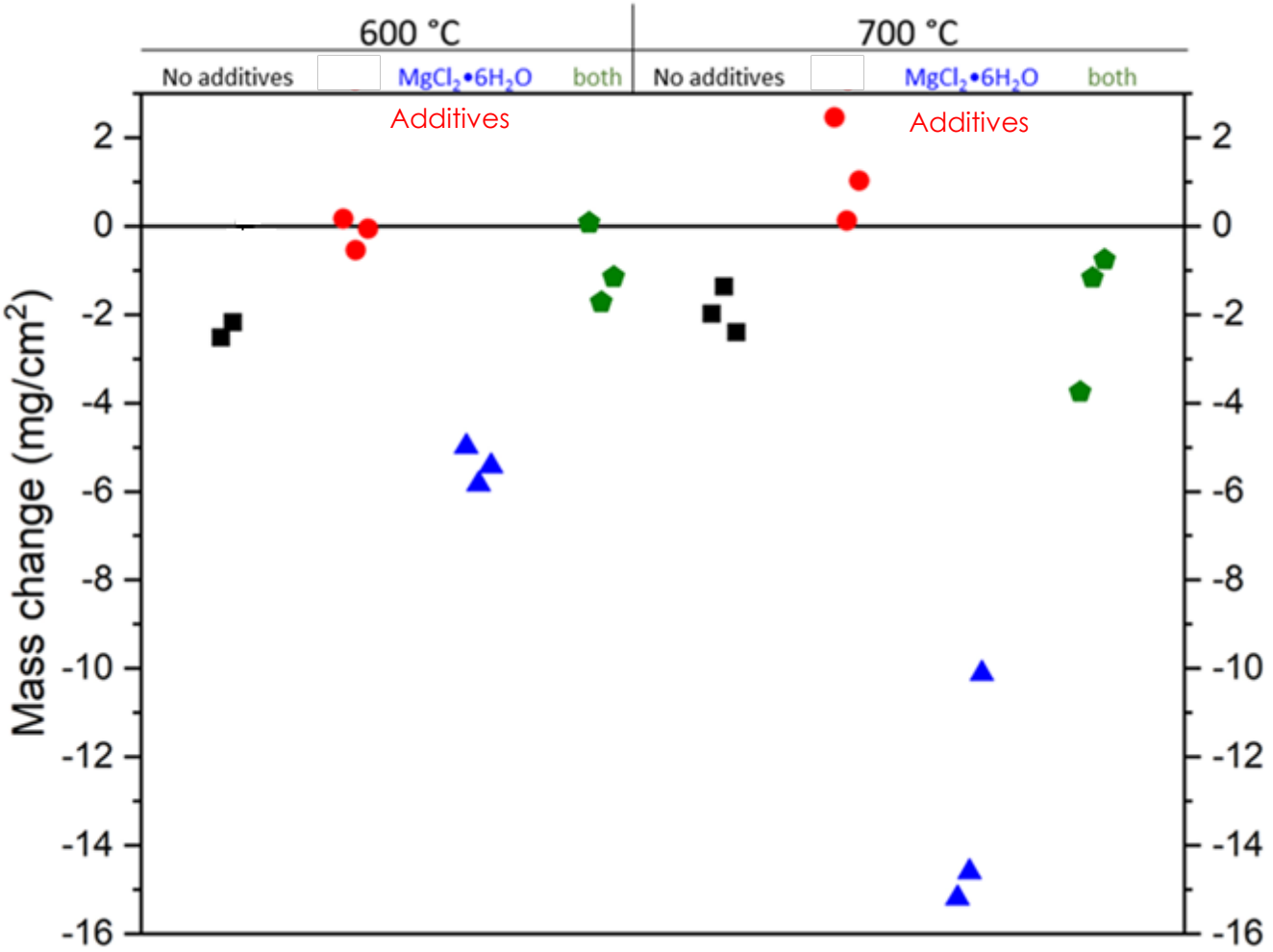


700°C
500h
Purified Cl salt
"aggressive" FLiNaK



Sulejmanovic et al. (unpublished)

Moisture? Redox control additives? They matter too



316 Stainless

Chloride salt with:

- Metallic additions
- 0.1% H_2O
- Both
- Neither

Raiman et al. (unpublished)

Conclusions (and a commercial)

- Consistent experiments are important
  - Control variables
- Salt chemistry matters most. When it's good, other data emerges
- DOE can provide characterized salts for research under certain circumstances