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Molten Salt Reactor PROGRAM

Argonne NATIONAL LABORATORY

Distributed Salt Monitoring and Corrosion Control

Nathaniel Hoyt (nhoyt@anl.gov)
Jicheng Guo
Nora Shaheen

Argonne National Laboratory

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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:

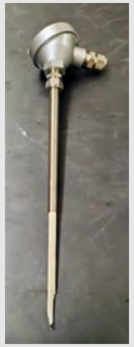
- Is the salt clean enough to avoid failure of the system?
- Is an O_2/H_2O ingression actively occurring?
- Are actinides and other species precipitating out of the salt?
- How quickly are the structural metals corroding?
- Are actinides plating into the structural metals?

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

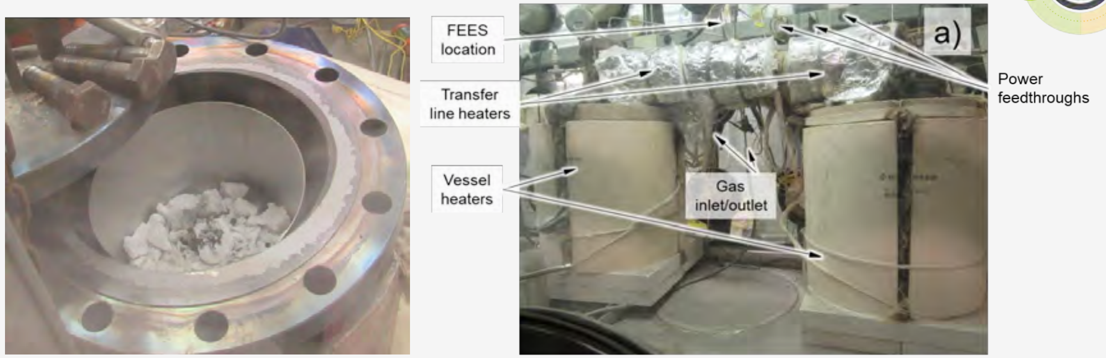
particulate monitoring

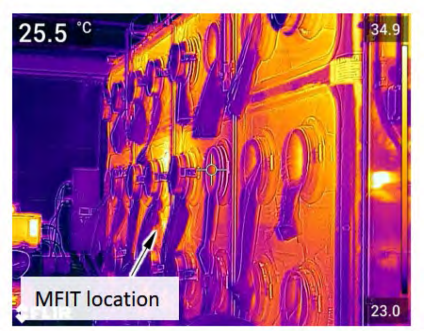


automated sampling

salt composition

Automated Operations of Molten Salt Systems

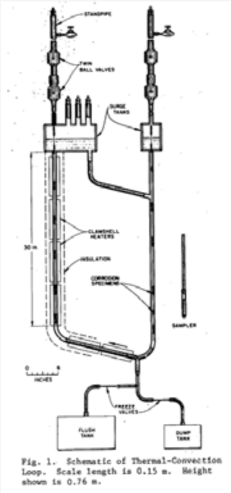




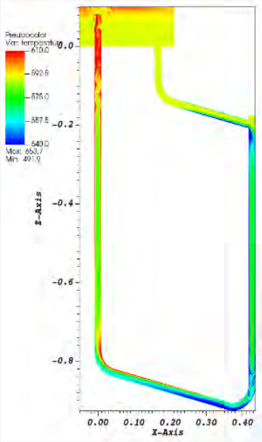
Operational Envelopes for Molten Salt Systems

Prior to running any molten salt equipment, it is important to define the operational limits needed to achieve successful thermodynamic/kinetic evolution of the system

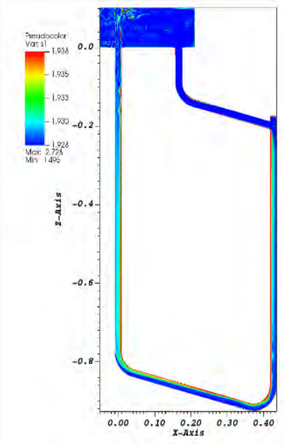
Modeling of Combined Thermodynamic/Kinetic Evolution of Salt-Alloy Systems



MSRE-era thermal convection loop[1]



Temperature contours

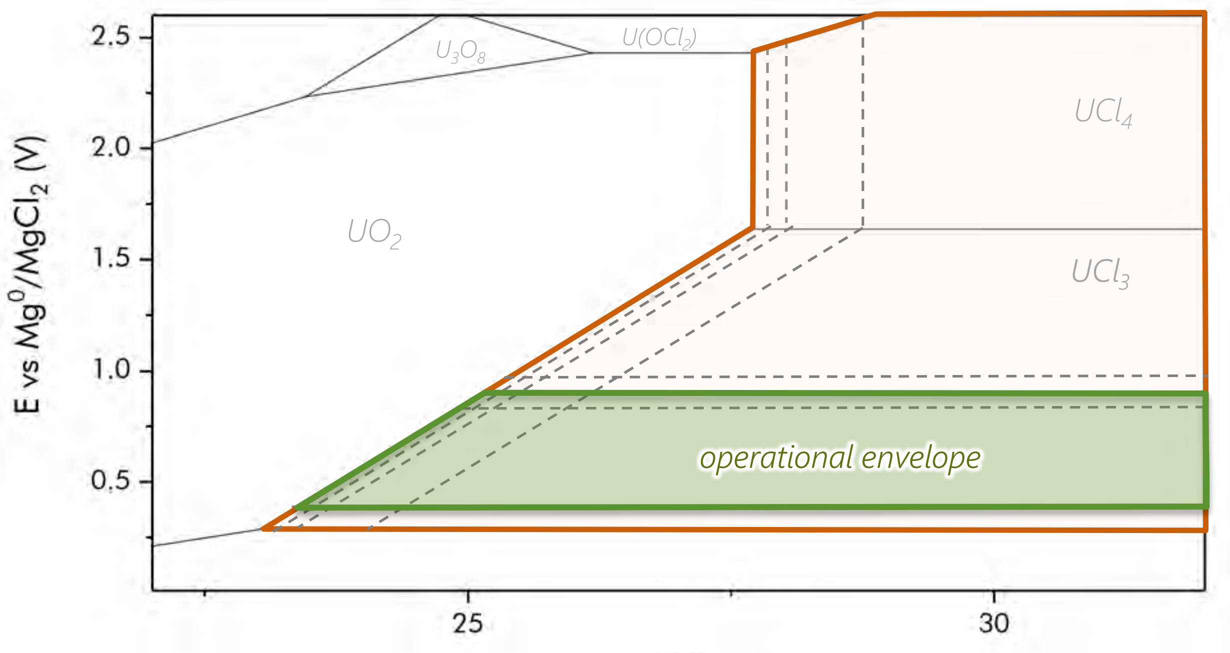


Cr^{2+} concentration contours

Three-dimensional engineering-scale simulations of coupled salt-alloy behavior

NEAMS

Salt Chemistry Operational Envelope



$MgCl_2$-KCl-NaCl-UCl_x at 500 °C

Approaches for Salt Excursion Recovery

Alongside monitoring, it is essential to have capabilities to recover from operational envelope excursions

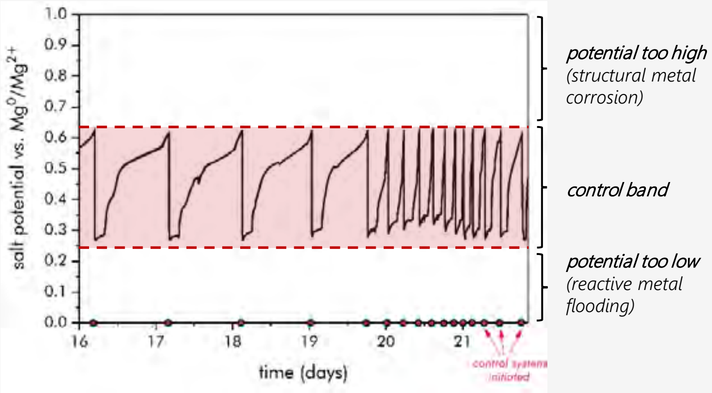
Argonne has developed systems to provide these capabilities

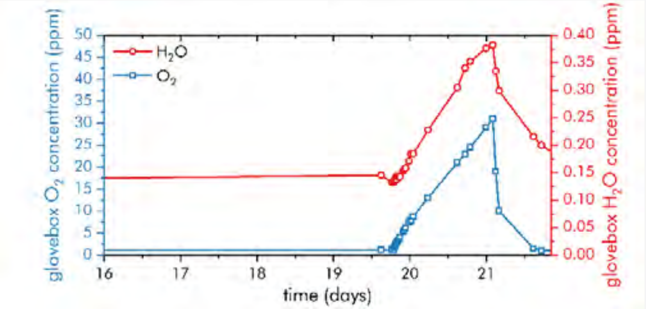
- Reactive metal contacting
- Automated electrolysis
- Particulate removal systems

Monitoring and control are crucial to be able to properly respond to off-normal events that can occur with molten salt systems

Reactive Metal Contacting

Automated Electrolysis for Redox Control





Vortex Separation / Filtering

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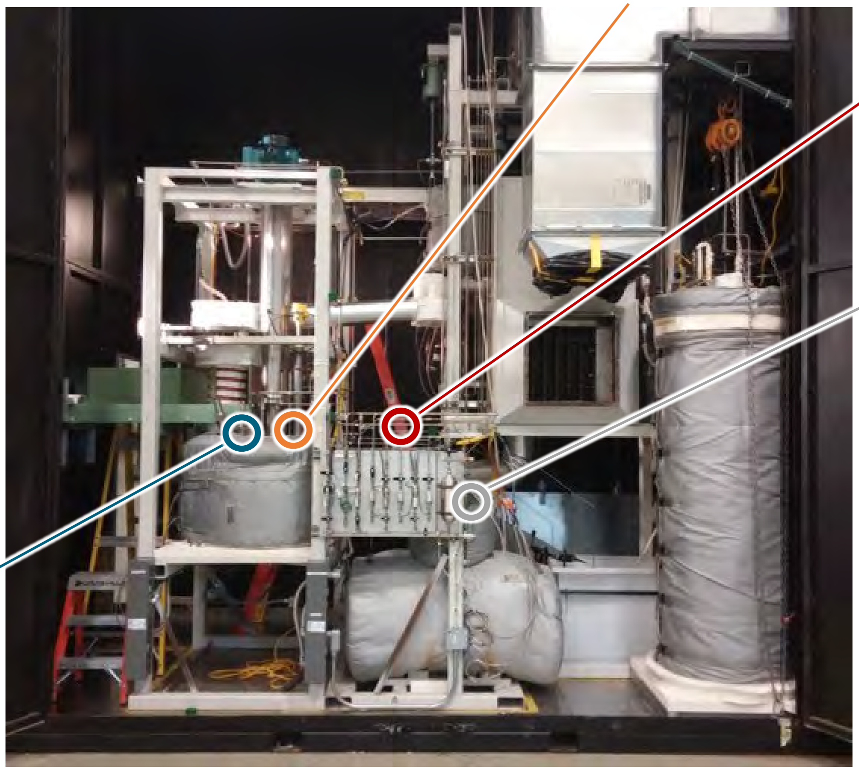
Chemistry Monitoring and Control System Integration

FY23 Goals

Deploy salt monitoring and control technologies for use in the LSTL

- **Distributed Sensors**
  - Multielectrode electrochemical sensor installed along transfer line
  - Auxiliary electrode in pump tank
  - Targeting the LSTL’s FLiNaK (with unknown impurity levels)
- **Integrated Salt Chemistry Control**
  - Chemistry control unit will be installed into LSTL pump tank



Liquid Salt Test Loop at ORNL

Salt Monitoring and Control for the LSTL

Sensors have been deployed to facilitate distributed monitoring of the LSTL transfer line and pump tank. A full multielectrode array sensor was installed in the transfer line, while the other locations used individual auxiliary electrodes.

Multielectrode Array Sensor

- Species concentrations (Cr^{2+}, Fe^{2+}, Ni^{2+}, O^{2-}, OH^{-}, etc.)
- Salt potential
- Salt level

Auxiliary Distributed Electrodes

- Local salt redox potential

Multielectrode Array Voltammetry Sensor (MAVS)
[LSTL Transfer Line]

Auxiliary Distributed Electrodes
[LSTL Pump Tank]

Updated Sensor Materials

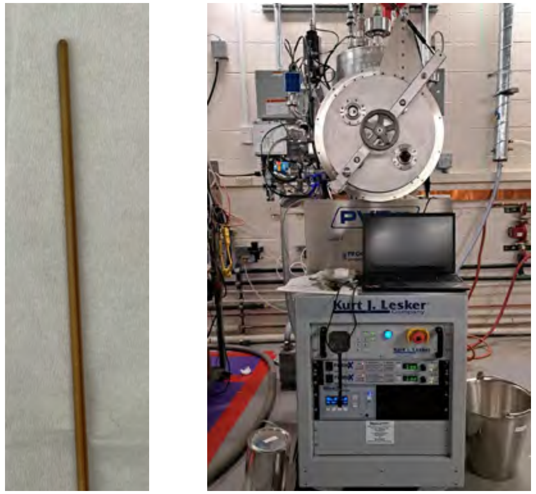
Argonne's electroanalytical sensors have been used for long durations in a wide variety of coolant and fuel salts

- Be-bearing salts
- U/TRU-bearing salts
- High concentration fuel salts

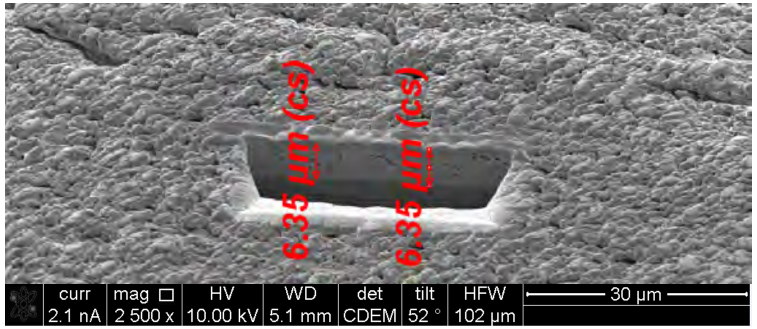
Continued improvement to the sensor designs have been made in FY22 and FY23

- Previously-developed electrodes showed consistent results over very long durations in FLiNaK, FLiBe, and other fluoride salts
- Transition to coated electrodes in FY23 for greater mechanical robustness

FY22: compound electrodes

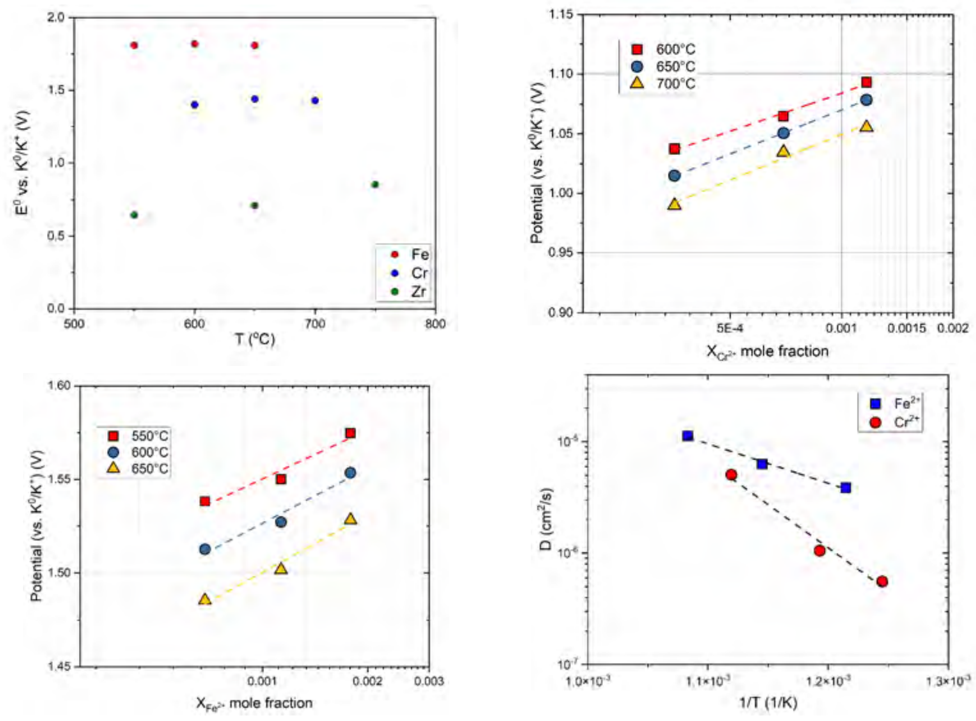


FY23: vapor deposition coated electrodes

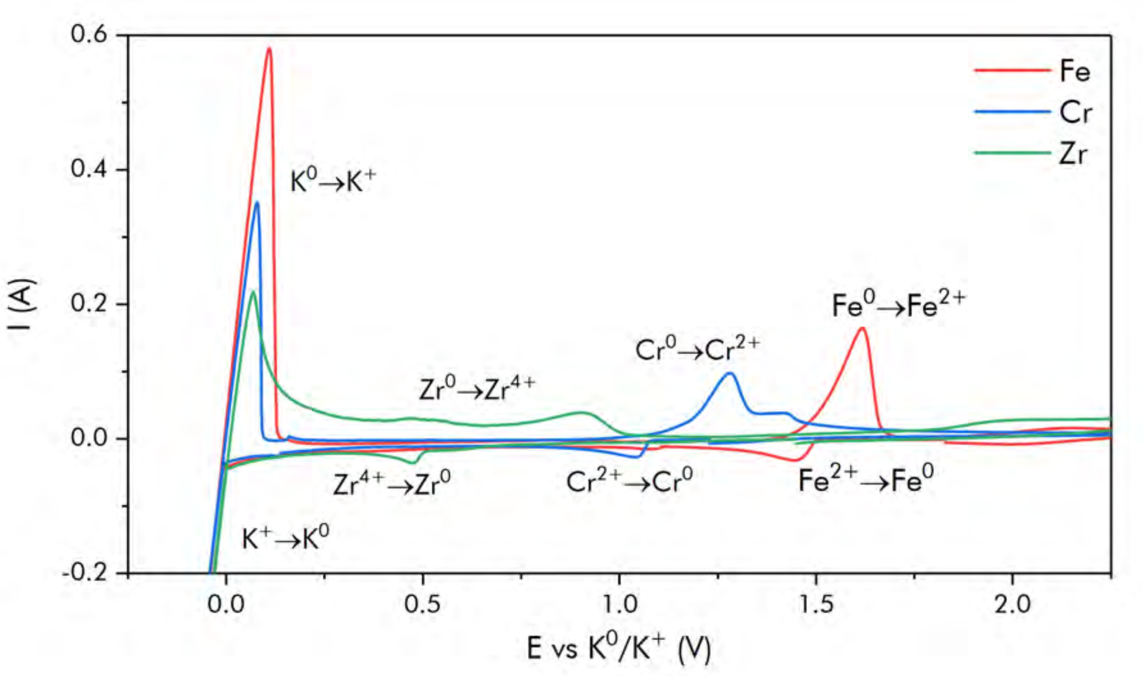


Corrosion Control in FLiNaK

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



Typical fundamental values for key species



Raw electrochemical data for key corrosion products and corrosion control species

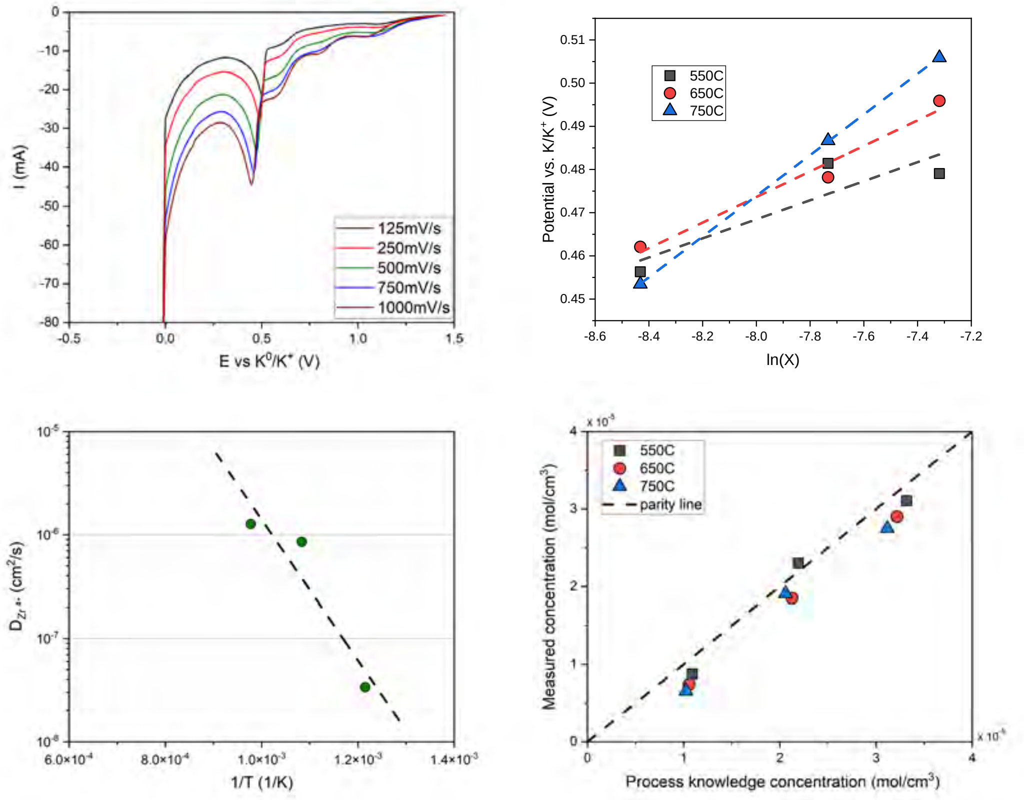
Properties of Zr/ZrF_4 in FLiNaK

Zr has been selected as a candidate corrosion control additive for several molten salt loops

Fundamental thermodynamic and kinetic properties have been measured in support of its use in loop environments

- Suitable redox potential
- Significant precipitation of ZrO_2
- Issues with volatility of ZrF_4

Capabilities for ZrF_4 measurements have also been established to assess consumption of the additive



Raw Zr^{4+}/Zr^{0} LSVs (top left); Potentiometric relationship for Zr^{4+}/Zr^{0} (top right); Diffusion coefficients for Zr^{4+} (bottom left); Measurements of Zr^{4+} concentration (bottom right)

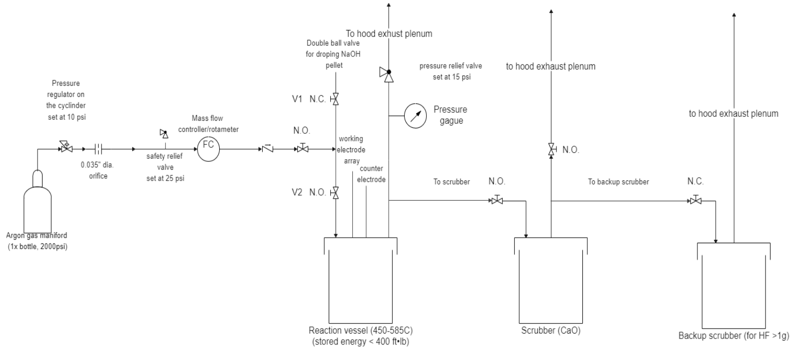
Extrinsic Impurities in Molten FLiNaK

Extrinsic impurities from moisture and oxygen ingressions play a substantial role in determining the success of a given salt/alloy combination

Experiments to establish fundamental properties of salt impurities and structural materials are essential to quantify and understand corrosion interactions

We have developed a number of experimental apparatuses devoted to extrinsic salt impurity studies

- Due to aggressive off-gas products, these experiments are prepared in gloveboxes and later run inside fume hoods



System designed at ANL to perform in situ impurity additions to molten FLiNaK and electrochemical measurements

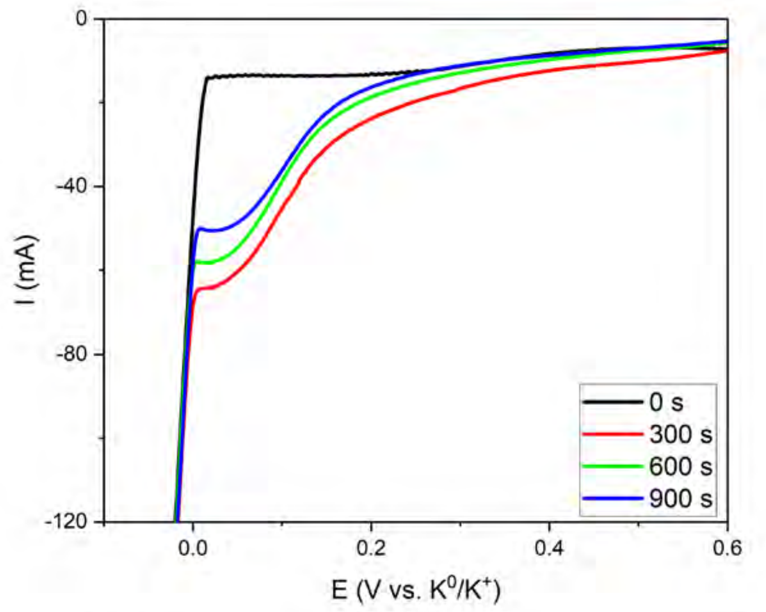
Hydroxides in Molten Fluoride Salts

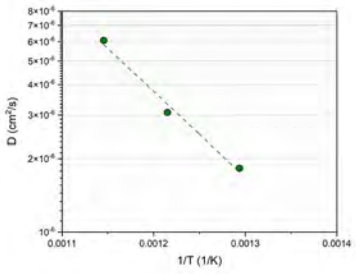
- Using impurity injection systems, detailed electrochemical investigations of salt chemistry interactions have been conducted
- Hydroxide arising from water has been a particular focus

$$OH^- + e^- = \frac{1}{2}H_2 + O^{2-}$$

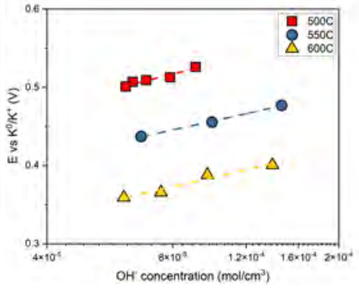
- Fundamental properties such as the diffusion coefficients and thermodynamics values for OH^- in molten FLiNaK have been measured

$$\log(D_{OH^-}) = -1.222 - \frac{3503.0}{T}$$





The diffusion coefficient of hydroxide in molten FLiNaK at various temperatures



Hydroxide reduction potential vs concentration in molten FLiNaK at various temperatures

Temp (C)	$E^{0'}$ (V vs. K/K+)
500	0.872
550	0.767
600	0.707

Formal potentials for OH^- in FLiNaK

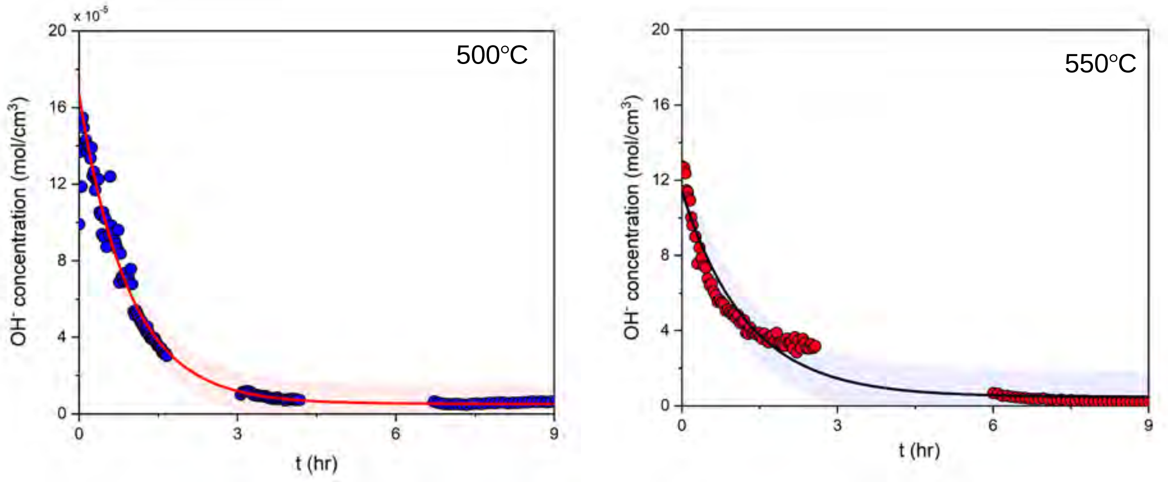
Hydroxides in Molten FLiNaK

- The behavior of OH^- in molten FLiNaK is complex and involves decomposition reaction mechanisms
- The decomposition typically generates corrosive HF which can attack structural metals

$$2OH^- \rightleftharpoons O^{2-} + H_2O(g)$$

$$2F^- + H_2O(g) \rightleftharpoons 2HF(g) + O^{2-}$$

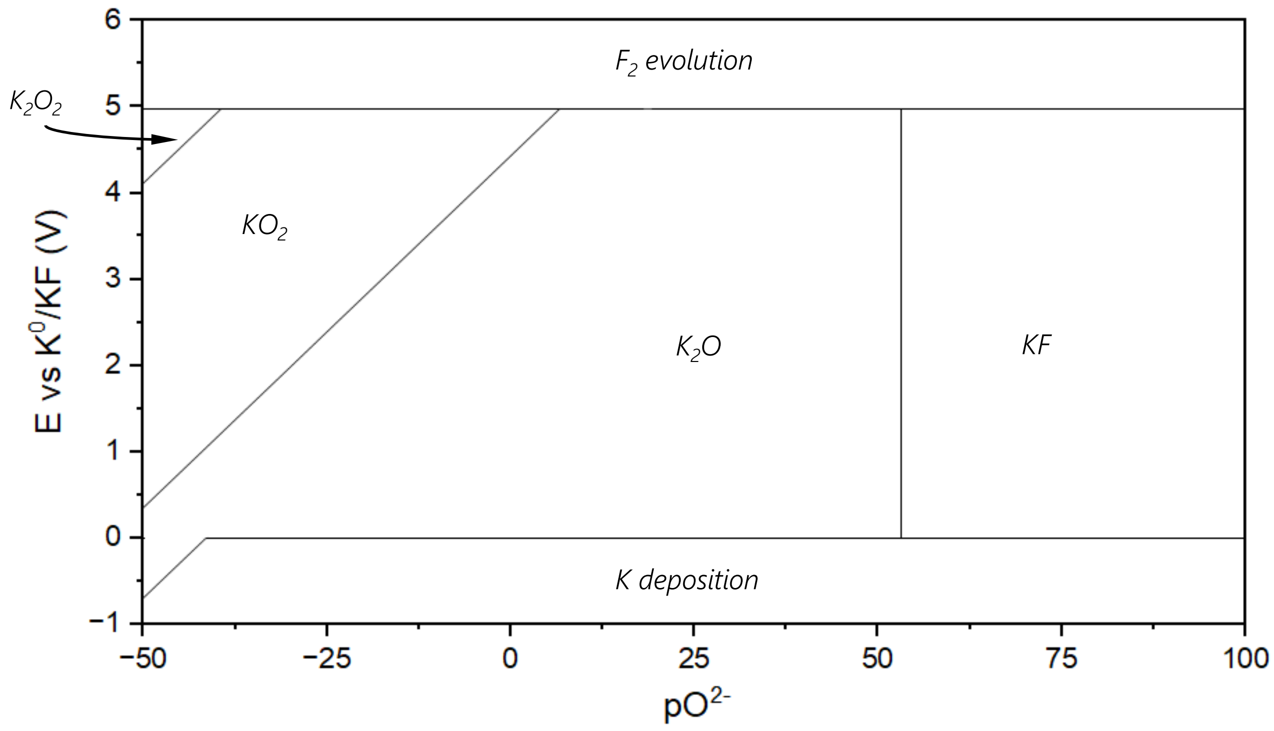
- The decomposition reaction shows distinctive first order reaction characteristics. Equilibrium concentrations of hydroxide therefore allow for estimates of water ingression rates.



Reaction rate constants (k) for hydroxide decomposition in FLiNaK	
Temperature (°C)	Reaction rate constant k (s^{-1})
500	$2.23\times10^{-4} \pm 9.36\times10^{-6}$
550	$2.94\times10^{-4} \pm 1.61\times10^{-4}$
600	$1.18\times10^{-3} \pm 4.47E\times10^{-5}$

Building an Operational Envelope for the LSTL

- Using data we've taken over the past several years, we have constructed an operational envelope for the LSTL
- Operational limits are constructed from thermodynamic and kinetic factors
- Ideal operating envelope lies at low oxide concentrations and low (but not too low) salt redox potentials
- Maintaining conditions within the envelope will help ensure acceptable corrosion rates



Pourbaix diagram and associated operational envelope for the LSTL

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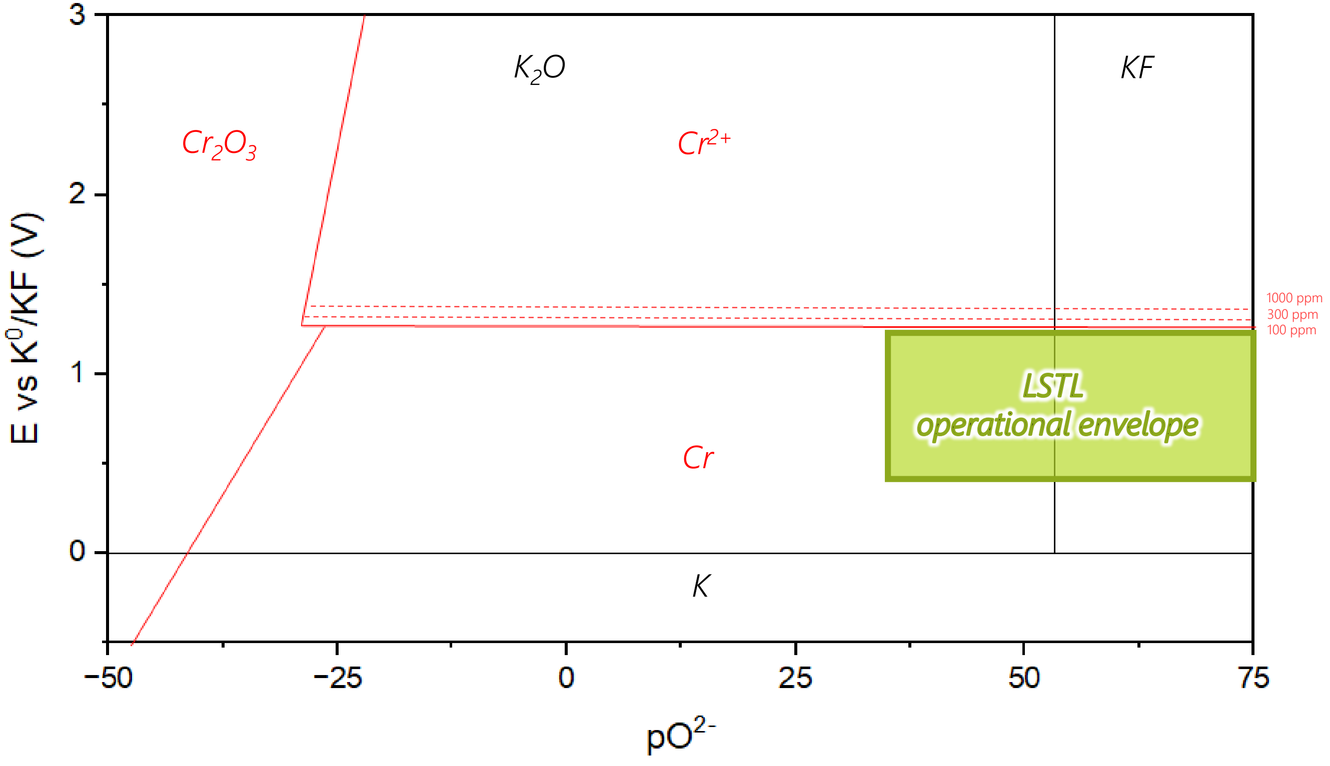


Pourbaix diagram and associated operational envelope for the LSTL

LSTL Sensor Operations

Sensor operations of the LSTL took place over two days during November 2022

The electrochemical sensors were used to characterize the salt condition, which was expected to have substantial impurities

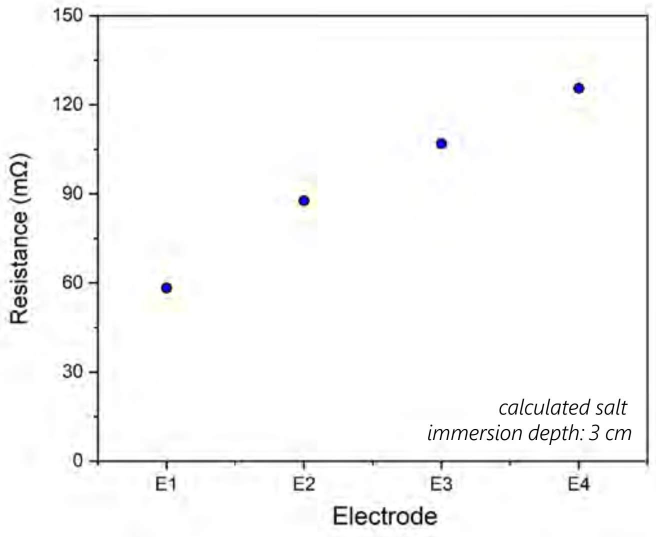
- Impurities such as hydroxide and oxide were expected from an earlier air/moisture ingression event

The sensor was operated completely autonomously using default settings

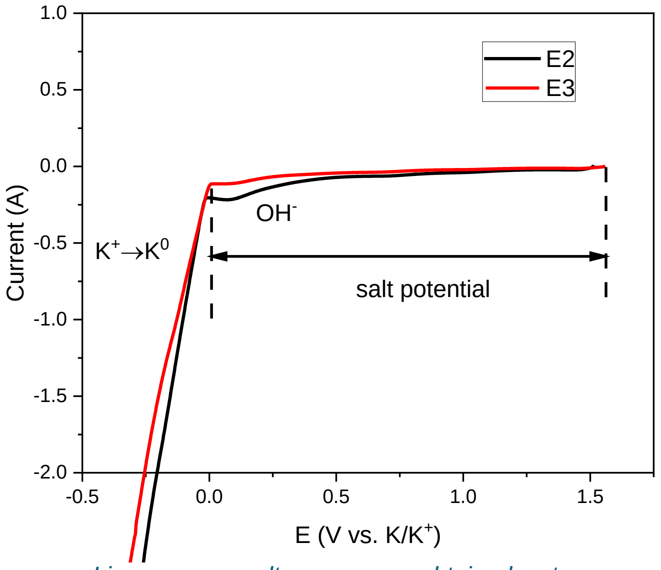
- No opportunities for adjustments to applied waveform parameters

Results from LSTL Sensor Operations

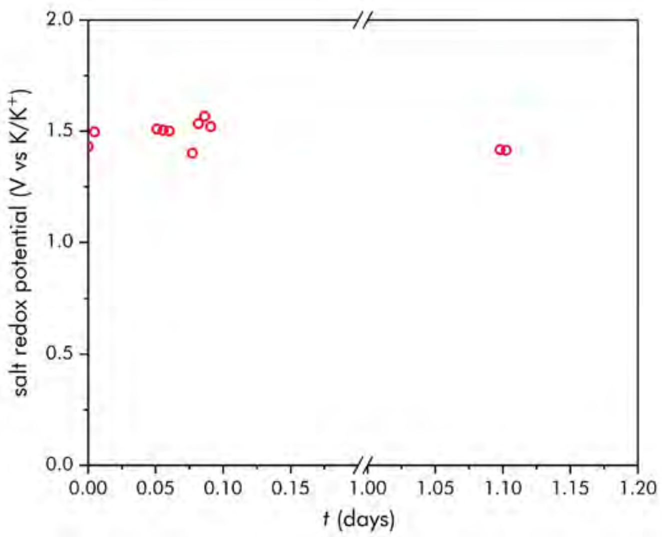
The multi-electrode sensor worked well over the short period of LSTL operations. The salt potential redox potential varied from 1.4 – 1.55 V vs. K^0/K^+ and hydroxide levels were >3200 ppm.



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

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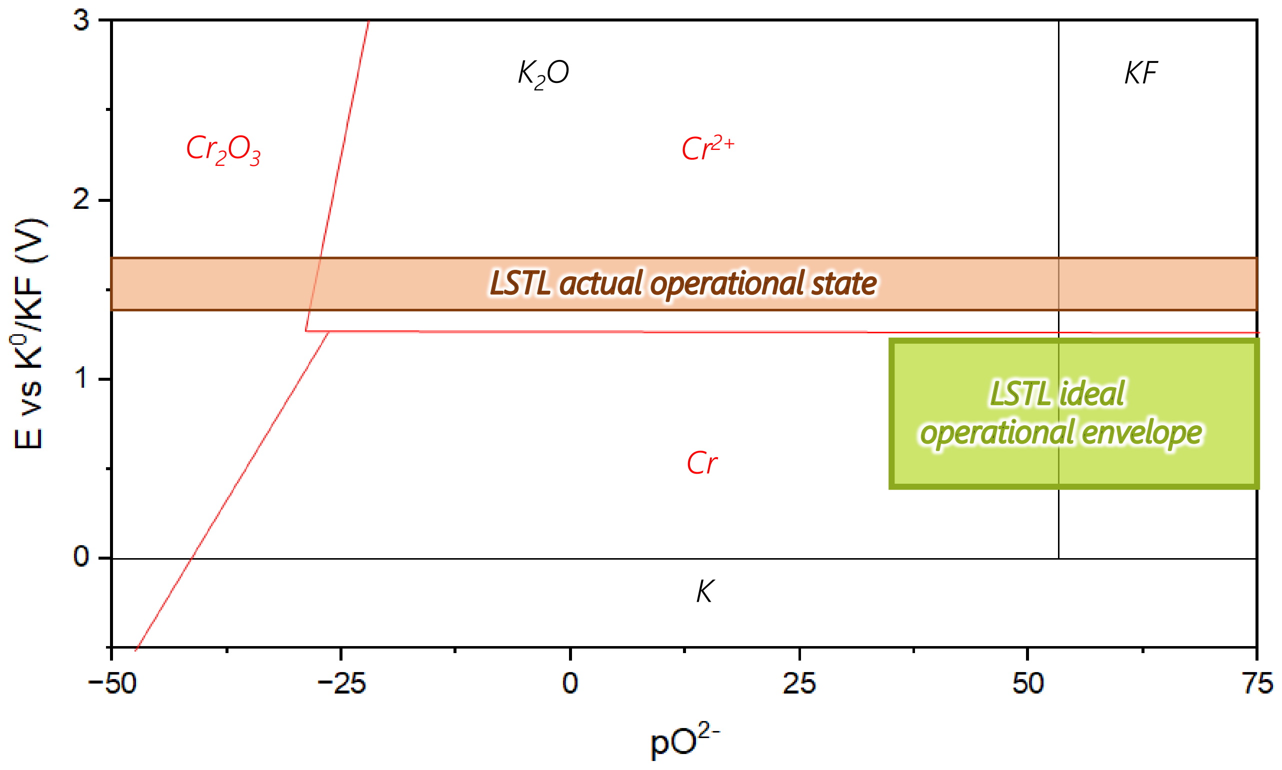
Operational Envelope for the LSTL

When the sensor measurements are shown relative to the operational envelope, it is clear that the LSTL operated well outside its optimal range

Argonne's corrosion control system cannot supply a sufficient quantity of redox agents to purify the salt

- Limitations based on available port size
- Full purification is instead needed (hydrofluorination)



Pourbaix diagram and associated operational envelope for the LSTL

Plan for the Remainder of FY23

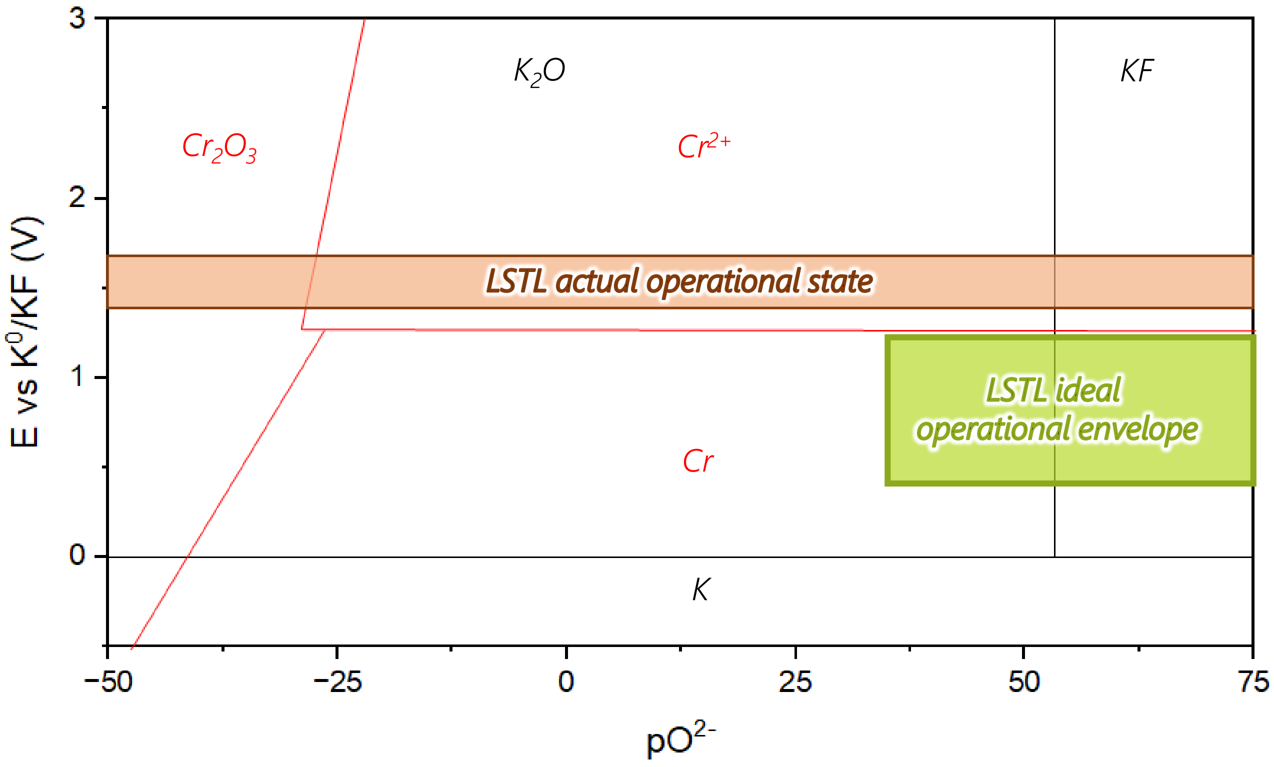
- **LSTL Operations**
  - Inline measurements over longer durations
- **Fundamental Properties Measurements**
  - Additional metal ion species
  - Finalize extrinsic impurity measurements
- **Sensor Operations in FLiNaK Purification Vessel**
  - Demonstrate capabilities for end-point determination
- **Sensor Operations with Deliberate O_2/H_2O Ingressions**
  - Demonstrate measurement of ingression rate through salt composition changes

Current Technology Deployment Activities

Funding Office	Program	Partner	Relevant Technologies
arpa·e CHANGING WHAT'S POSSIBLE	GEMINA (MARS)	Kairos Power	Electrochemical Sensors (and several other sensors)
GAIN Gateway for Accelerated Innovation in Nuclear	GAIN Voucher	Kairos Power	Hardware and Software for Automated Salt Sensing and Sensor Fusion
U.S. DEPARTMENT OF ENERGY Office of NUCLEAR ENERGY	Advanced Reactor Safeguards Program	Kairos Power	Inline Flow System Monitoring
arpa·e CHANGING WHAT'S POSSIBLE	GEMINA (APPLIED)	Moltex Energy	Salt Chemistry Monitoring and Control Technologies; Salt Chemistry Modeling Tools

Conclusions

- Monitoring and control of the salt combined with careful specification of an operational envelope will help ensure success of molten salt systems
- Sensors deployed to the LSTL worked well over the first two days of operations
  - Additional opportunities for operations in FY23 are expected
- Operations of the purification/de-purification cell will be continued throughout FY23.



Pourbaix diagram and associated operational envelope for the LSTL

THANKS TO:

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Thank you

Nathaniel Hoyt (nhoyt@anl.gov)

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