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

Molten Salt Reactor PROGRAM

Argonne NATIONAL LABORATORY

Distributed Salt Monitoring and Corrosion Control

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Molten Salt Technology Development at Argonne

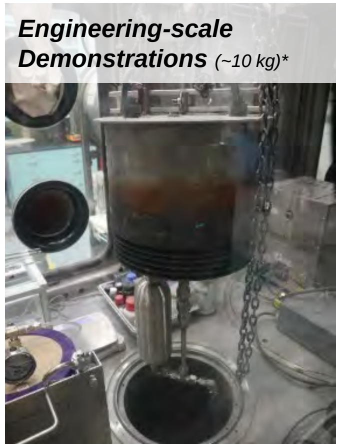
Argonne National Laboratory has a broad array of molten salt activities from small-scale fundamental investigations up through engineering-scale demonstrations.

Activities include fundamental chemistry, thermophysical and thermochemical property measurements, flowsheet demonstrations, process scale-up, thermal hydraulics, and the development of process monitoring and control technologies.

Supported Salts

- Chloride salts
- Fluoride salts
- Be-bearing salts
- U/TRU-bearing salts
    - Fuel reprocessing salts
    - MSR fuel salts

Pilot-scale Demonstrations
*(> 100 kg)**



Engineering-scale Demonstrations *(~10 kg)**

Bench-scale Process Development *(~100 g)**

Fundamental Chemistry
*(~1 g)**

In-situ HEXRD of molten salt chemical and electrochemical processes

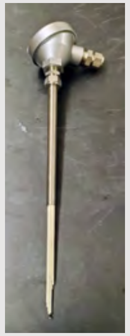
**quantity of molten salt*

Monitoring and Control of Molten Salt Systems

Monitoring and control technologies are essential to achieve successful years-long operations of molten salt reactors.

Monitoring and Control Technologies

particulate monitoring



DOE NE-4: MRWFD

automated sampling

DOE NE-4: MPACT

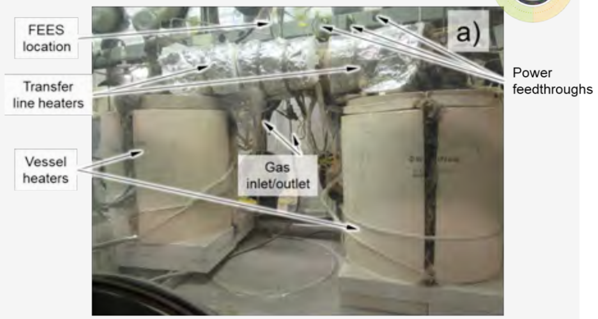
electrochemical

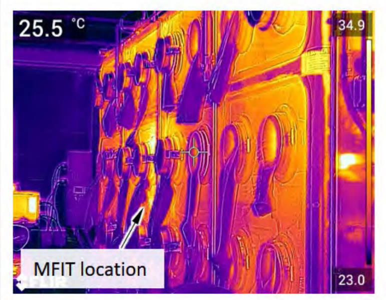
MSR Campaign, ARPA-E

windowless optical cell

NA-22

Automated Operations of Molten Salt Flow Systems

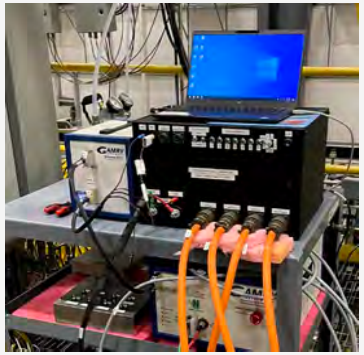




DOE NE-5: ARSS

Large-Scale Deployments

https://www.ans.org/news/article-5541/kairos-power-begins-loading-14-tons-of-flibe-into-molten-salt-test-loop/



DOE NE: GAIN

Motivation and Objectives

Motivation

Monitoring and control of salt chemistry is essential for successful long duration operations of molten salt reactors. In the absence of chemistry control, vendors will not be able to satisfy evolving NRC licensing requirements for advanced reactor corrosion and criticality safety (e.g., 10CFR50, 10CFR72).

Objectives

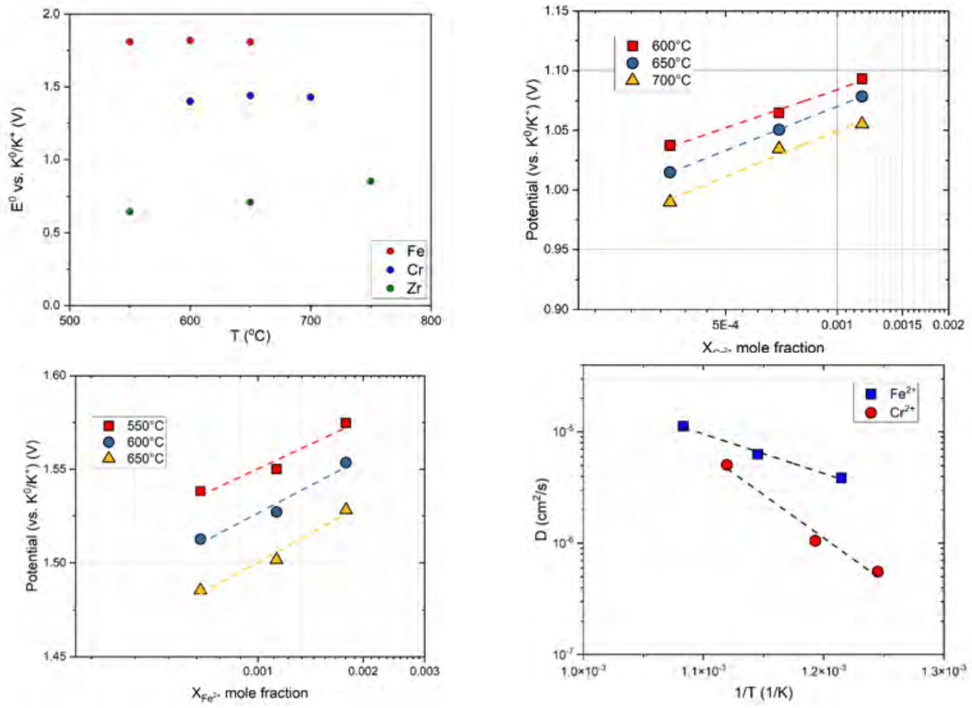
1. Develop, deploy, and demonstrate distributed salt monitoring capabilities for pilot-scale forced-flow salt loops
2. Develop, deploy, and demonstrate distributed salt chemistry control capabilities for pilot-scale forced-flow salt loops
3. Measure key fundamental chemical and electrochemical data to enable successful long-duration operations of molten salt flow systems

Questions Operators of Molten Salt Systems Need to Ask Themselves:

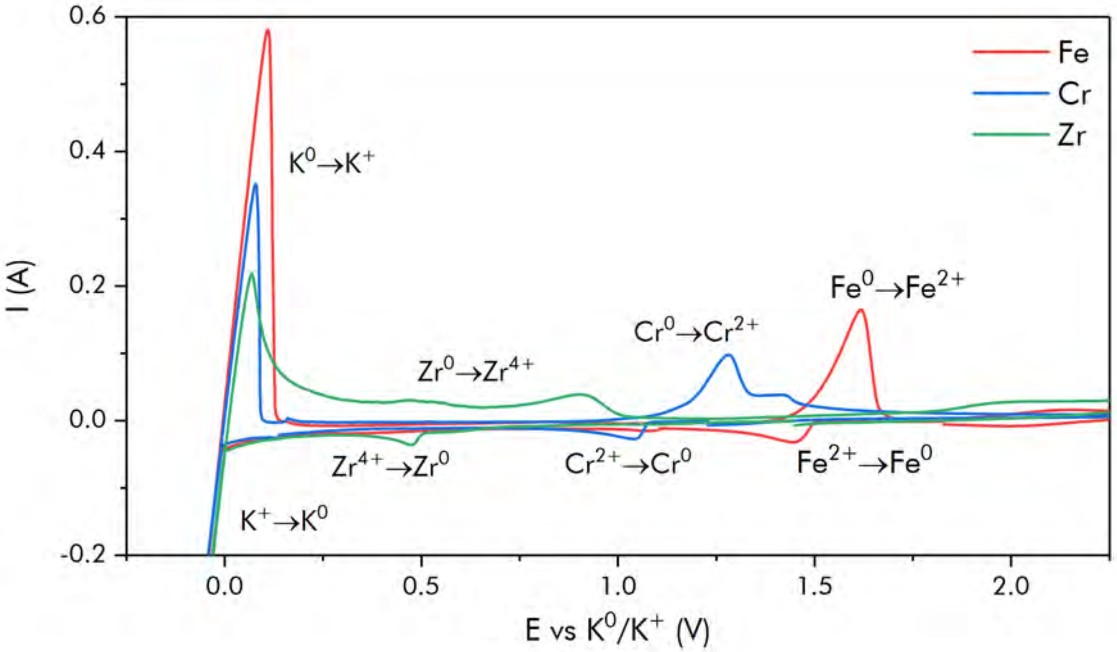
- Is the salt clean enough to avoid failure of the system?
- Is an O_2/H_2O ingression actively occurring?
- Are actinides and other species precipitating out of the salt?
- How quickly are the structural metals corroding?
- Is the loop becoming clogged from mass transfer effects?
- Are actinides plating into the structural metals?

Fundamental Properties to Enable Technology Development and Deployment

We have measured key thermodynamic and kinetic properties for most of the corrosion products and corrosion control species that are important for MSR-relevant alloys in salts such as FLiNaK.



Typical fundamental values for key species

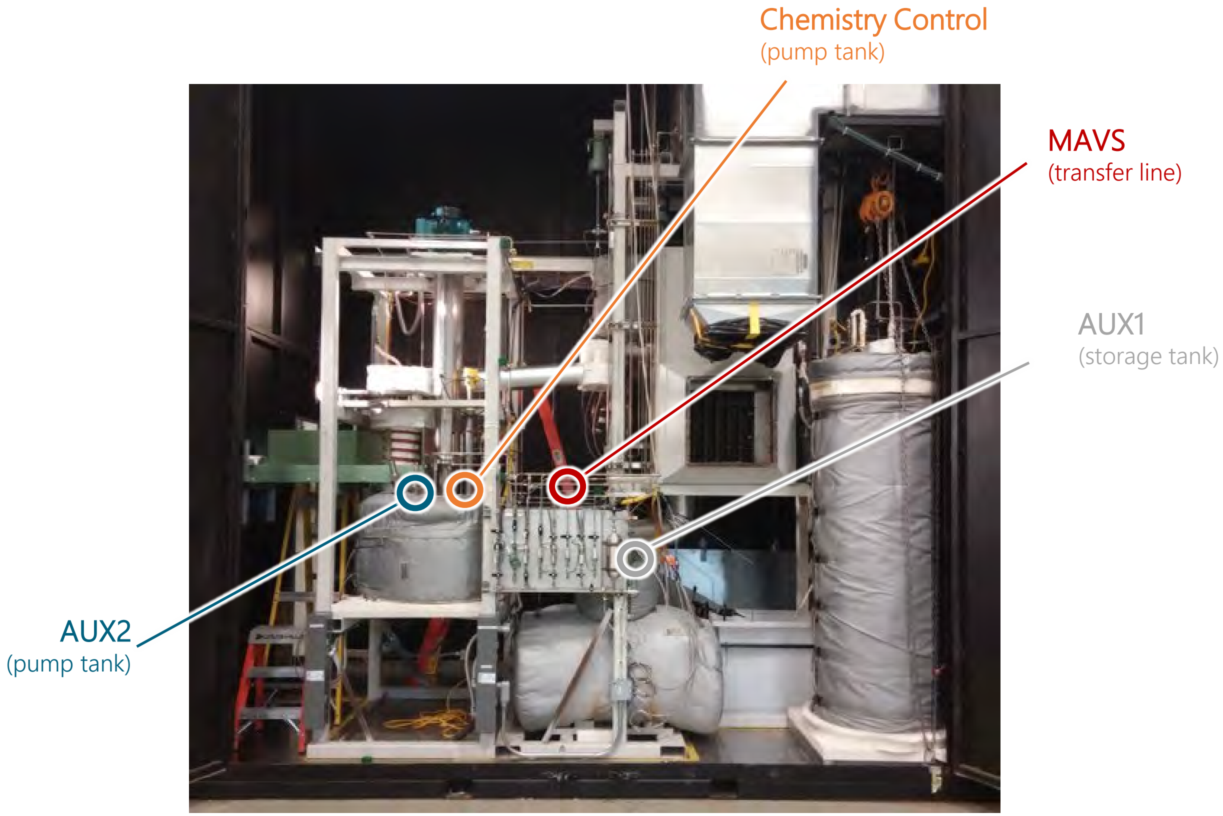


Raw electrochemical data for key corrosion products and corrosion control species

Previous Work for the MSR Campaign:

Chemistry Monitoring and Control System Integration Activities

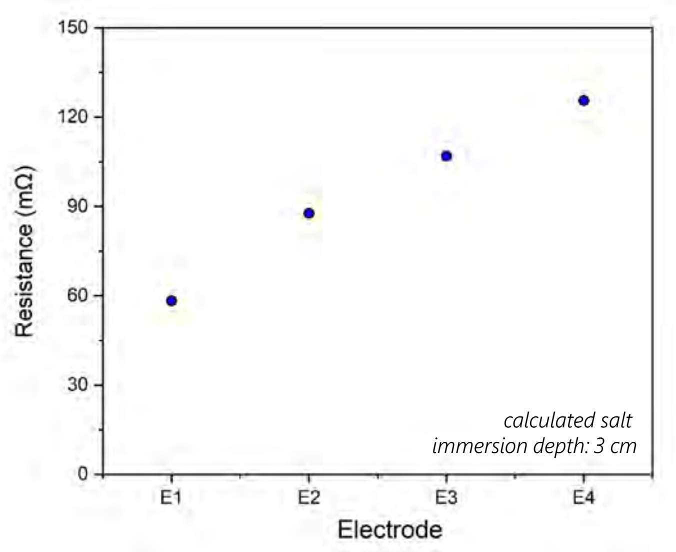
- Argonne deployed distributed sensors to ORNL's Liquid Salt Test Loop (LSTL) in FY23
  - Multielectrode electrochemical sensor installed along transfer line
  - Auxiliary electrode in pump tank
  - Targeting the LSTL's FLiNaK (with unknown impurity levels)
- During two days of operation, the distributed sensors were used to monitor LSTL's salt status including salt redox potential, salt level and impurity concentrations.



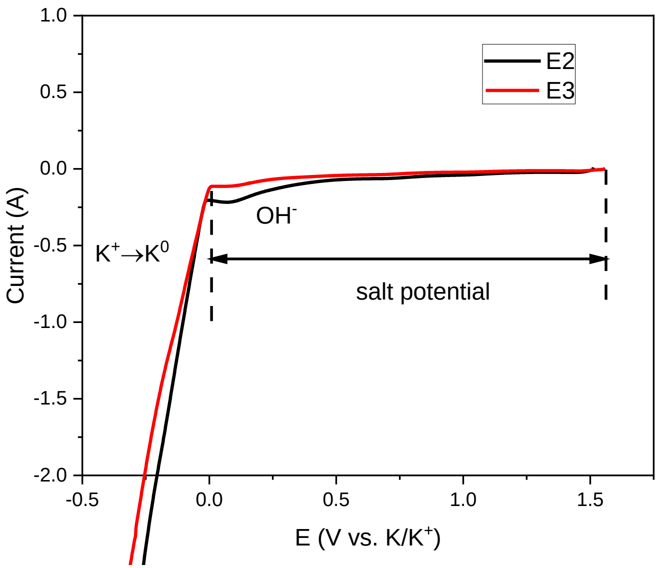
Liquid Salt Test Loop at ORNL

Results from FY23 LSTL Sensor Operations

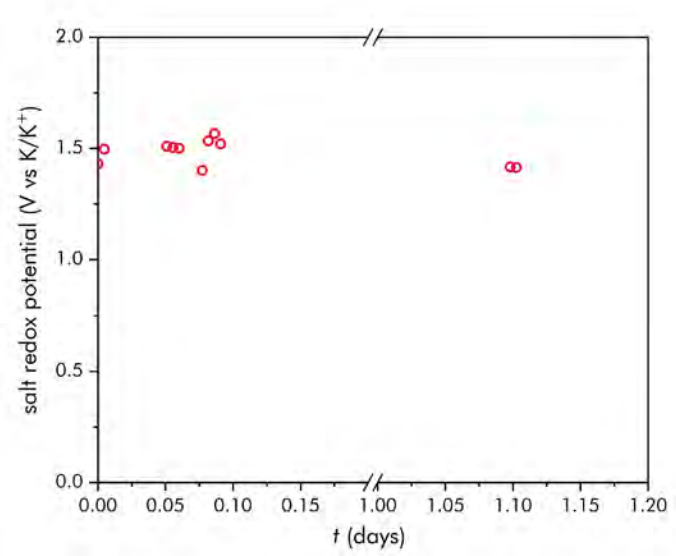
The multi-electrode sensor worked well over the short period of LSTL operations. The salt redox potential varied from 1.4 – 1.55 V vs. K^0/K^+ and hydroxide levels were >3200 ppm.



High-frequency resistance measured on each electrode (lower resistance means deeper immersion depth)



Linear sweep voltammograms obtained on two electrodes of the sensor installed on LSTL



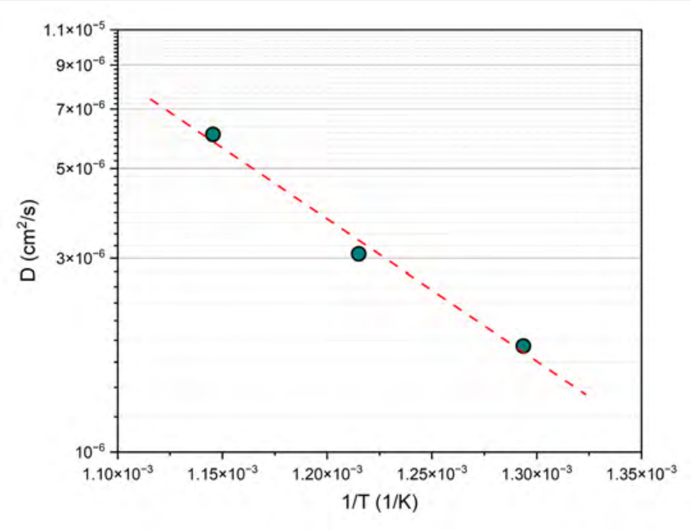
The salt potential throughout the operations of the LSTL

Electrode after operations in LSTL

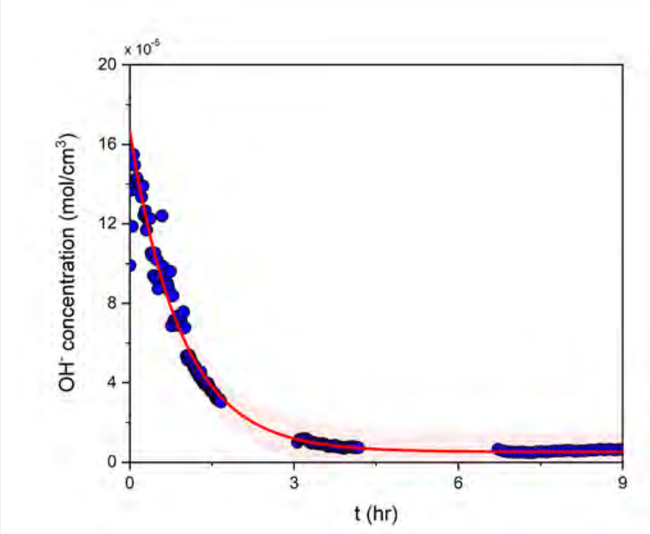
Results from FY23 LSTL Sensor Operations

- ANL previously investigated the electrochemical behavior of OH^- in molten FLiNaK and obtained fundamental information such as diffusion coefficients and decomposition reaction rates using benchtop scale experiment setup
- The OH^- in the LSTL behaved similarly to the experiments at smaller scales

Bench-scale Hydroxide Measurements

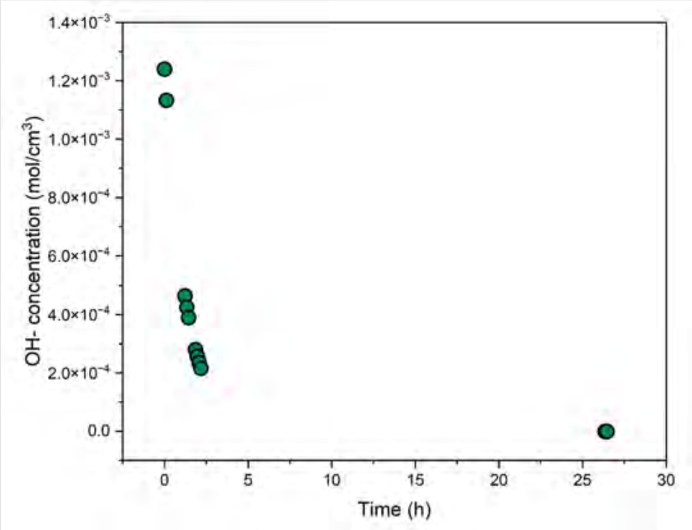


The variation of OH- diffusion coefficient in molten FLiNaK over various temperatures



The variation of OH- concentration in molten FLiNaK in molten FLiNaK over time at 500°C

LSTL Hydroxide Measurements



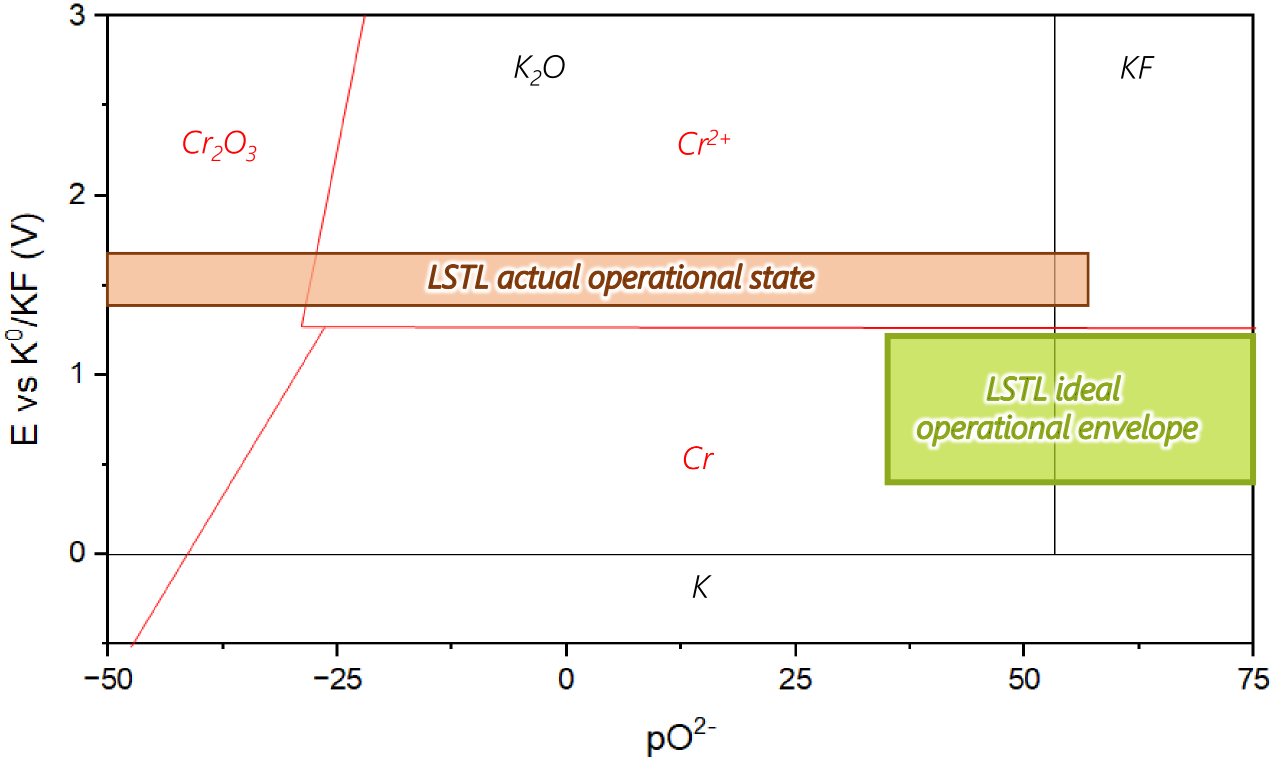
The variation of OH- concentration in LSTL during operations in FY23

Operational Envelope for the LSTL

Argonne established an operational envelope for the LSTL based on its salt and alloy compositions.

As measured by the in-situ sensors, the LSTL was operating outside its optimal range

- Salt redox potential in range where significant oxidation would occur
- High oxide levels from OH^{-} decomposition



Pourbaix diagram and associated operational envelope for the LSTL

Method development for contaminant quantification across complete concentration ranges

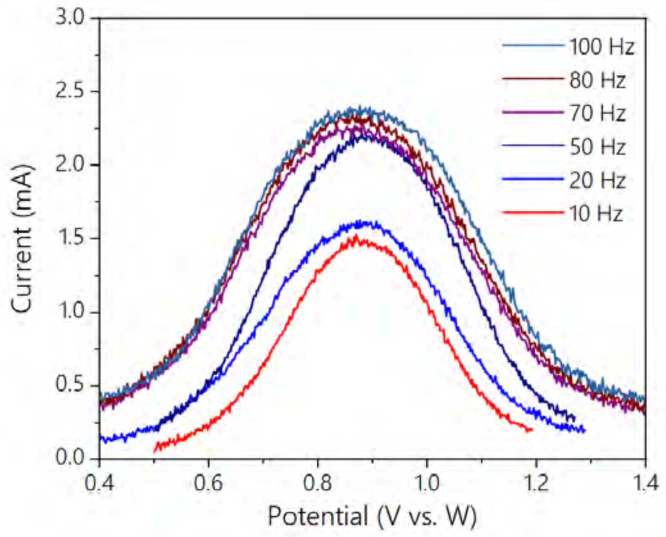
- Measurement capabilities for oxide and other species were enhanced after conclusion of the FY23 campaign

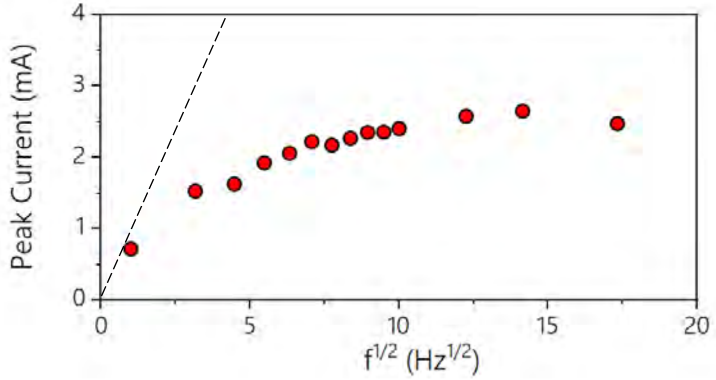
- Developing reliable techniques for use in molten salts at scale is important for monitoring corrosion products and contaminants from ppb scales through 10,000s of ppm

- Square wave voltammograms were collected for a model system

$$Cr^{2+} \rightarrow Cr^{3+} + e$$

- Anomalous relationship between peak current and frequency was observed
  - Deviation from theory indicate nonideal effects that limit the direct feasibility of pulse techniques in molten salts
  - Nonideal effects similar to or larger than earlier studies by Hoyt, et al. (2018)



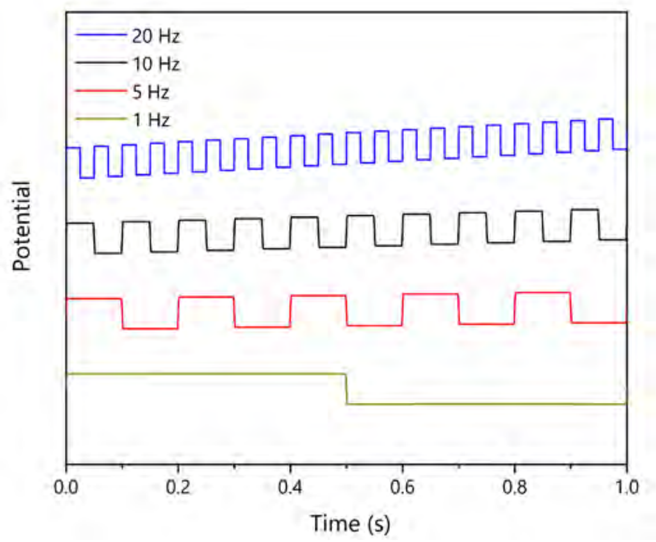


Representative square wave voltammograms of Cr oxidation (top) and anomalous relationship versus square root of frequency (bottom)

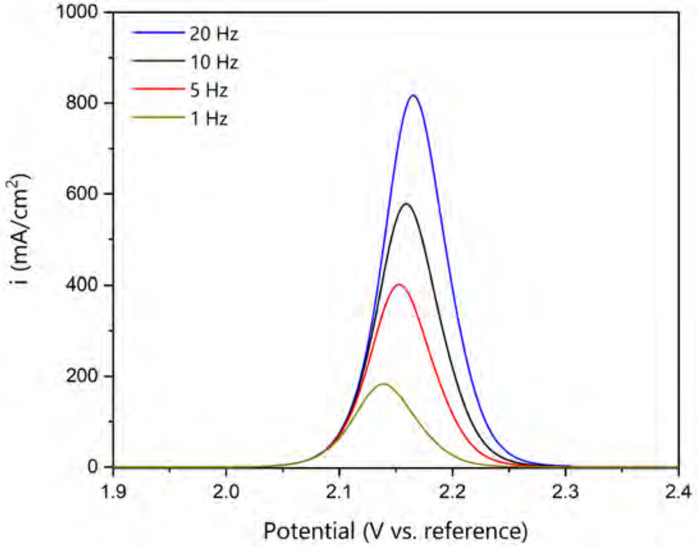
Supporting experiments through simulations

Numerical simulations of square wave voltammograms were created to support analysis and correction of the experimental data

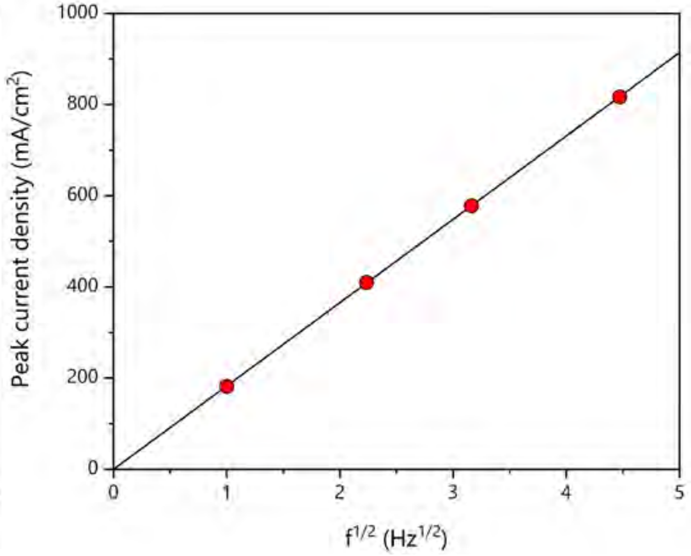
- User defined variables such as frequency, number of electrons transferred, and solution resistance are known to affect current-potential relationship



Potential-time profiles of simulated square wave voltammograms



Square wave voltammograms simulated at various frequencies



Linear relationship between peak current density and $f^{1/2}$

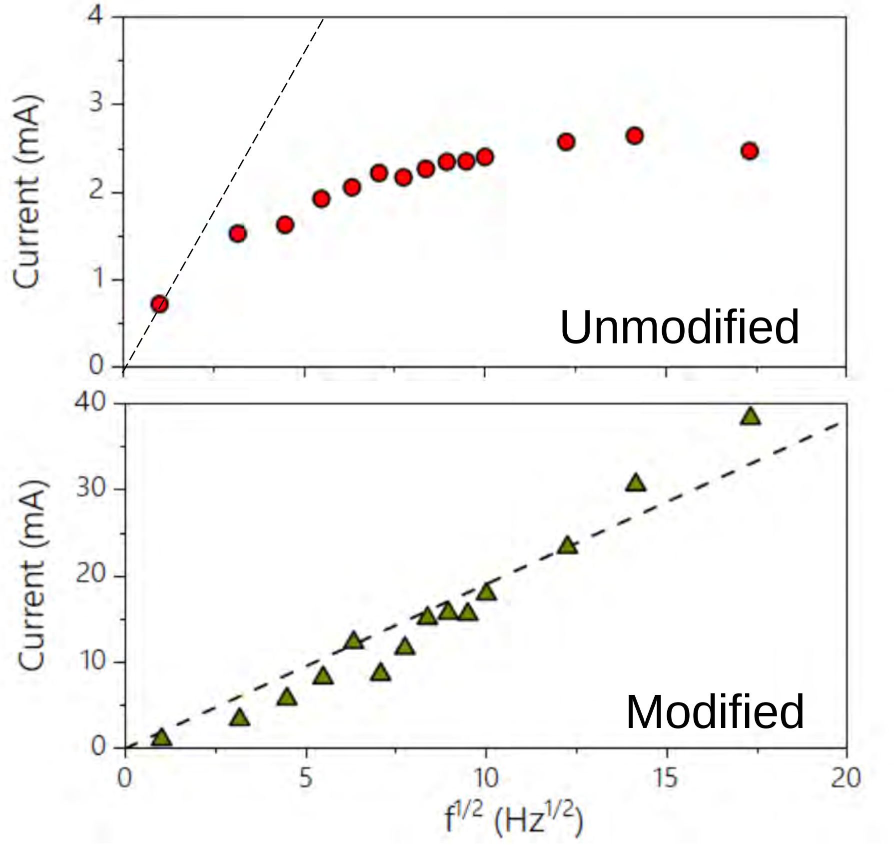
Correcting data through digital simulations produces reliable results

- Theory-based simulations developed to correct for nonideal contributions that can distort experimental measurements

- Modified Krause and Ramaley formula
  - ϕ is the current multiplier calculated from digital simulations

$$I_p = \phi \frac{nFAD^{\frac{1}{2}}C_b\psi_p}{\pi^{1/2}t_p^{1/2}}$$

- Using our approach, we are able to calculate fundamental properties that agree well with literature and other electrochemical techniques



Peak current versus square root of frequency of chromium oxidation in chloride salts – unmodified (top) and modified (bottom)

Enhanced measurements of contaminants in molten fluorides

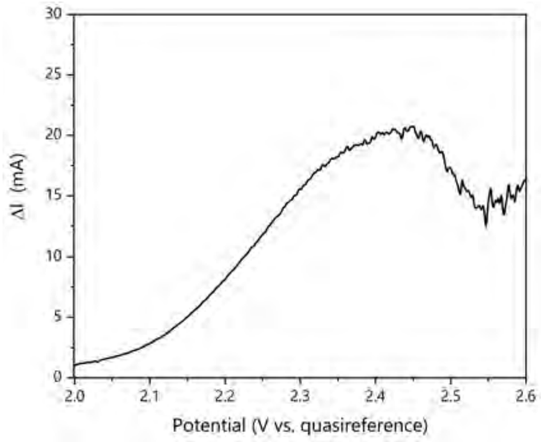
Oxide measurements are important as these impurities can be introduced to molten salt flow systems through a number of routes, including:

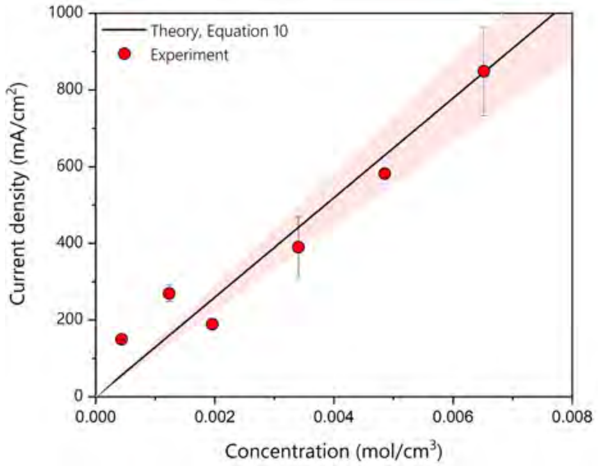
- Oxygen/moisture ingressions
- Selective dissolution of oxides present in structural alloys
- Residual oxide impurities in the bulk.

Oxide quantification is of interest via

$$2O^{2-} \rightarrow O_2 + 4e$$

By leveraging our modified Krause and Ramaley formula, proper quantification of O^{2-} can be achieved over broad concentration ranges

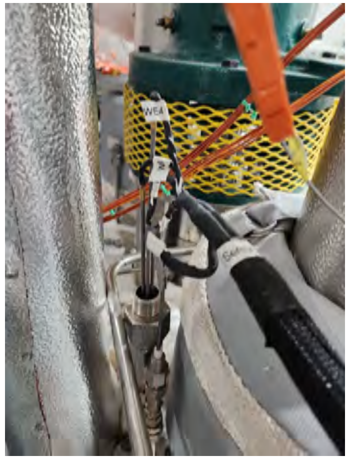




Representative square wave voltammogram of oxygen evolution (top) and peak current density versus bulk concentration (bottom)

FY24 MSR Campaign Sensor Operations

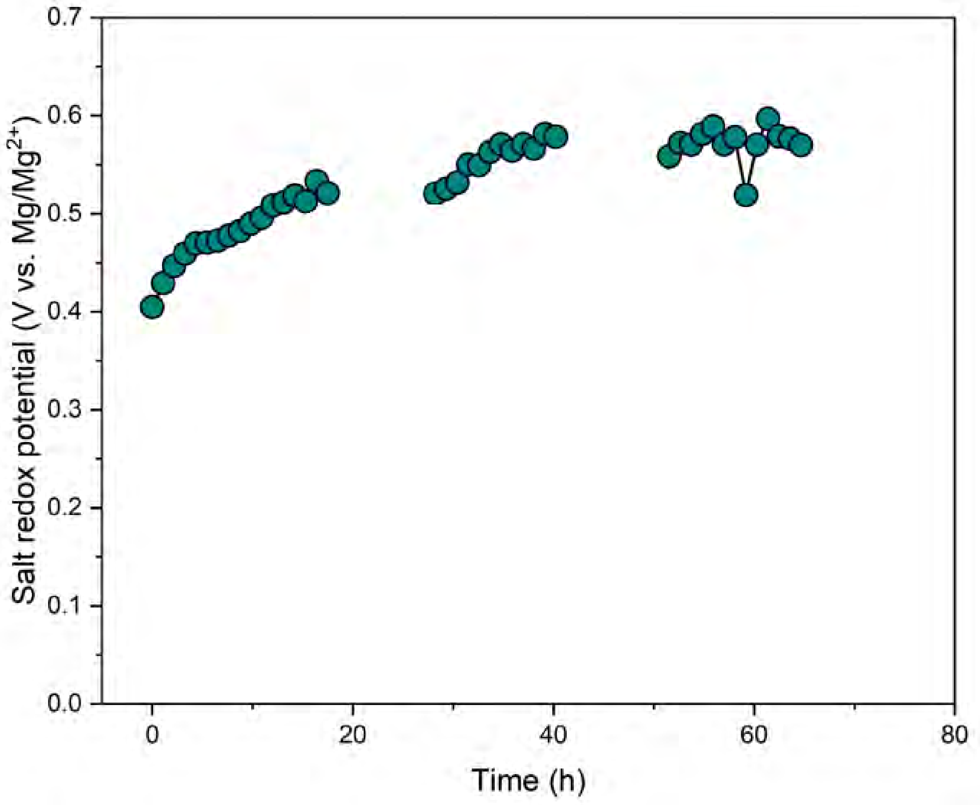
- For FY24, the FASTR loop at ORNL is being used to support MSR-relevant technology demonstrations
- Initial resumption of operations for FASTR took place over a period of three days using molten $MgCl_2$-KCl-NaCl
- An Argonne electrochemical sensor was used to monitor the salt status in the loop
  - The sensor features multielectrode sensor arrays connected to a customized multiplexer
  - The salt status was periodically monitored throughout of the loop operations (~70h)



sensor probe assembly after operations

Initial Monitoring of the FASTR Loop

- **Electrochemical Monitoring**
  - The ANL sensor provided crucial information for loop operations such as the salt redox potential and impurity concentrations
  - The result obtained from the sensor indicates that salt was clean with <1 ppm Cr^{2+}, Fe^{2+}, and OH^-
  - The salt potential increased modestly as O_2 and H_2O gradually entered the salt
    - Any leaks were likely extremely minor (est. << 1×10^{-5} mbar L/s)

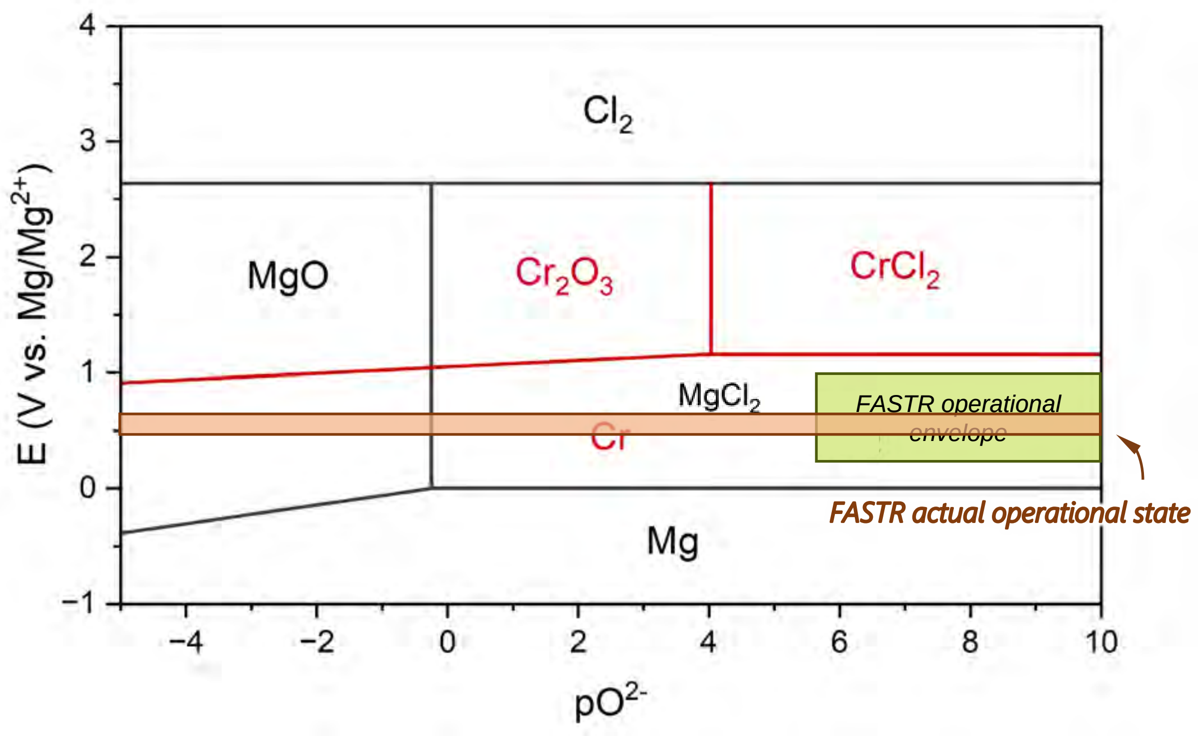


Salt redox potential variation over time within FASTR during preliminary operations

Operational Envelope for FASTR

- Similar to the LSTL, the salt redox state in FASTR could be compared to its operational envelope
  - Envelope for $MgCl_2$-KCl-NaCl is slightly more constrictive due to the relatively high formal potential of Mg deposition
- Even though the salt redox potential was above 0 V vs Mg^0/Mg^{2+}, Mg metal from the original purification procedure is still likely present in salt (non-equilibrium conditions)

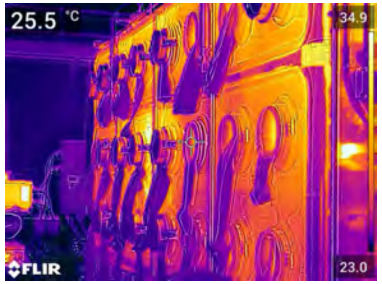
The FASTR loop's salt is in good condition to support future technology demonstrations for the MSR Campaign



FY24 Activity – Pumped Actinide Loop

Moving into the second half of FY24, Argonne is working to construct a pumped actinide loop

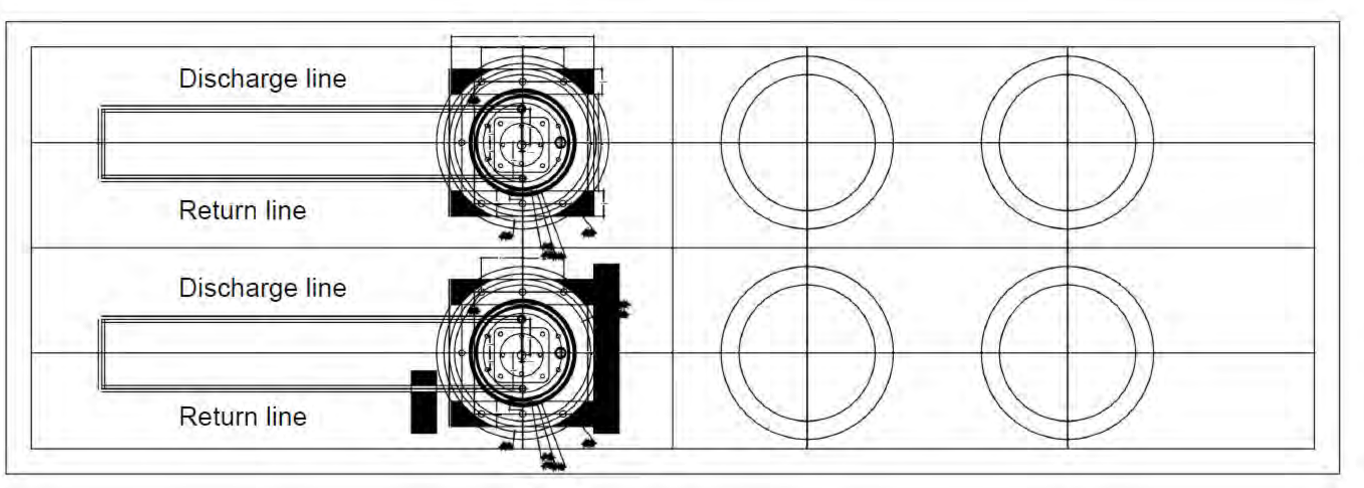
- Small-scale loop installed within flow systems glovebox
- Glovebox infrastructure in place to support electrical, thermal, and radiological protection requirements
- Glovebox includes five well furnaces capable of supporting salt operations
- Located in Pu/TRU laboratory



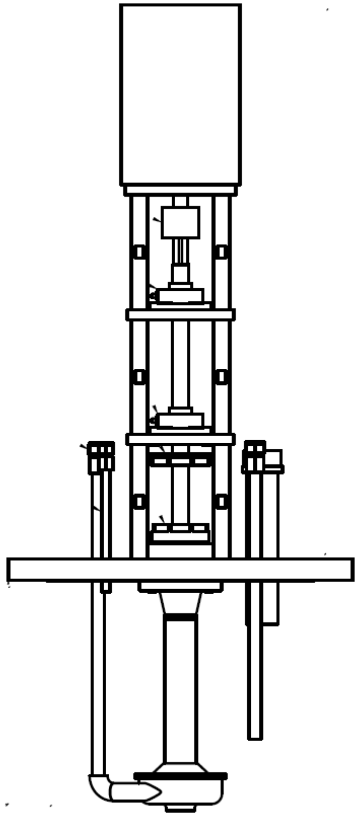
FY24 Activity – Pumped Actinide Loop

Preparation for loop integration is underway. The loop will ultimately support:

- Technology demonstrations in flowing actinide salts
- Corrosion studies in nonisothermal, pumped conditions
- Demonstrations of flow system automation



Overhead view of salt loop installed into glovebox furnace wells

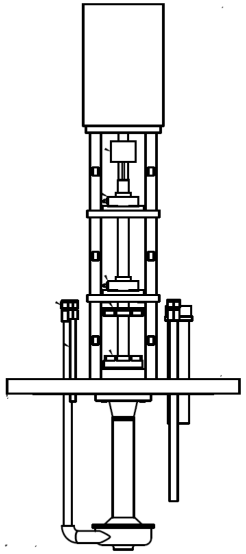


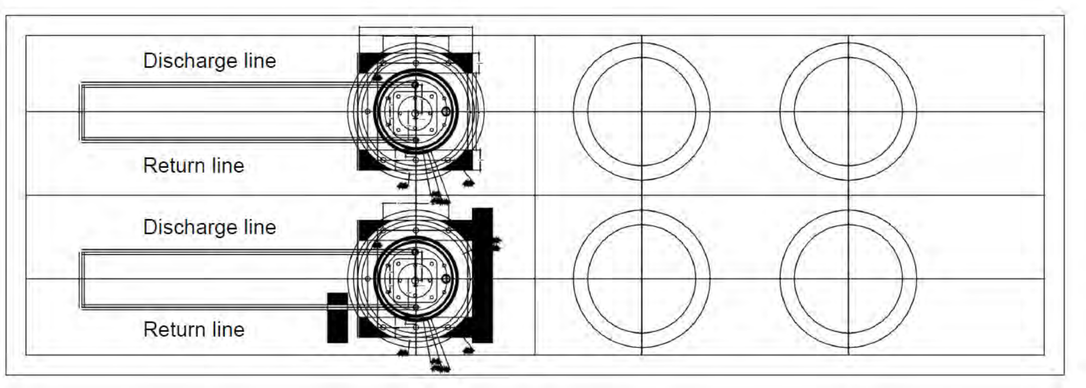
Cantilever pump for furnace well operations[1]

[1]Pump to be procured from High Temperature System Designs, Inc.

Conclusions

- Monitoring and control of the salt are essential for successful operations of molten salt systems
- Argonne has developed and deployed electrochemical sensors in support of a variety of flow systems including ORNL's LSTL and FASTR
  - Various enhancements are required to achieve accurate salt measurements in realistic, at-scale environments
- Argonne is working to develop new versatile pumped loops to close technology gaps related to actinide-bearing fuel salts





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THANKS TO:

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Thank you

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