U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY

Molten Salt Reactor PROGRAM

Salt and Materials Interaction

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Acknowledgments

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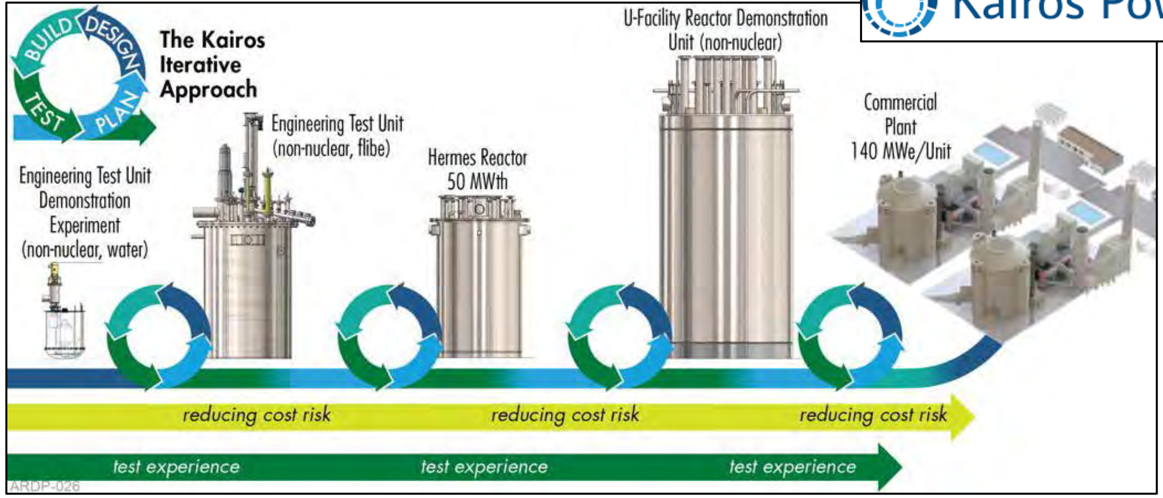
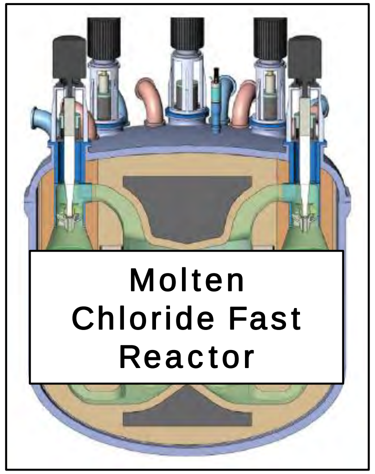
- **ORNL team**
  - Dino Sulejmanovic: salt purification, handling and characterization
  - Adam Willoughby: thermal convection loops
  - Brandon Johnston, John Wade, Kelsey Epps: Creep tests
  - Yi-Feng Su, Michael Lance and Tracie Lowe: characterization
  - Jim Keiser, David Holcomb, Lou Qualls: consulting
- **Kairos Power: salt (A. Kruizenga) and feedback (G. Young)**

Molten salt reactors are on their way primarily driven by extensive legacy knowledge

Kairos Power



TerraPower
A Nuclear Innovation Company


Molten Chloride Fast Reactor

- ➢ **Impact of long-term operation in different salts?**
- ➢ **Role of impurities?**
- ➢ **Material degradation due to coupled extremes of stress, corrosion and irradiation?**
- ➢ **Enough information to predict material performance over reactor operating lifetimes of 30-50 years?**

Providing critical data on structural materials compatibility and lifetime in molten halide salts

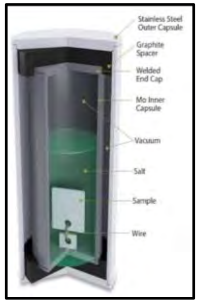
Specification

- Salt chemistry
- Fuel salt vs Coolant salt
- Allowable impurities
- Redox control

Purification + Testing

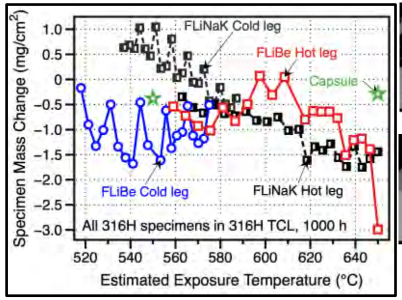
Static capsule testing

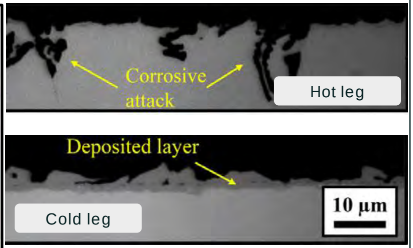
Thermal Convection loops



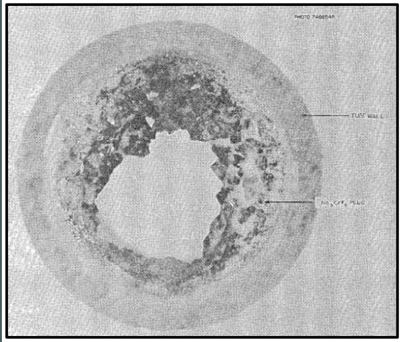
Mass Transfer

- Corrosion
- Deposition
- Temperature dependence





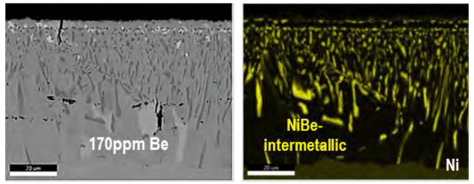
*Raiman et al. 2022



Hastelloy N, $NaBF_4$-NaF-KBF_4
8760 h, TCL 605º460C
- J. Koger, Corrosion, 1974

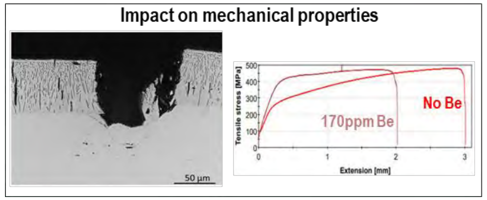
Long-term operation

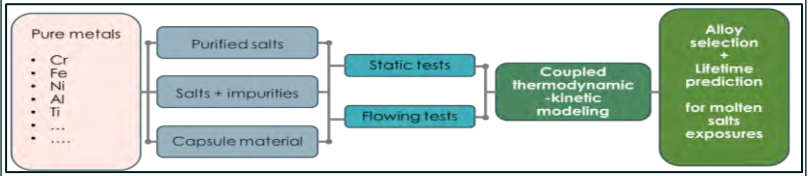
- Transmutation performance
- Salt chemistry (changes?)
- Redox control (how much?)
- Useful predictive models



316H, FLiBe, 1000h capsule test, 650 °C

- Keiser et al., JNM, 2022





Salt and Materials Interactions: FY23-24 R&D Goals

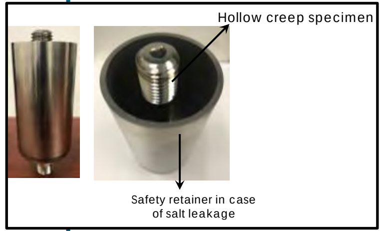
FY22 Carryover
M3RD-23OR0603031: Measure Cr/Fe dissolution in FLiNaK and FLiBe

- Three temperatures (550°, 650°, 750°C) and three times (500-2000 h)
- Completed Cr and Fe in FLiNaK
- Completed Cr and Fe in FLiBe

M3RD-23OR0603032: Measure Cr/Fe dissolution at 850°C in two halide salts

- Completed three times (100, 500, 2000 h) in FLiNaK and FLiBe
- Repeating Fe in FLiNaK and FLiBe with pure Fe capsules

M3RD-24OR0604042: Measure the effect of molten halide salt exposure on creep rupture lifetime (316H, 709 and 617)



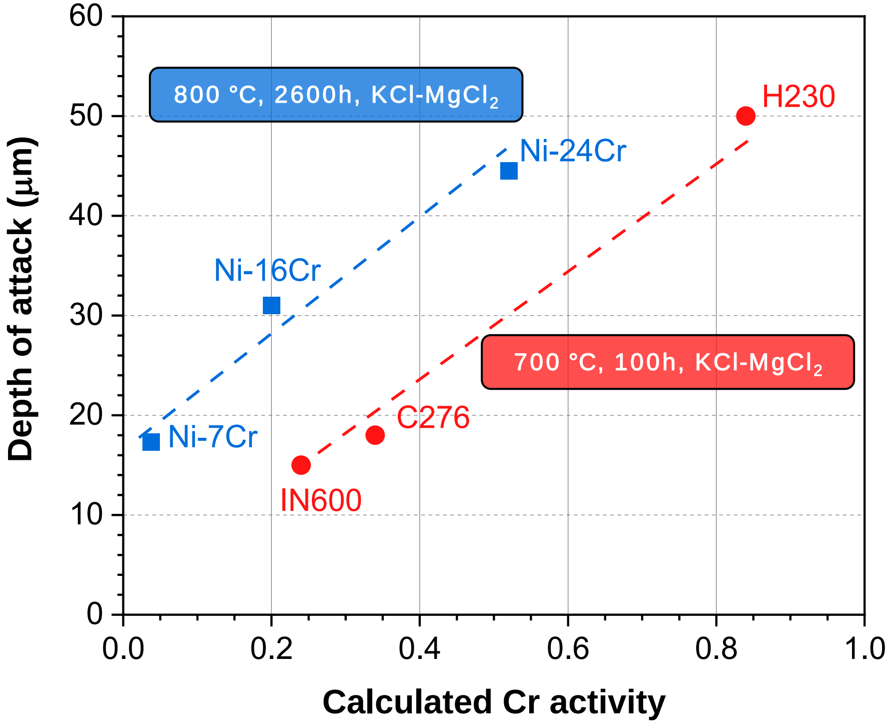
- Initiated creep testing for 617 (baseline and in FLiNaK) and 709 (baseline)

✓ **Extend previously developed and validated model for predicting molten-salt corrosion degradation of structural materials to flowing conditions**

✓ *Pillai et al., JNM 2021, JOM 2023*

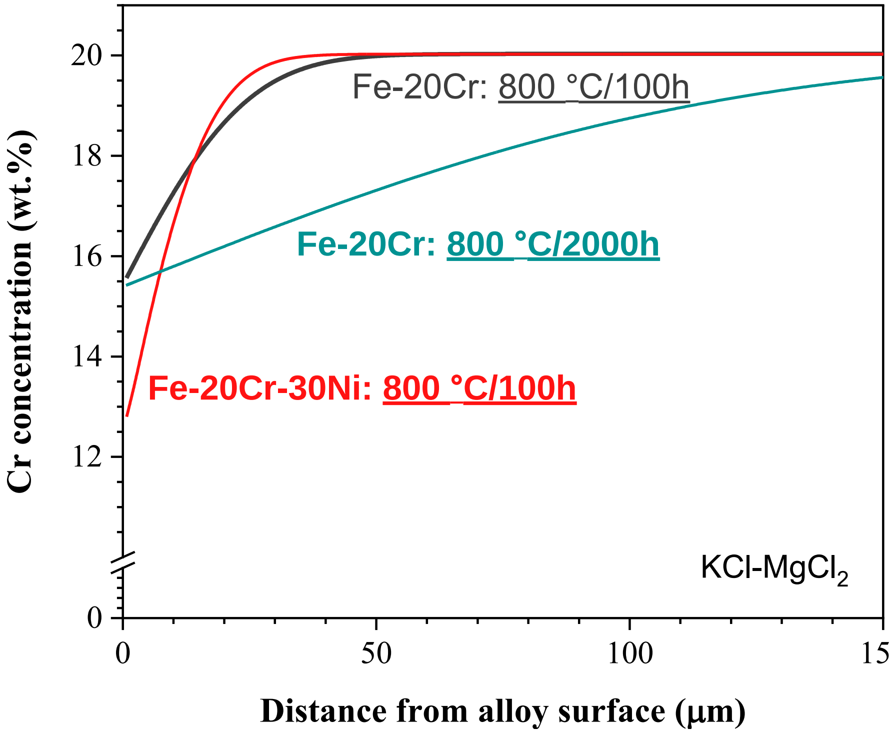
First stage* of model development involved using the experimentally measured corrosion rates as input

Alloy Thermodynamics



- Susceptibility to molten salts corrosion is proportional to the alloy Cr activity
  - *for similar transport kinetics in the alloy*

Alloy transport kinetics



- Transport in the alloy is rate-limiting
- Accurate description of long-term material behavior

How can we extend this to a more generic approach for multicomponent-multiphase technically relevant alloys?

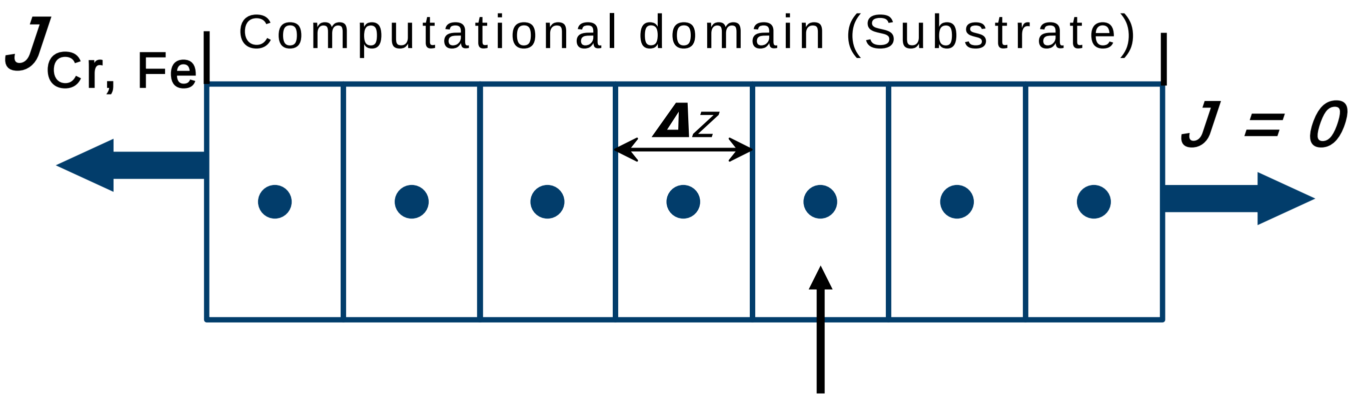
*Pillai et al. , JNM, 2021

Setting a key hypothesis for the One-dimensional Physics-based Modeling approach

- If Cr/Fe concentrations in the salt are measured for exposures of pure Cr/Fe as a function of time and temperature, the dissolution rate $\boldsymbol{k(T)}$ can be estimated

- For a multicomponent alloy, the Cr/Fe depletion can then be scaled based on the surface Cr/Fe activity (since $a_{\mathrm{Cr}} = 1$ for pure Cr) and defined as a flux boundary condition,

$$J_{\mathrm{Cr}} \propto \boldsymbol{k(T)} * a_{\mathrm{Cr}}$$



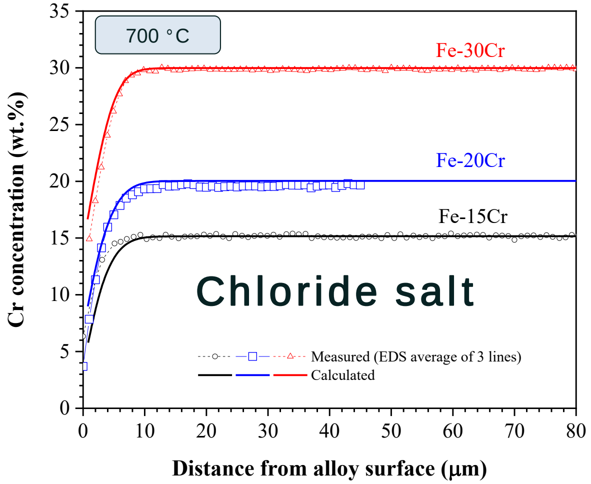
- Calculation of element fluxes
- Calculation of phase equilibria

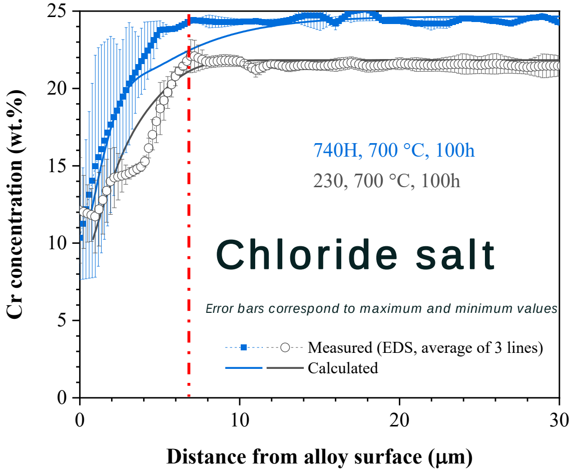
– **Calculate microstructural evolution in the alloy**
  - Using measured concentrations of pure elements after exposure in purified halide salts
  - Use of independent thermodynamic-kinetic data (Thermo-Calc)
  - Empirical description of grain boundaries (e.g., accelerated diffusion)
  - Consideration of relevant elements & phases in commercial high temperature alloys and coating systems
  - Thermodynamic calculations on multiple cores → <u>30,000h simulation of multicomponent-multiphase alloys in < 1 week</u>

**Pillai et al. , JOM, 2023*

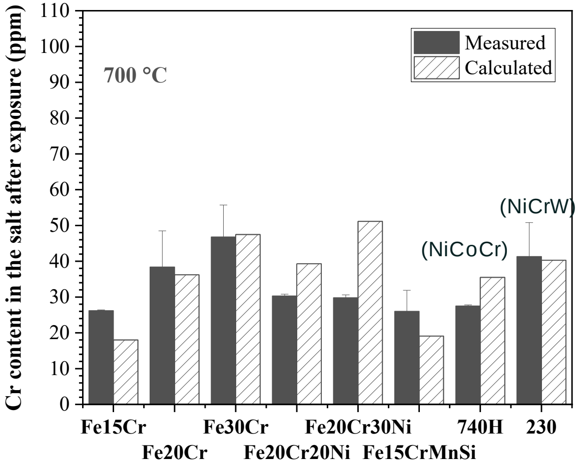
Established a validated physics-based approach to predict molten salts corrosion in multicomponent and multiphase alloys under static test conditions

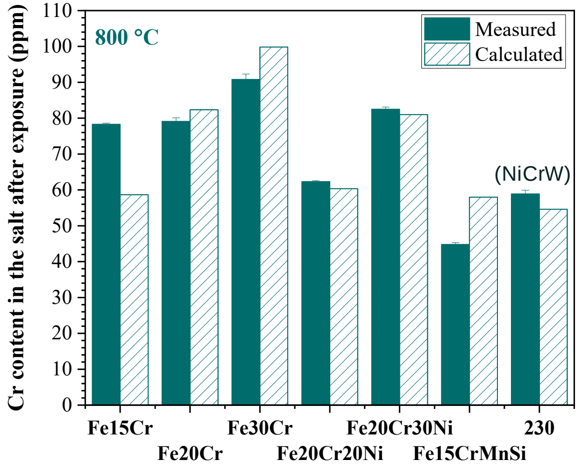
Comparison between measured and calculated compositional changes



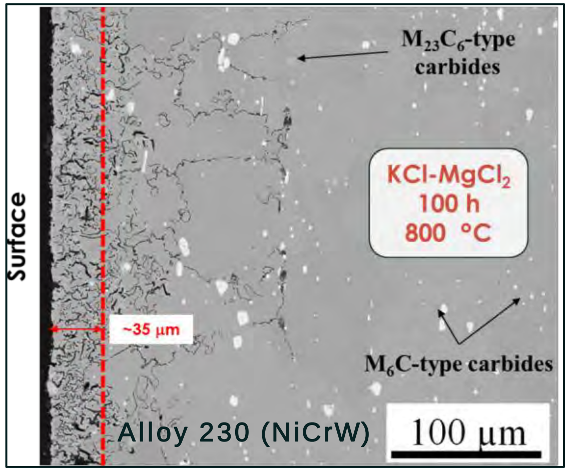


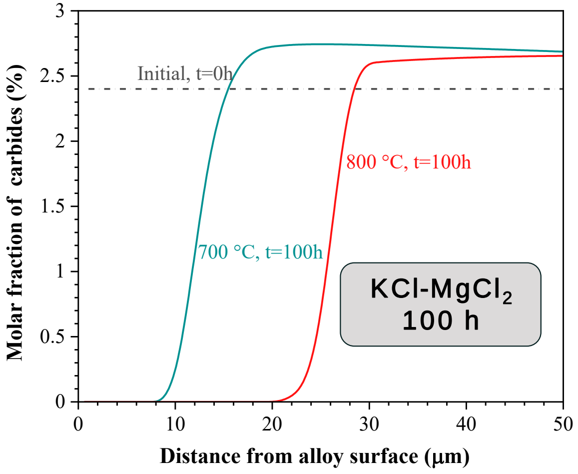
Model correctly predicts dissolved amounts of Cr in the salt





Modeling approach allows predicting dissolution of key phases

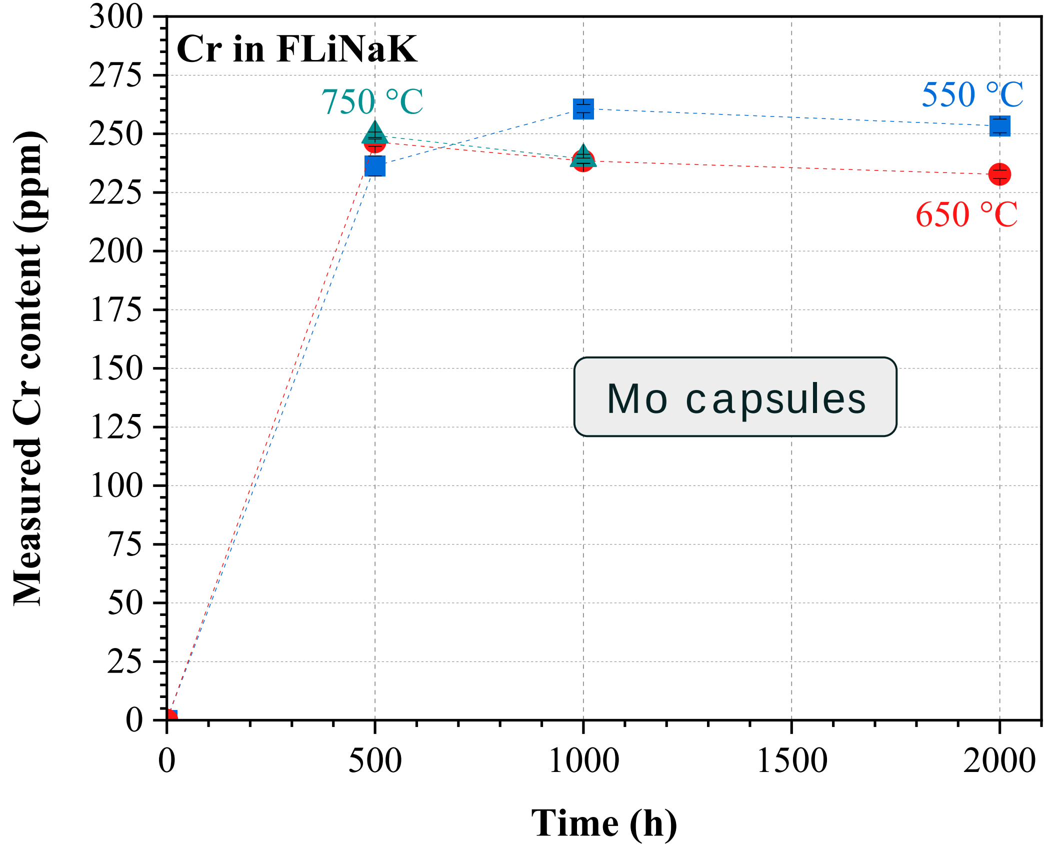


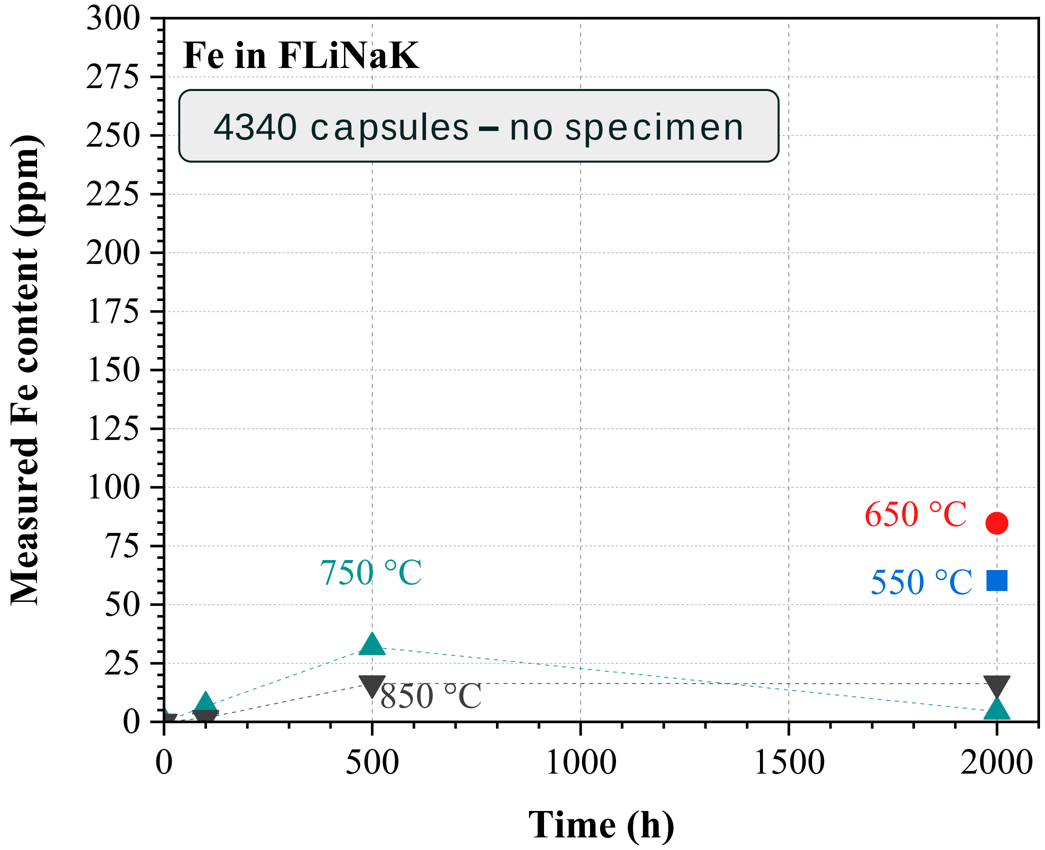


*Pillai et al. , JNM, 2021 and JOM 2023

Key model input : Acquire dissolution data for Cr and Fe in different candidate salts (FLiNaK, FLiBe and NaCl-$MgCl_2$)

Negligible temperature dependence of Cr Dissolution in FLiNaK (ECS*)

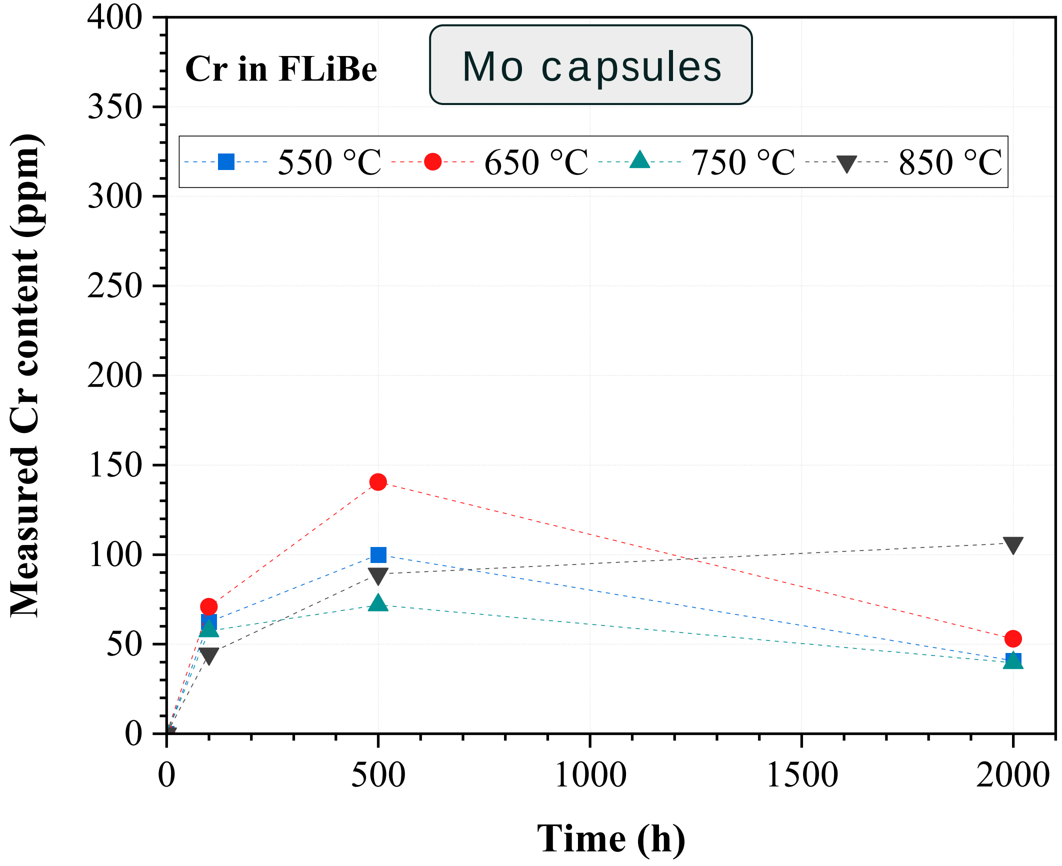


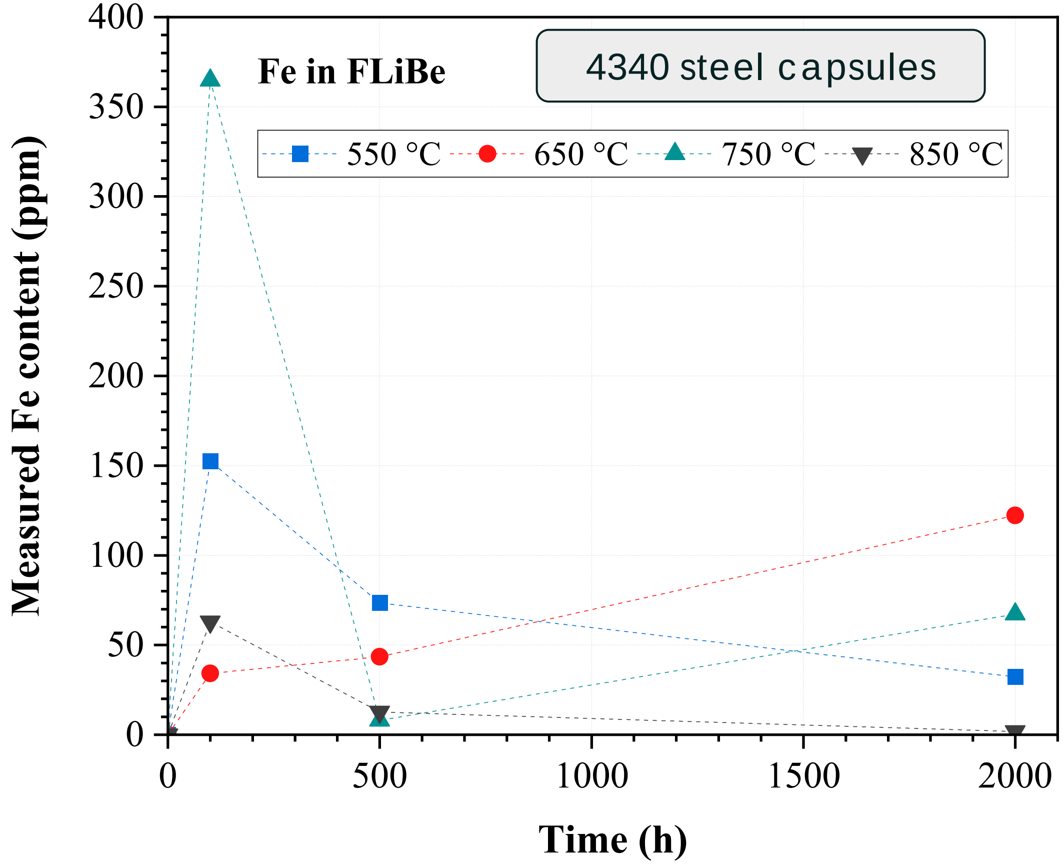


- ➢ **Data indicates temperature independent Cr dissolution (salt saturated after 500h)**
- ➢ **Mn dissolution from 4340 capsules influencing Fe dissolution at higher temperatures**
  - ❑ *Tests will be repeated with pure Fe capsules*

**Publication in preparation*

Weak temperature dependence for Cr dissolution in FLiBe similar to the FLiNaK case

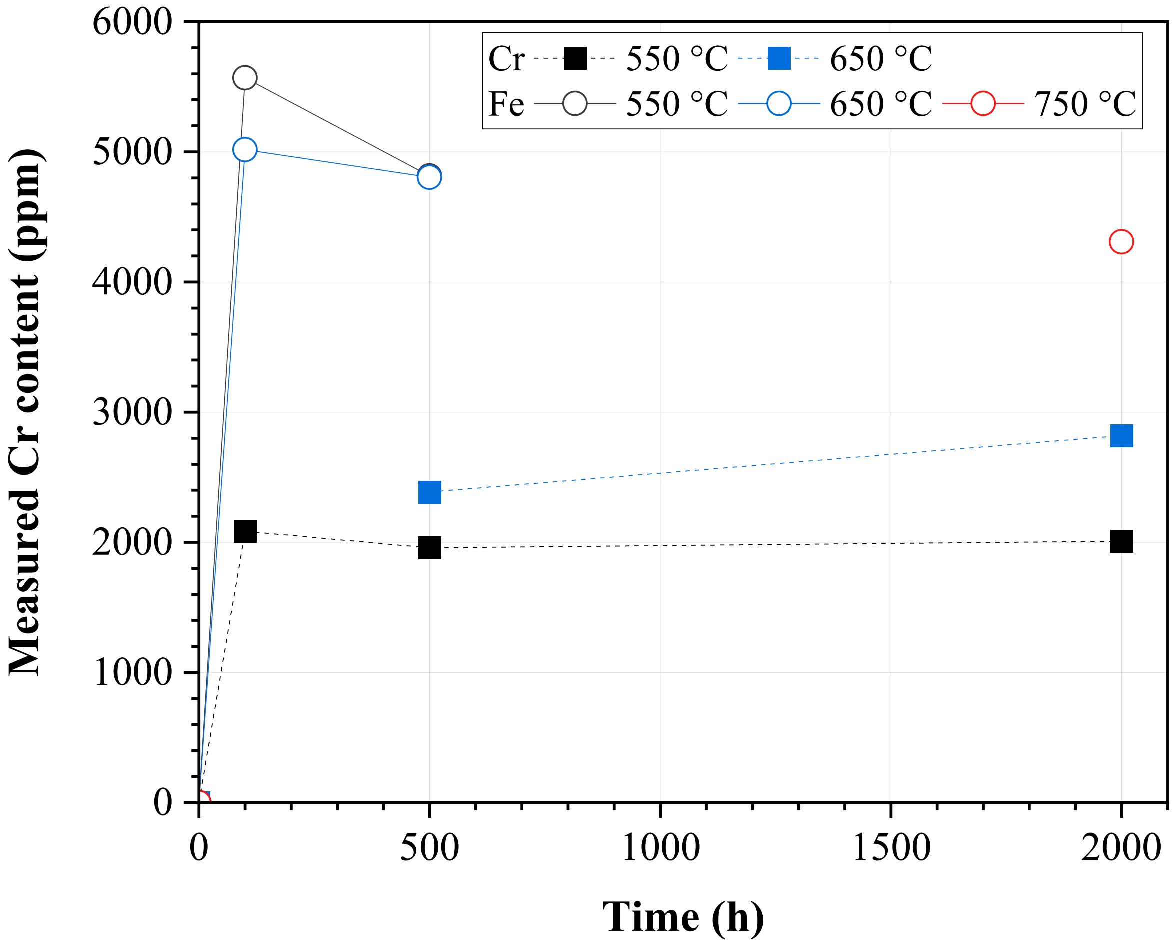




- **Data indicates slightly lower Cr dissolution in FLiBe than in FLiNaK (salt saturated after 500h)**
- **Mn dissolution from 4340 capsules influencing results**
  - *Tests will be repeated with pure Fe capsules*

**Publication in preparation*

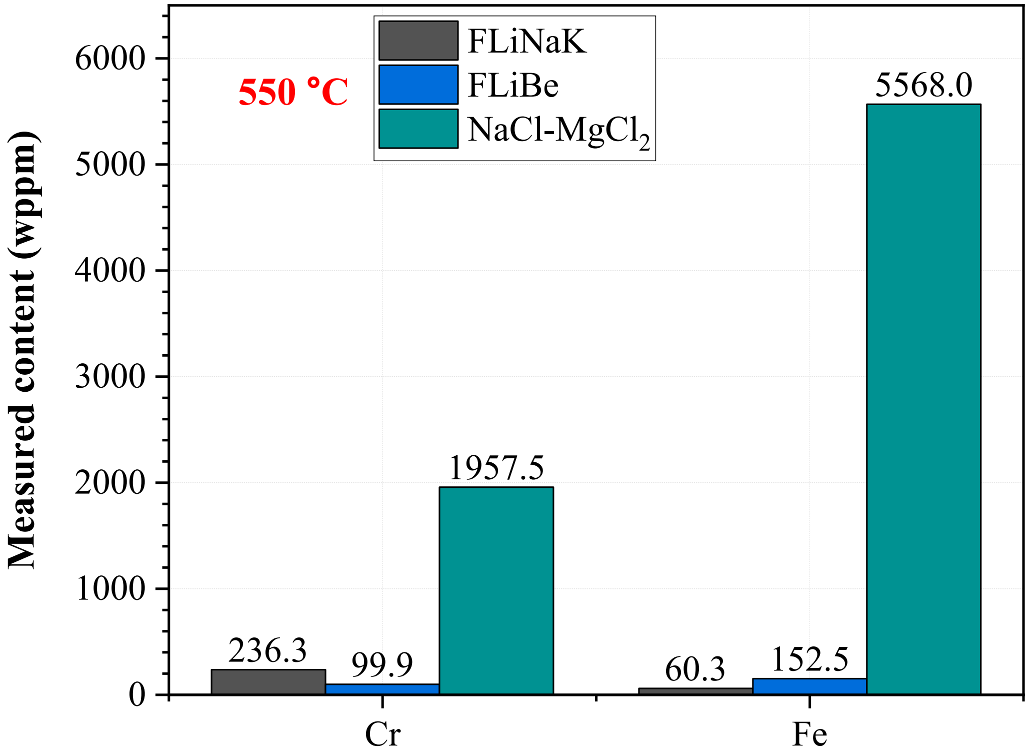
Observed Cr dissolution rates suggests stronger temperature dependence for Cr in the purified* binary eutectic NaCl-$MgCl_2$ salt compared to FLiNaK and FLiBe

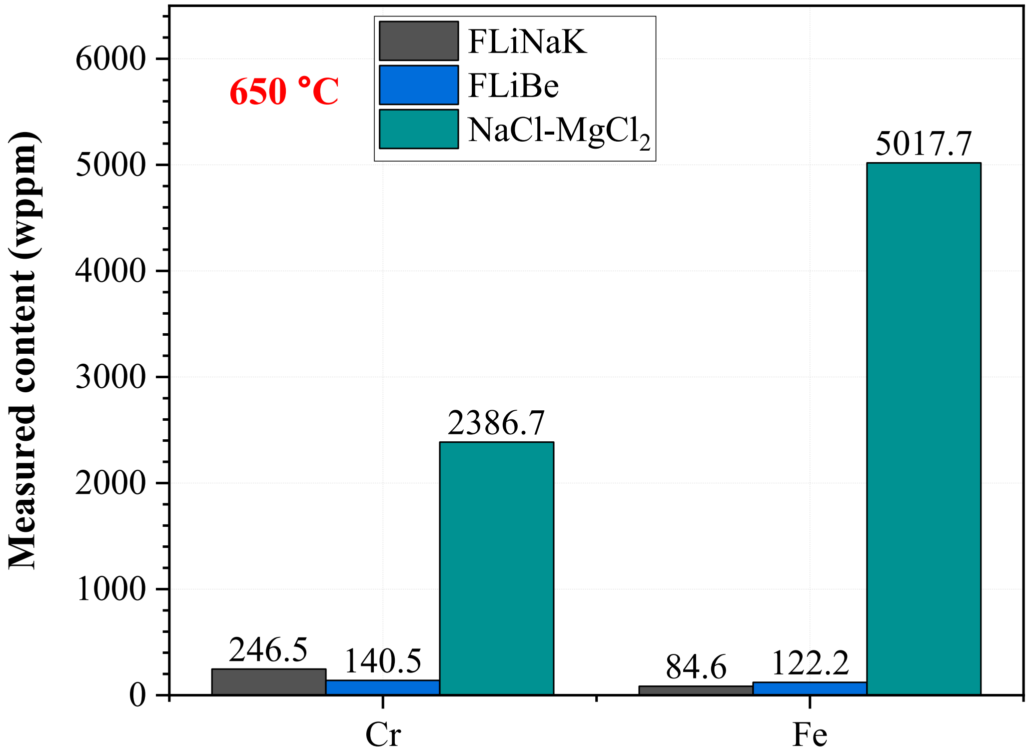


- Pure Cr specimens in Mo capsules
- 4340 steel capsules for measuring Fe dissolution
  - ***Mn dissolution*** *from the steel potentially skewing results at 750 ° C*
  - *Repeat with high purity Fe is planned*
- Noticeable **temperature dependence for Cr** dissolution
- Need lower temperature data (e.g., 500 °C)

**Publication in preparation*

Significantly higher dissolution rates were measured for Cr and Fe in the purified binary eutectic NaCl-$MgCl_2$ salt compared to FLiNaK and FLiBe



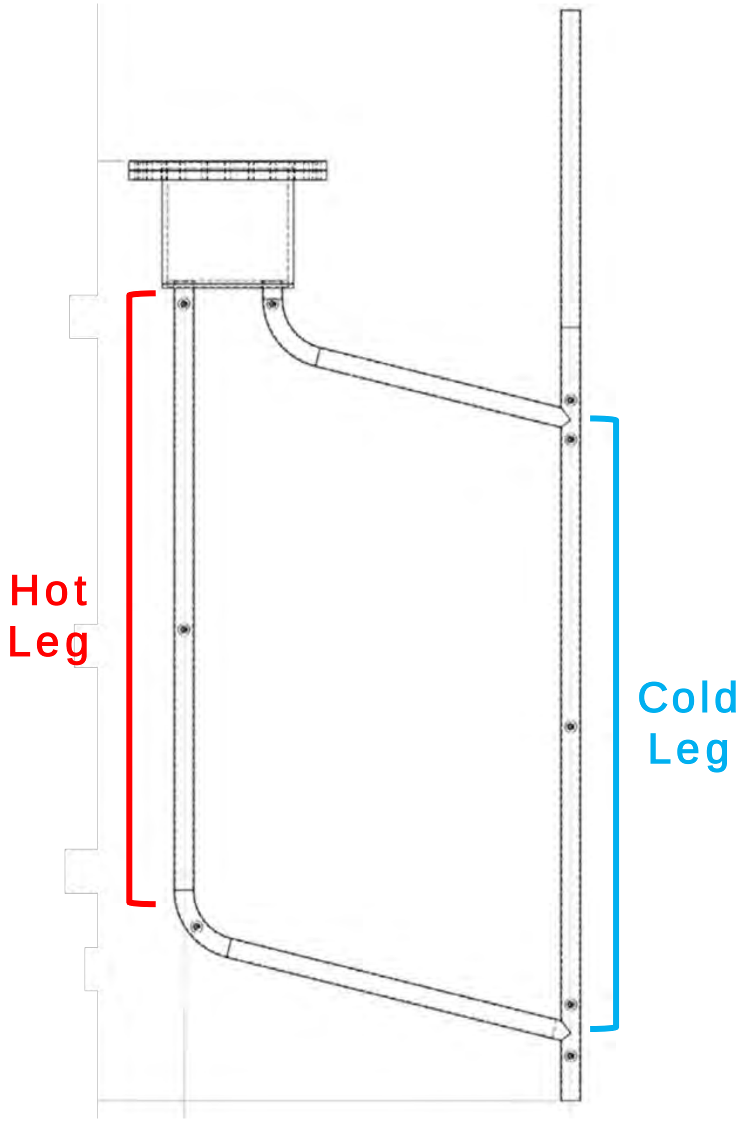


- **~10X higher Cr** content in NaCl-$MgCl_2$ than in FLiNaK and FLiBe (after 500h)
- **~90X higher Fe** content in NaCl-$MgCl_2$ than in FLiNaK and FLiBe (after 100h)

**Publication in preparation*

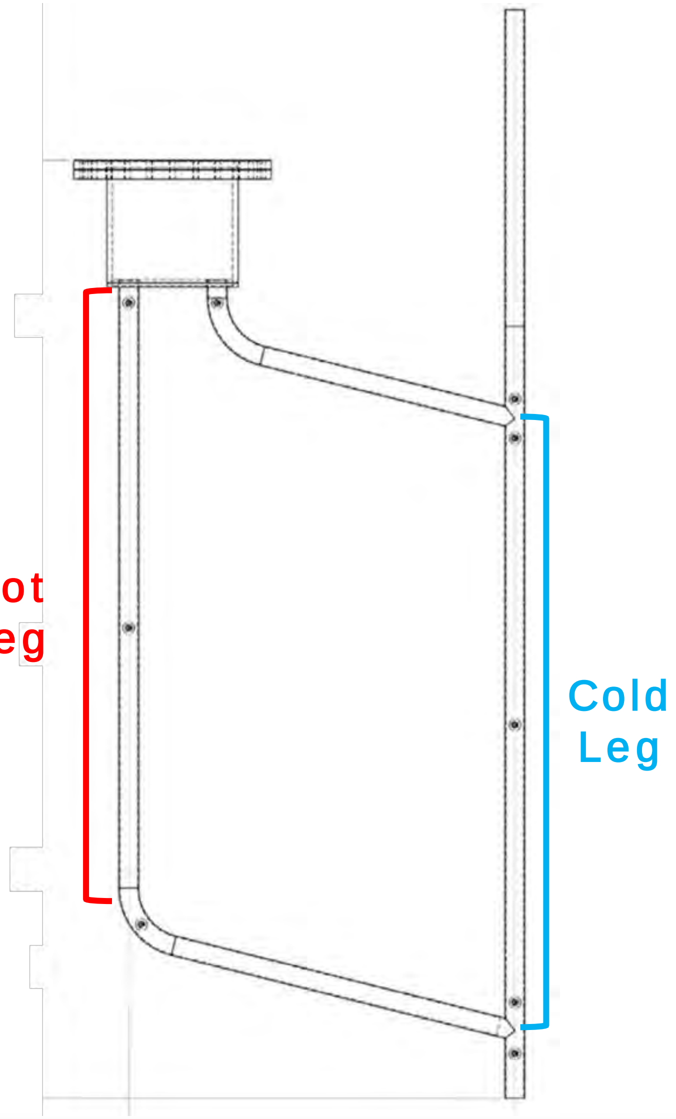
Can we leverage the success of predicting corrosion behavior in static tests to describe corrosion behavior under flowing conditions?

What is the model expected to capture to describe the corrosion behavior in thermal convection loops?

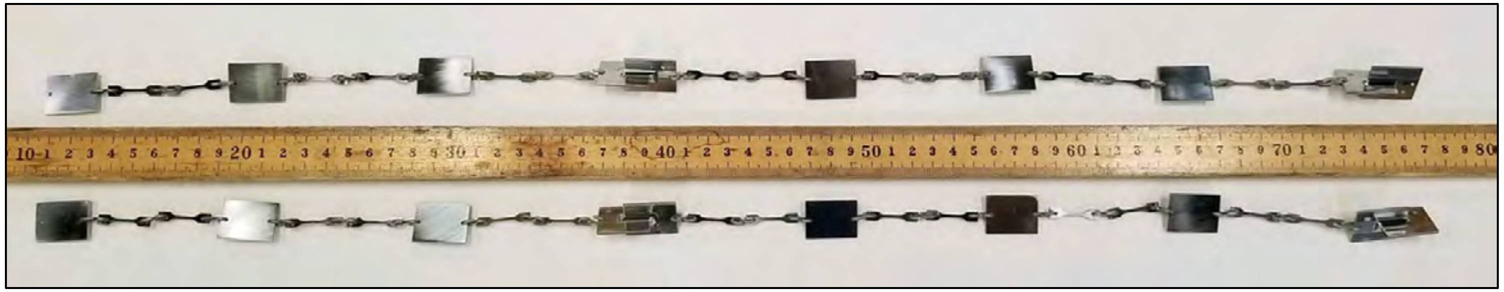


- Temperature dependent dissolution and redeposition
- Presence of different materials
- Account for total corroding surface area (loop and specimens)
- Mass transfer across hot and cold legs

Operation of a Thermal Convection Loop (TCL)* at ORNL provides good experimental data for model validation



Loop material	316H*
Salt	FLiNaK* (commercial from ECS)
Total salt amount	~ 5kg
Highest temperature in the hot leg	647 °C
Coldest temperature in the cold leg	552 °C
Specimen material	316H
Total number of specimens	12 coupons, 28 SS-3 tensile
Duration of test	1000h (continuous operation)



Alloy	Fe	Ni	Cr	Mo	Mn	Si	C
316H	64.5	13.3	17.2	2.3	1.9	0.5	0.06

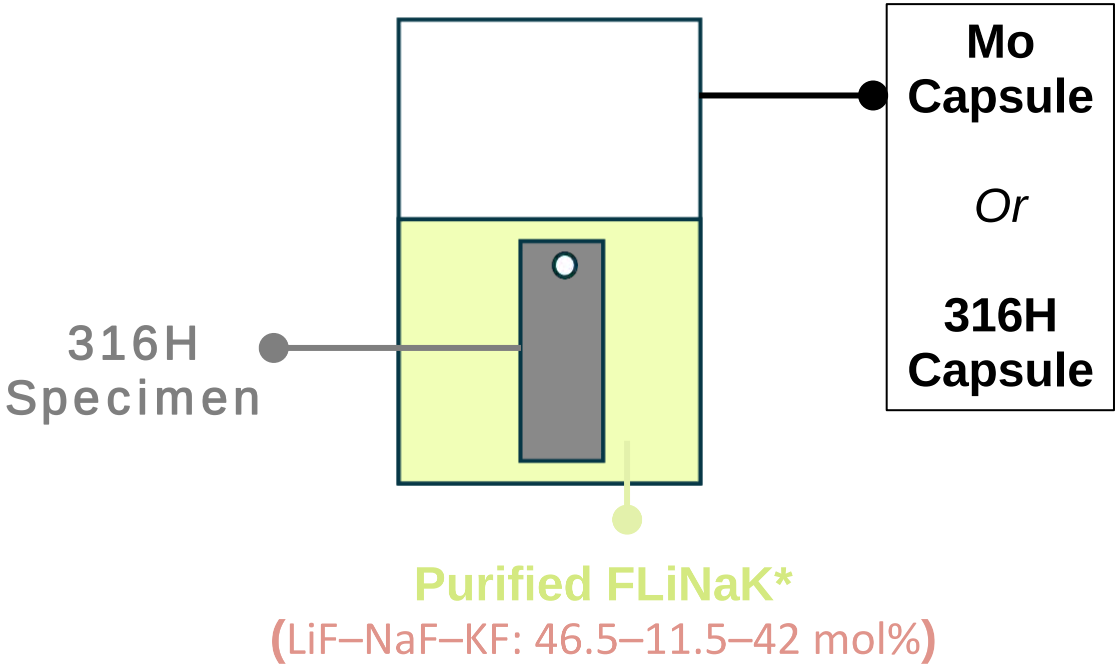
*Raiman et al. 2022

The model should first successfully demonstrate the impact of corroding surface area on corrosion kinetics in static capsule experiments

Alloy chemical composition (wt. %)

Alloy	Fe	Ni	Cr	Mo	Mn	Si	C
316H	64.5	13.3	17.2	2.3	1.9	0.5	0.06

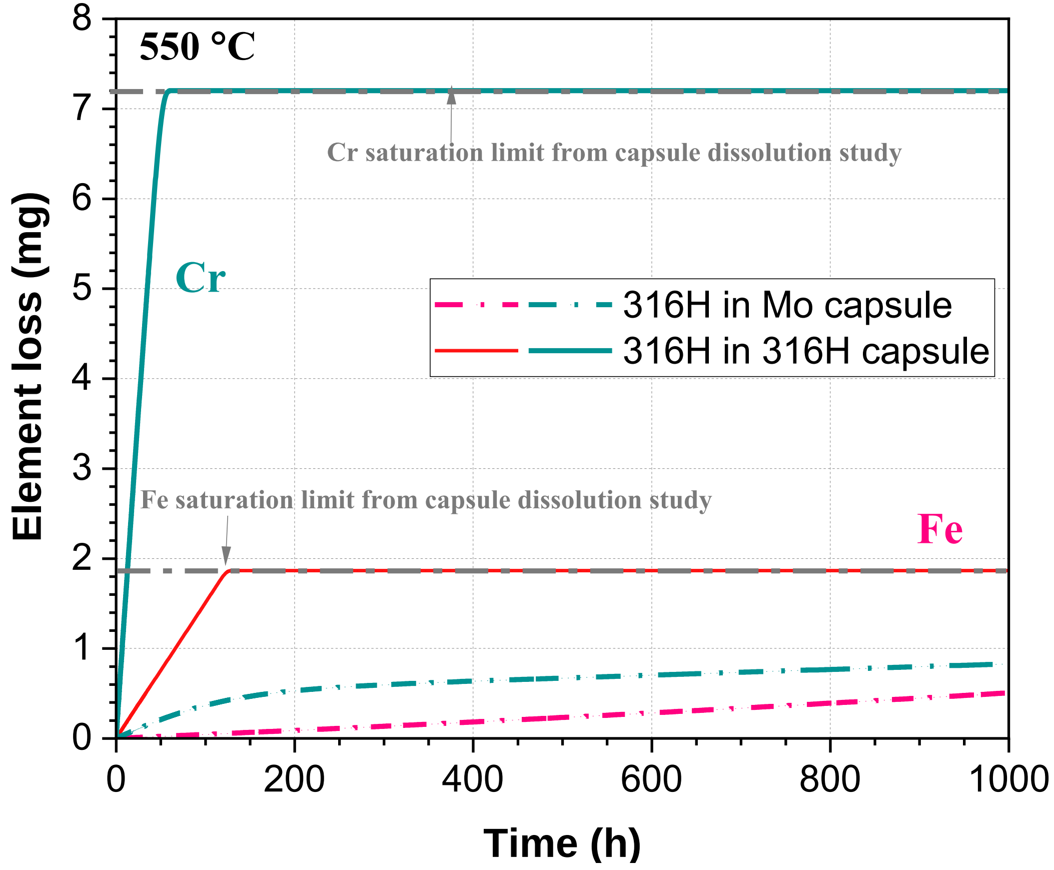
Exposures at 550 and 650 °C for 1000 h

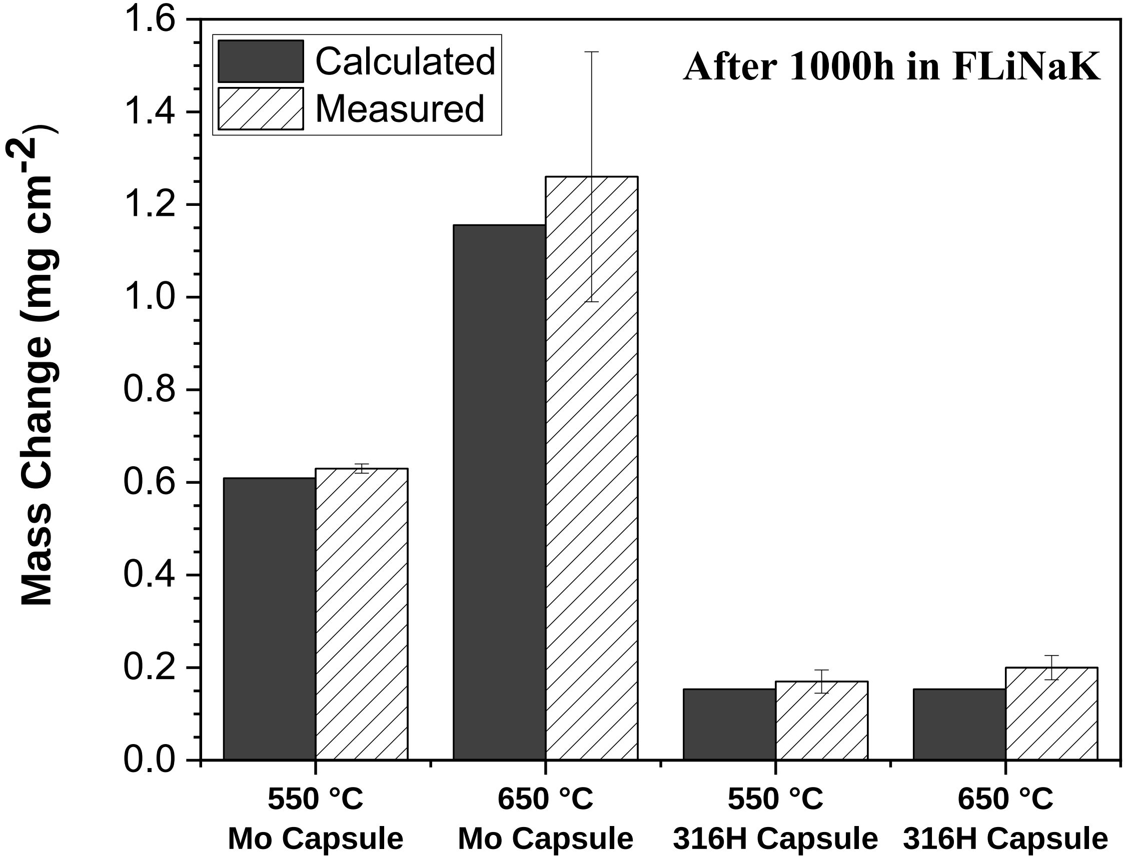


*Publication in preparation

*Salt provided by ECS, Raiman et al. 2022

Model accurately predicts mass change of multicomponent 316H in FLiNaK with different capsule materials

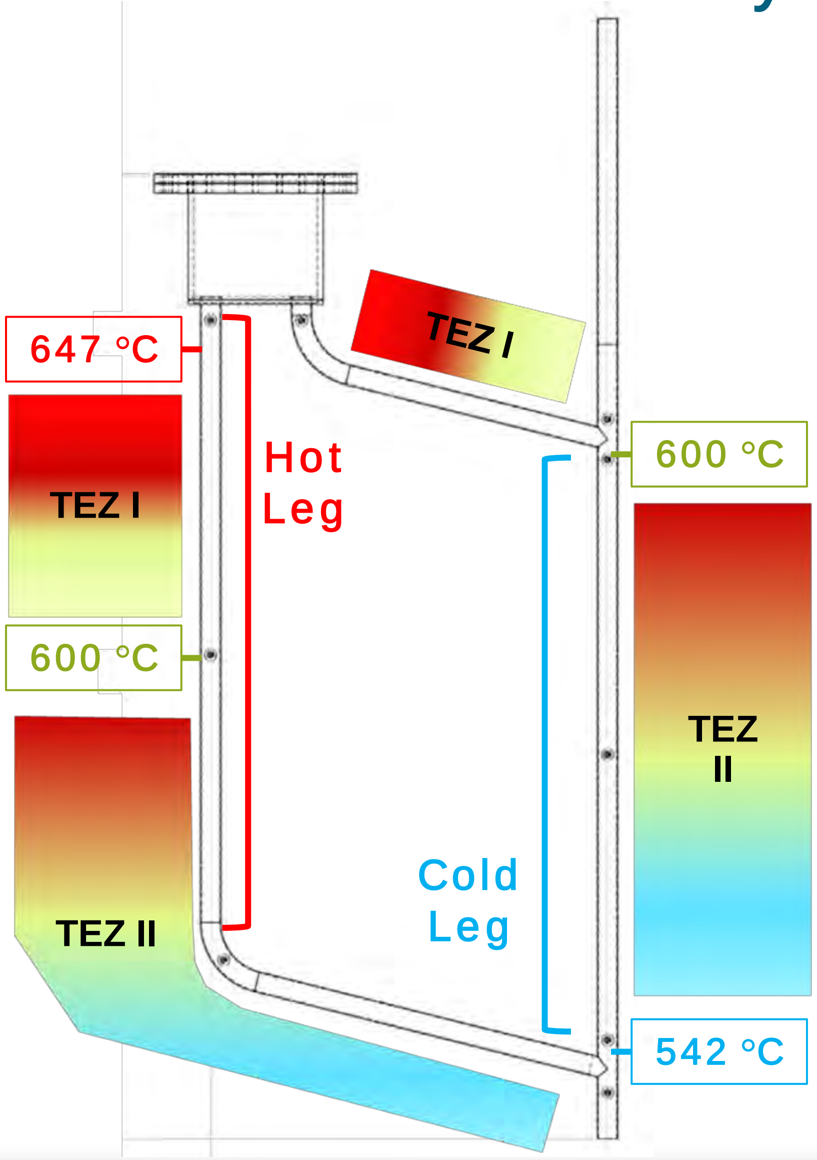




- Saturation limits for Fe and Cr are attained after 48 and 125h respectively for the tests in 316H capsules

*Publication in preparation

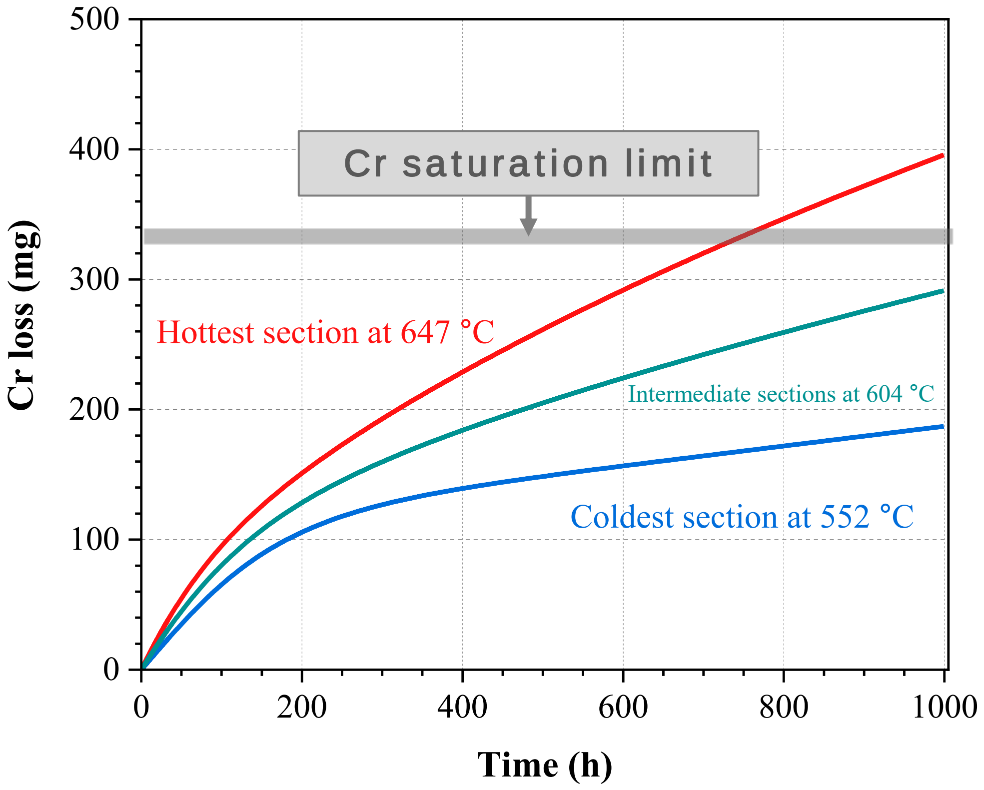
Simplify the underlying problem by dividing the TCL into thermodynamically equilibrated zones (TEZ)?

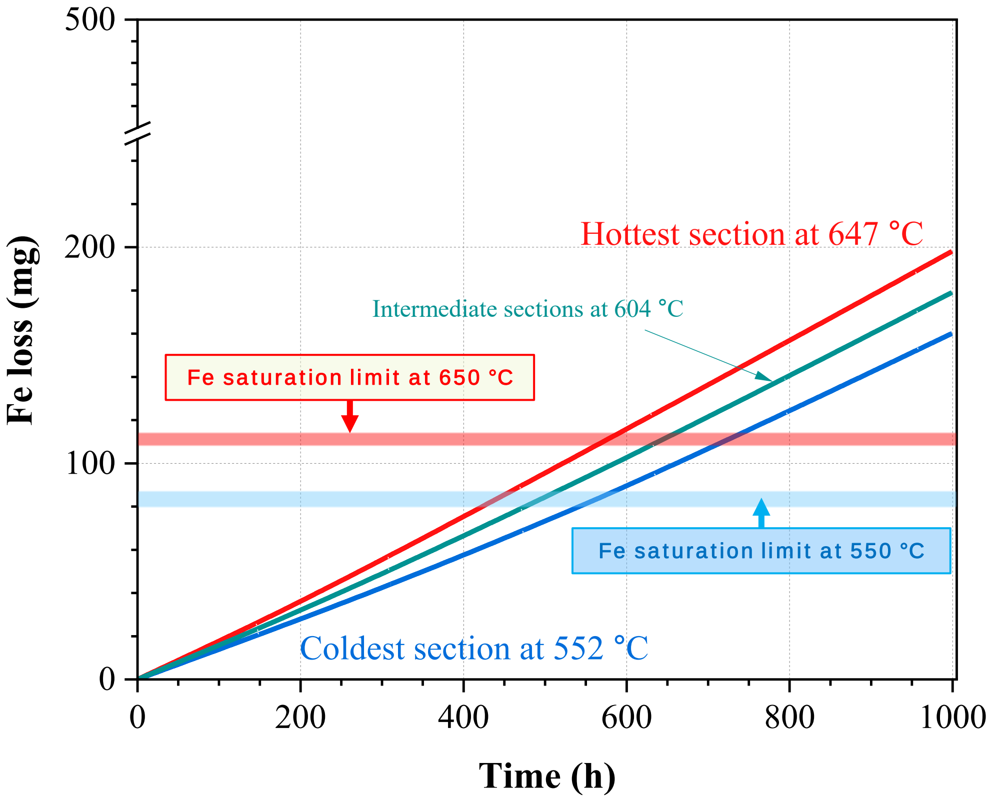


- Assume local equilibrium in temperature zones with $\Delta T = \sim 50$ °C
- TCL is divided into 4 sections
- Saturation limits of Cr and Fe correspond to the temperatures in each section
- Model in each section the temporal evolution of
  - *alloy compositional changes*
  - *dissolved Cr and Fe contents in the salt*
- Account for total surface area of loop section and contained specimens
- Allows the estimation of redeposition in the cold sections

**Publication in preparation*

Calculated temporal evolution of Cr and Fe dissolution in the salt in the thermodynamically equivalent sections



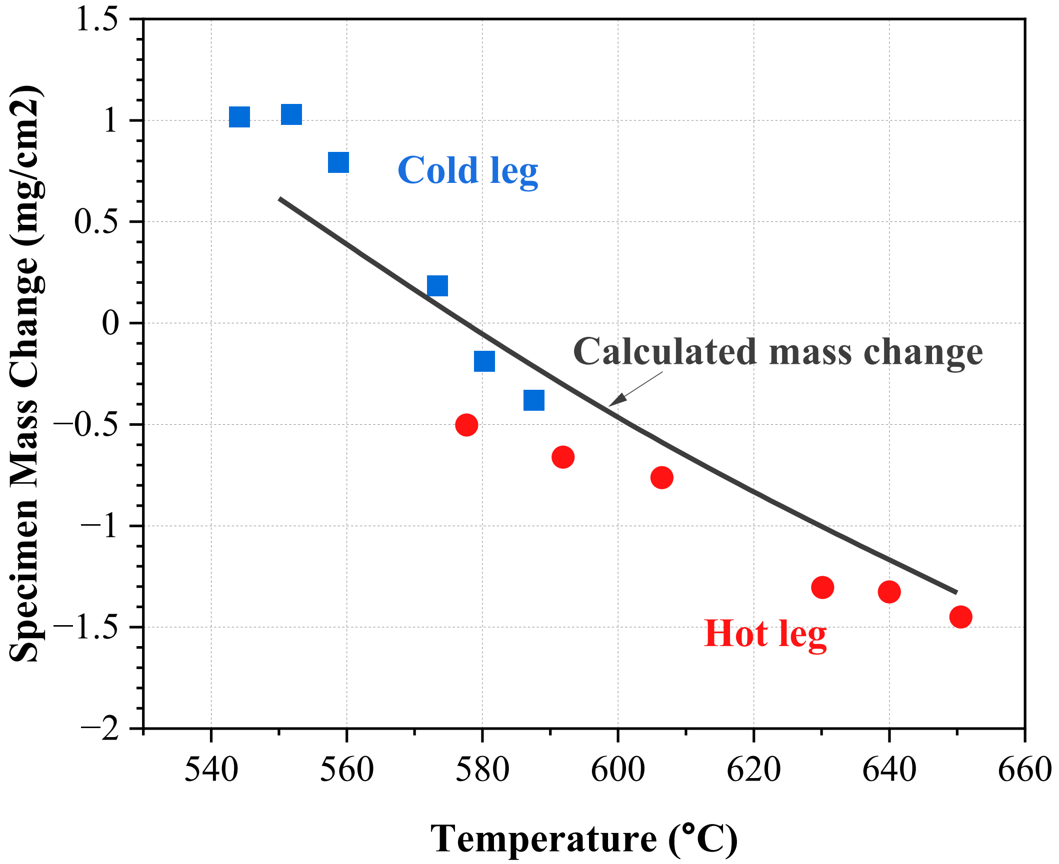


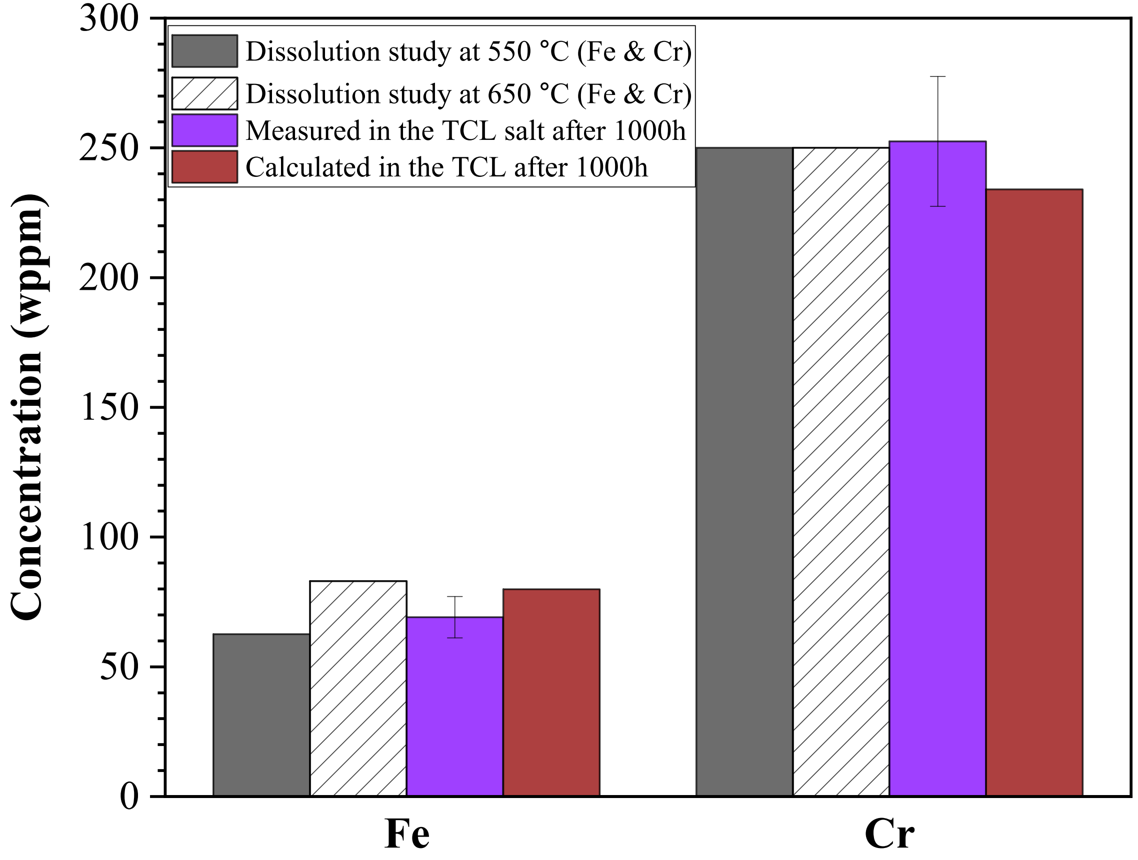
- Cr dissolution will cease in the hottest section after ~ 800h
- Cr dissolution will continue in the 2 intermediate sections

- Fe saturation expected in the coldest section after ~600h
- Fe dissolution in the hotter sections can continue beyond the saturation limits due to redeposition in the colder sections
- Fe-redeposition in the coldest sections will suppress Cr dissolution

*Publication in preparation

Modeling approach correctly predicts the observed gravimetric trends

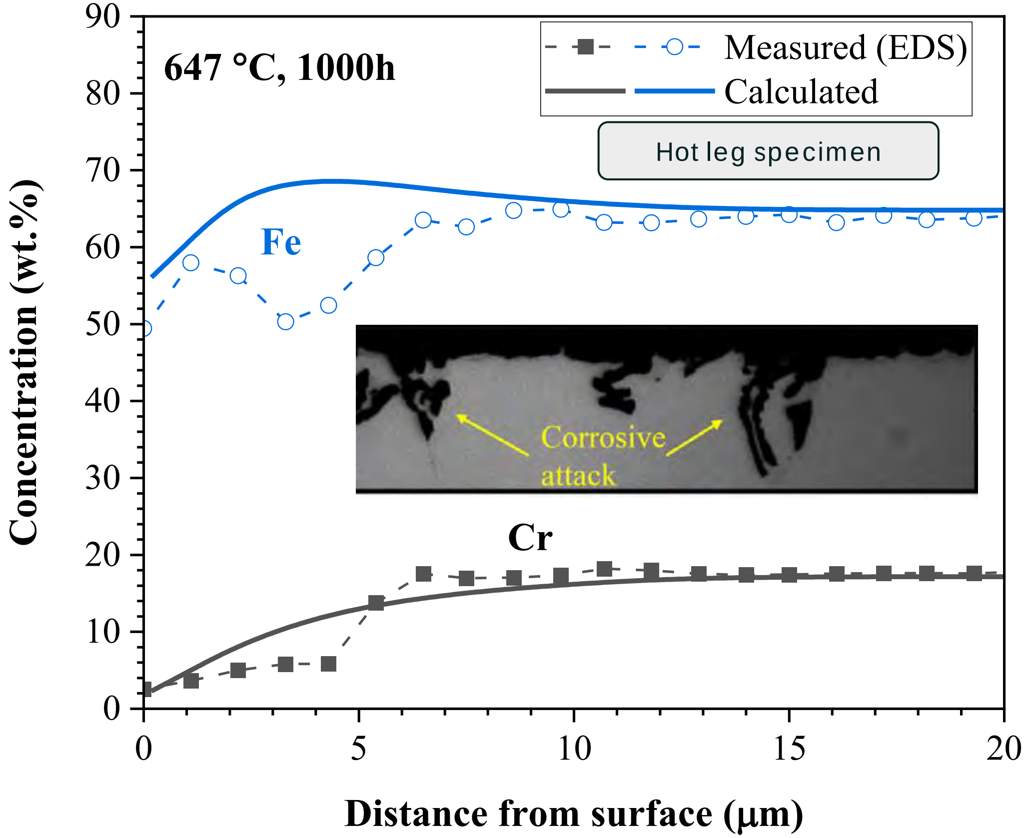


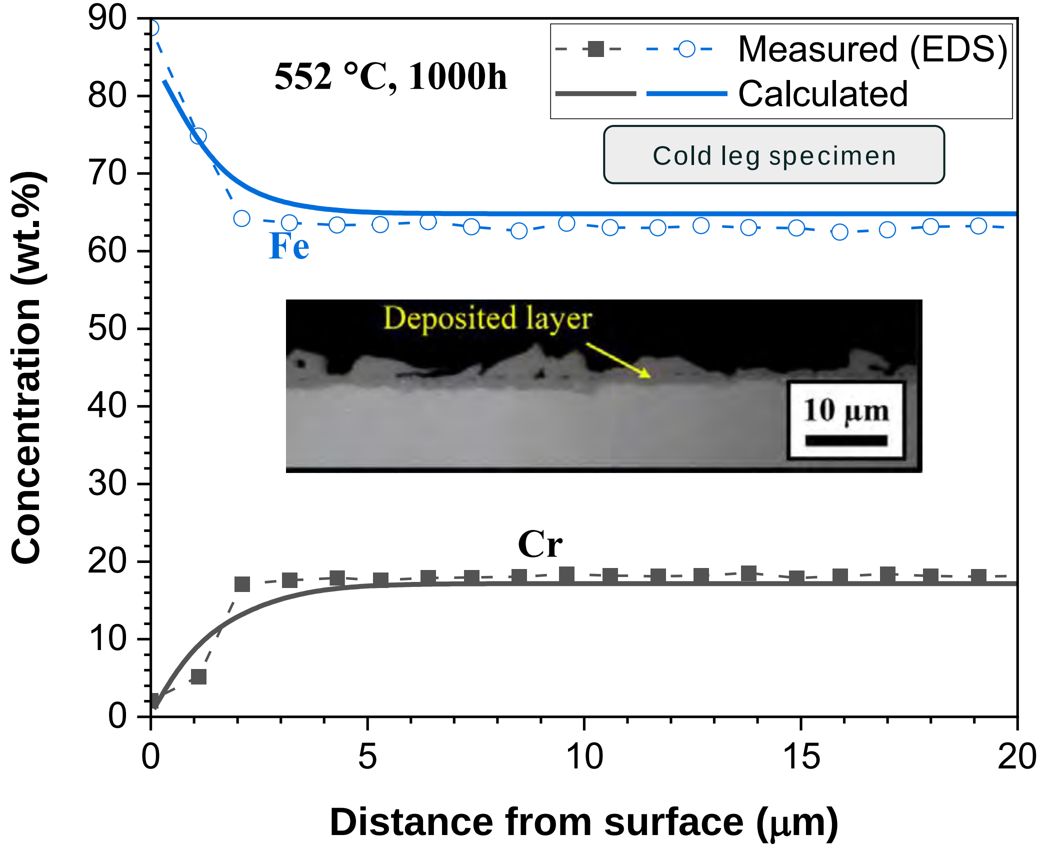


- Measured Cr and Fe contents in the 316H TCL after 1000h are in good agreement with values from the dissolution studies with pure Cr and Fe
- Model confirms the reason for Fe rather than Cr deposition in the cold leg of the TCL

*Publication in preparation

Excellent prediction of material behavior in hottest and coldest legs of the TCL



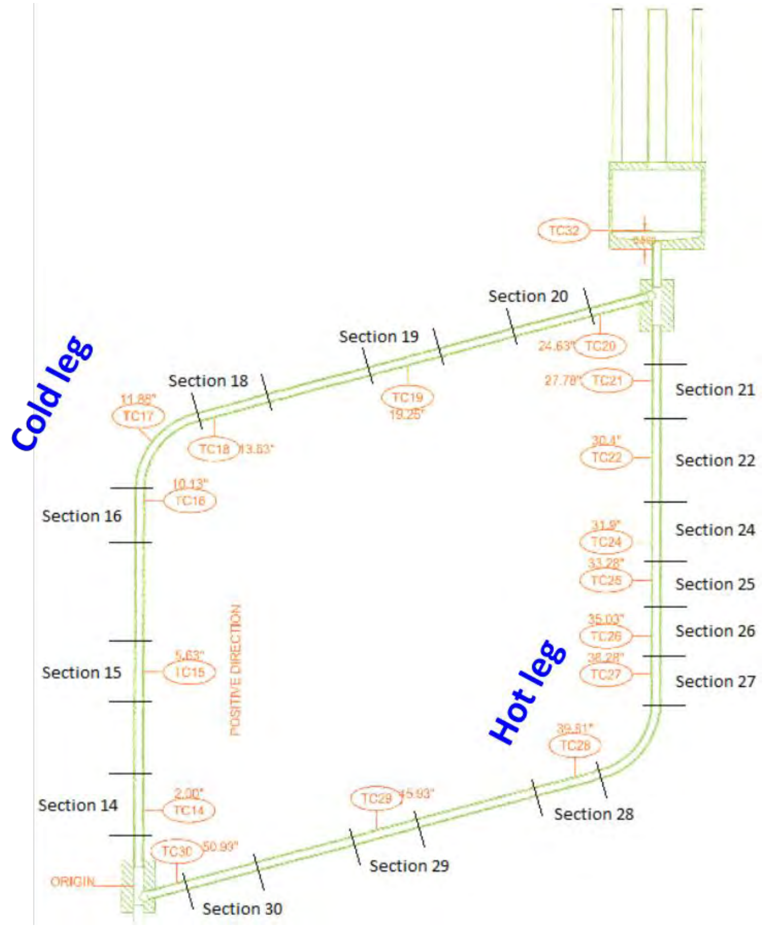


- Significantly less depth of attack in the cold leg (10 vs 2 μm)
- Fe depletion in the hot leg but redeposition in the cold leg which retards Cr dissolution

*Publication in preparation

Will the approach work for another material and salt?

Corrosion of Alloy-625 under natural circulation of molten salt in microloop



Loop material	625*
Salt	Eutectic NaCl-$MgCl_2$ *(58-42 mol%)
Total salt amount	320g
Highest temperature in the hot leg	620 °C
Coldest temperature in the cold leg	500 °C
Duration of test	2565h (continuous operation)

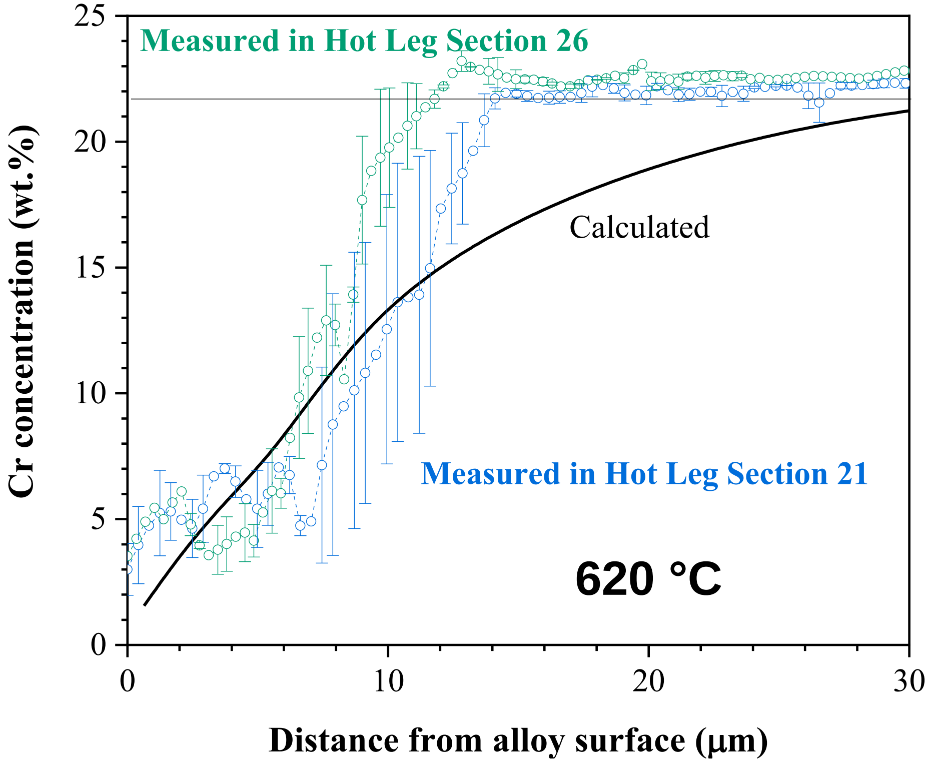
- **Measured dissolution rates of Fe and Cr in NaCl-$MgCl_2$ will be used to model the corrosion behavior**

**In collaboration with Jagadeesh Sure and Adrien Couet*

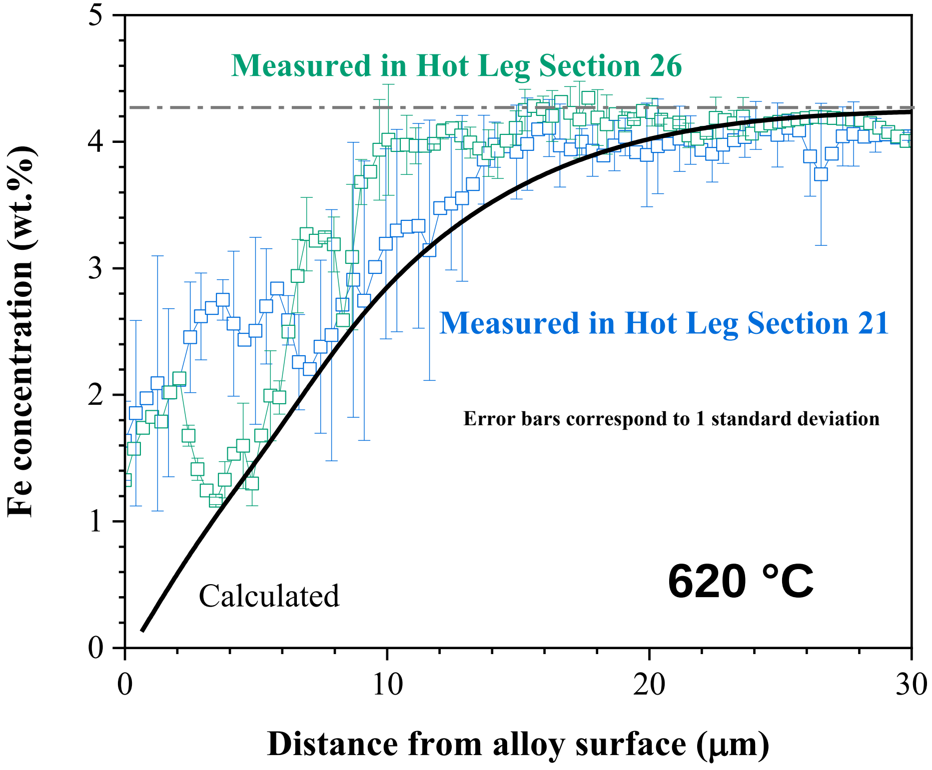
*Salt provided by Terrapower

Initial results are encouraging and demonstrate the applicability of the approach to different salts and alloys (after 2565 h at 620 °C)

Cr concentration profiles



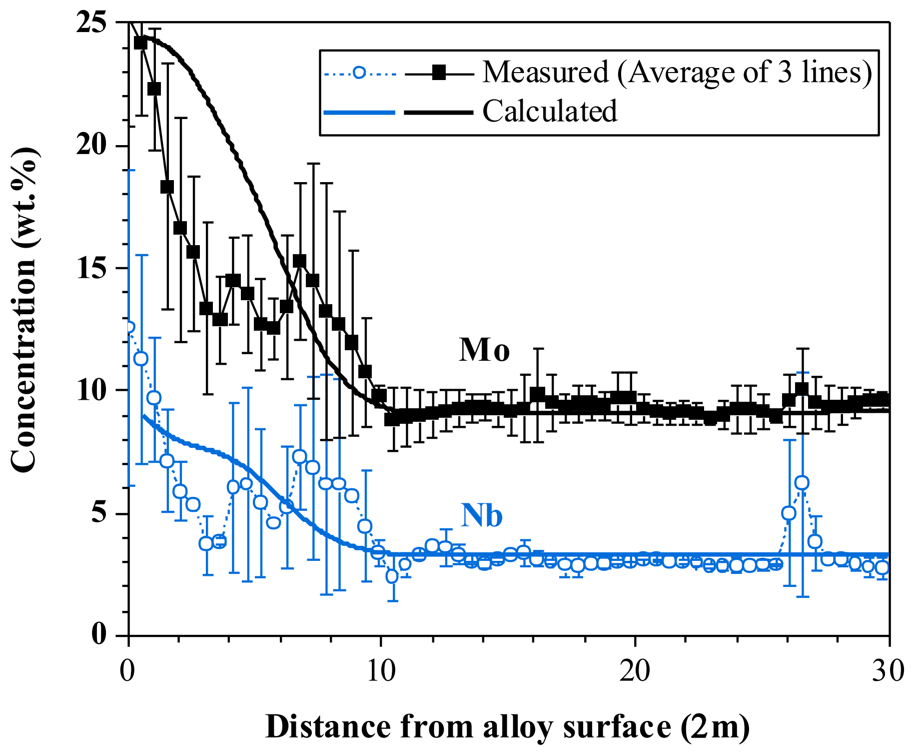
Fe concentration profiles

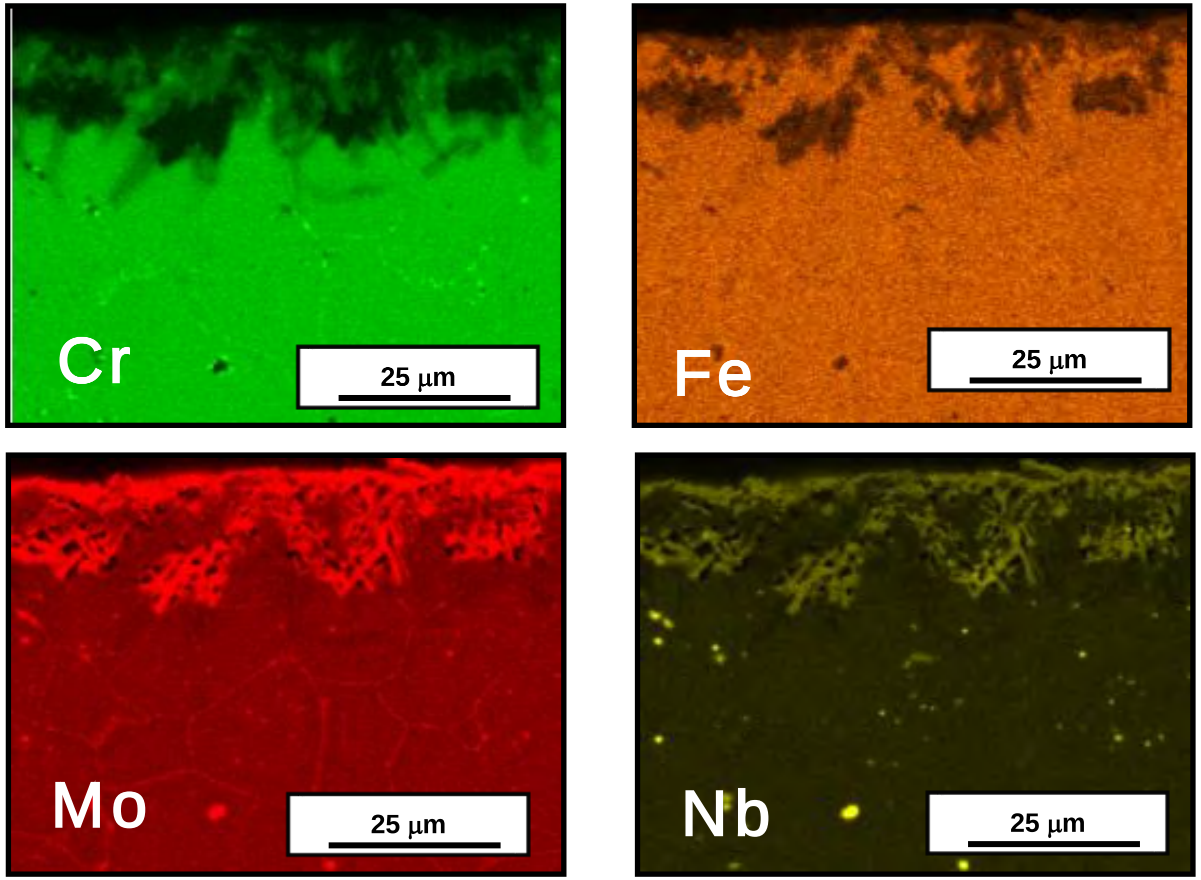


- Simultaneous dissolution of Cr and Fe can be expected in the NaCl-$MgCl_2$ salt
- Redeposition is a concern (need dissolution data at T < 550 °C)

**Publication in preparation*

Model correctly predicts the simultaneous enrichment of Mo and Nb on the alloy surface





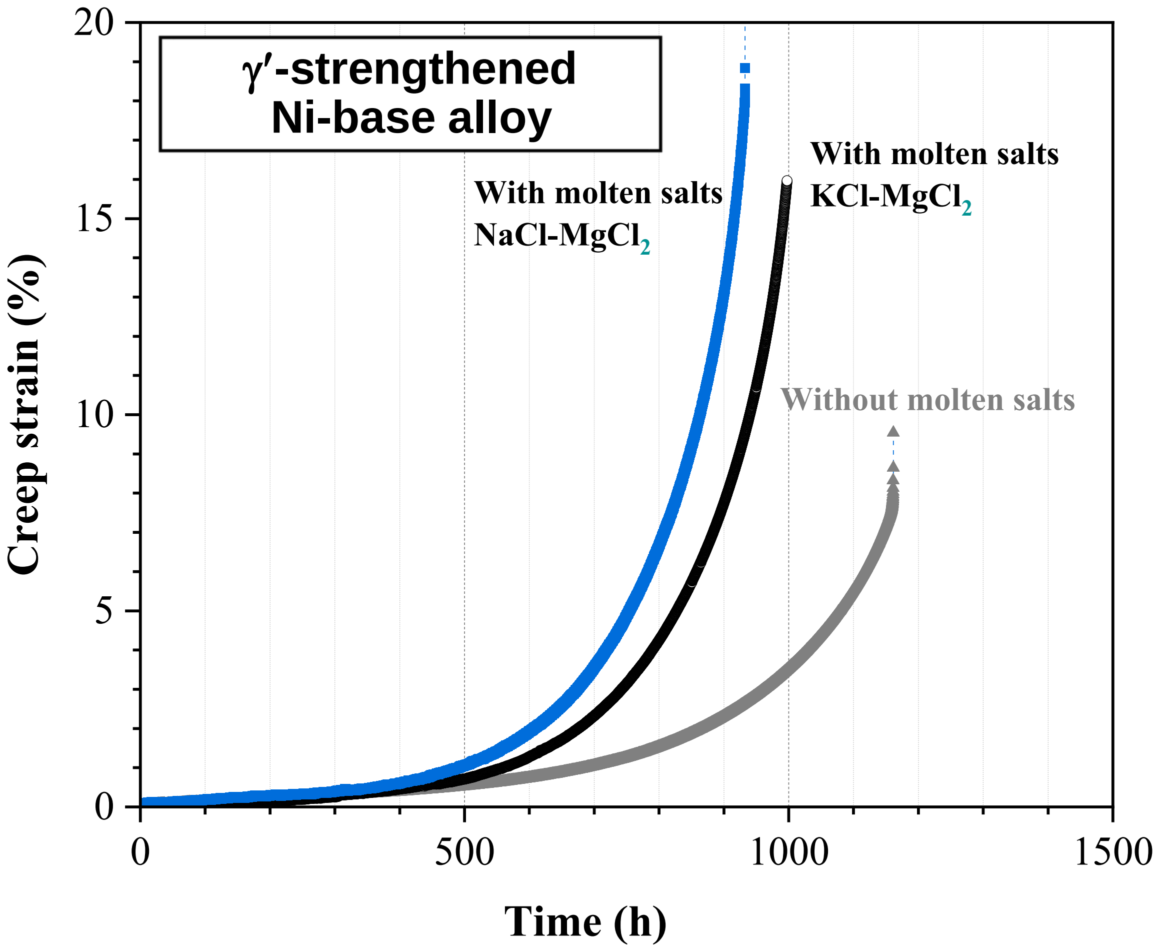
- The effect has been previously* observed and correctly predicted for other Ni-base alloys (IN600, C276)
- Potential to suppress further Fe and Cr dissolution but what about behavior under simultaneous stress?

*Pillai et al. , JNM, 2021

*Publication in preparation

Do we know how the relatively brittle subsurface might behave under stress?

Observed impact of the molten salt environment on creep behavior of some alloys motivated the need to test candidate materials for MSRs



- Chloride salts evidently accelerating creep rates
- Limited short-term tests showed impact
  - *lower stresses and longer times expected to have a higher impact*

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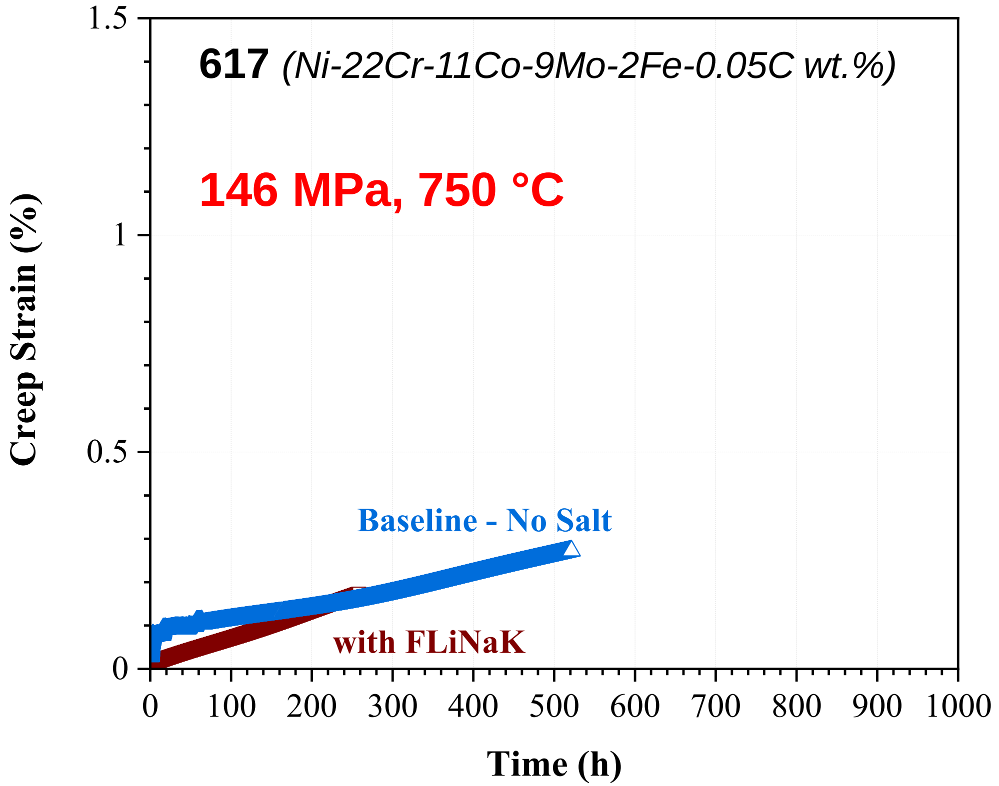
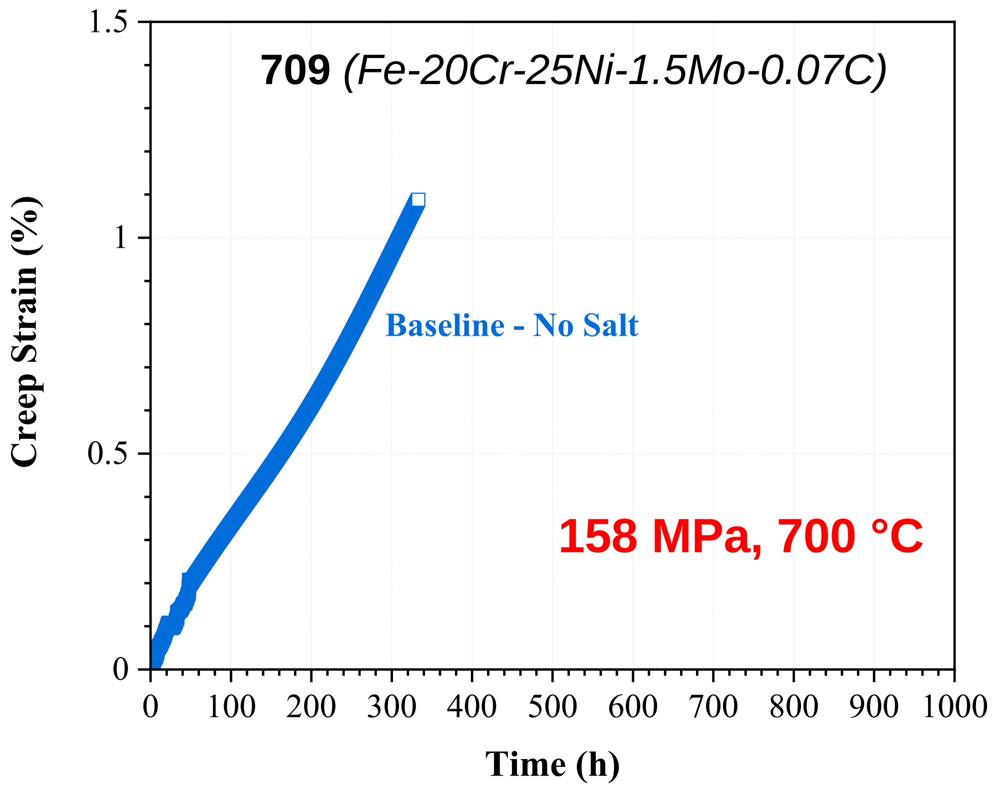
Initiated creep testing of 617 (baseline and with FLiNaK) and 709 (baseline) for a planned rupture time of 1000 h

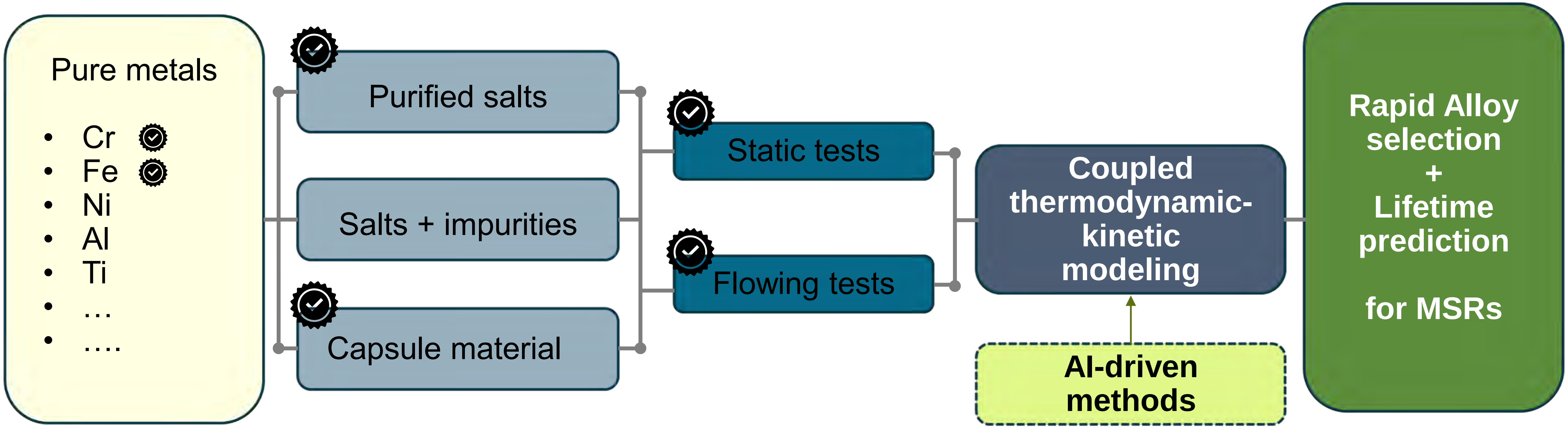




- Test conditions chosen based on data generated in the code case efforts for 617[a] and 709[b]
- Testing for 709 with FLiNaK and 316H (baseline, FLiNaK and in $NaCl$-$MgCl_2$) to follow

[a]INL Report (Wright, INL/EXT-15-36305)
[b]ORNL Report (Wang et al., ORNL/TM-2022/2593)

Continuously evolving modeling approach to enable prediction of salt induced corrosion of multicomponent and multiphase alloys



➢ **Impact of stresses? →** *Ongoing Creep testing in fluoride and chloride salts of 316H, 709 and 617*

Salt and Materials Interactions: Future Goals

Future topics

- ✓ FLiBe/316H interaction: higher temperatures/accident scenario TCLs
  - ✓ Feedback from MSR developers
- ✓ Further development of corrosion sensors/electrochemistry aspects
- ✓ Similar studies for Cl salts
- ✓ Model corrosion behavior of 709 in different salts and compare with 316H

FY25 goals

- ✓ De-risk the transition from **316H** to higher performance alloys **709** and **617**
- ✓ Compatibility (corrosion and mechanical) effect of impurities/additives (salt purity standards)
- ✓ Continue to develop material degradation model
  - ✓ Modeling the <u>effect of impurities/additives</u> on material degradation and lifetime
  - ✓ Focus on <u>higher temperature operation</u> and <u>lifetime modeling</u>
  - ✓ Combining <u>AI + Physics based models</u>* into reduced order models
    - ✓ Integration into existing NEAMS or other codes

* **NRC Report**: *Preliminary Assessment of Models for Generating Long-term Corrosion Predictions in Molten Salts*, Rishi Pillai, Aditya Savara, 2024

Thank you

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