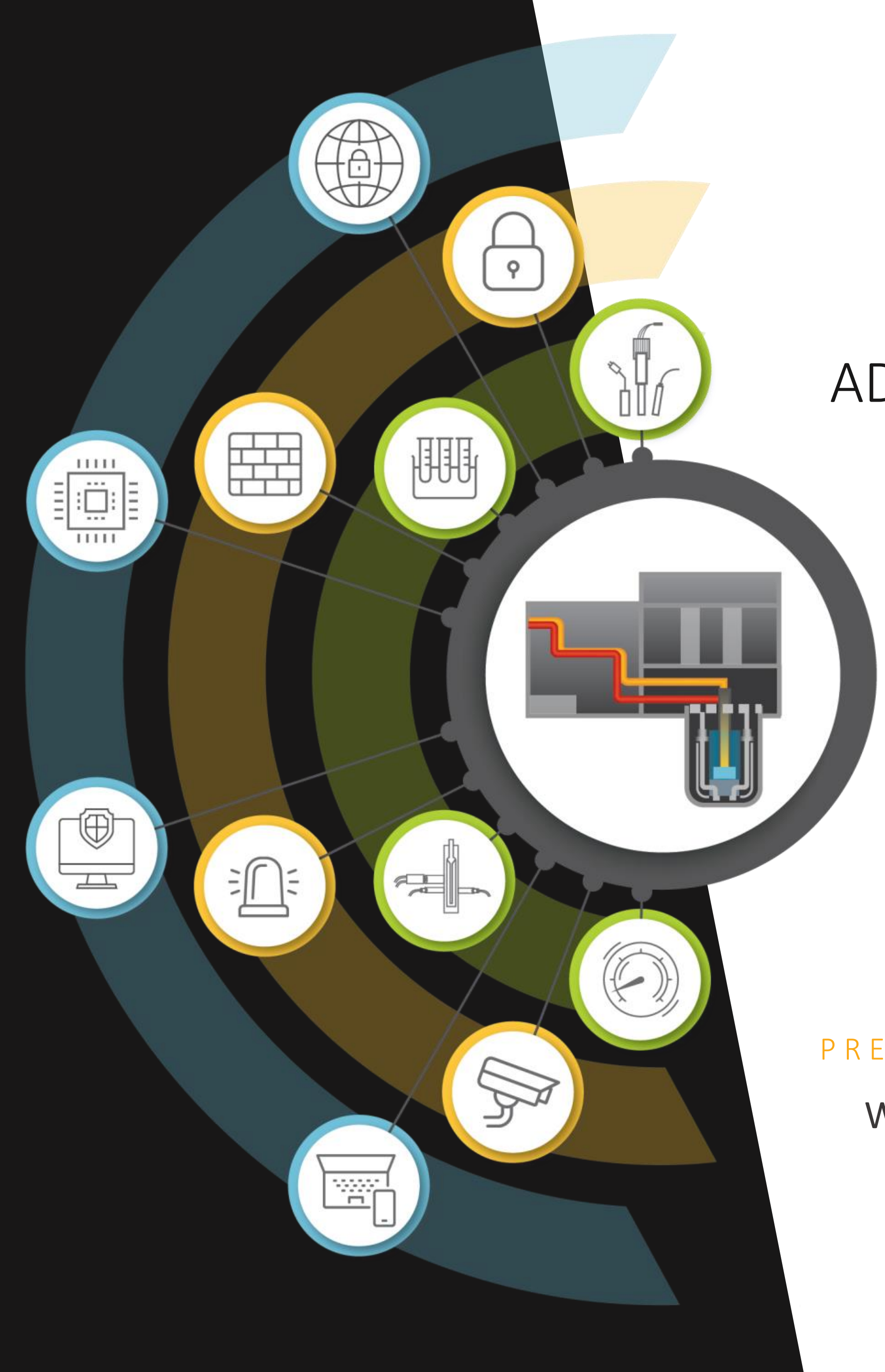


ADVANCED REACTOR SAFEGUARDS & SECURITY

In-line Flow-Enhanced Electrochemical Sensors for MSR Mass Accountancy

Sensor updates and deployment activities

PRESENTED BY

William Doniger, Nathaniel C. Hoyt

May 15, 2024

Argonne Publication Tracking #: 189078

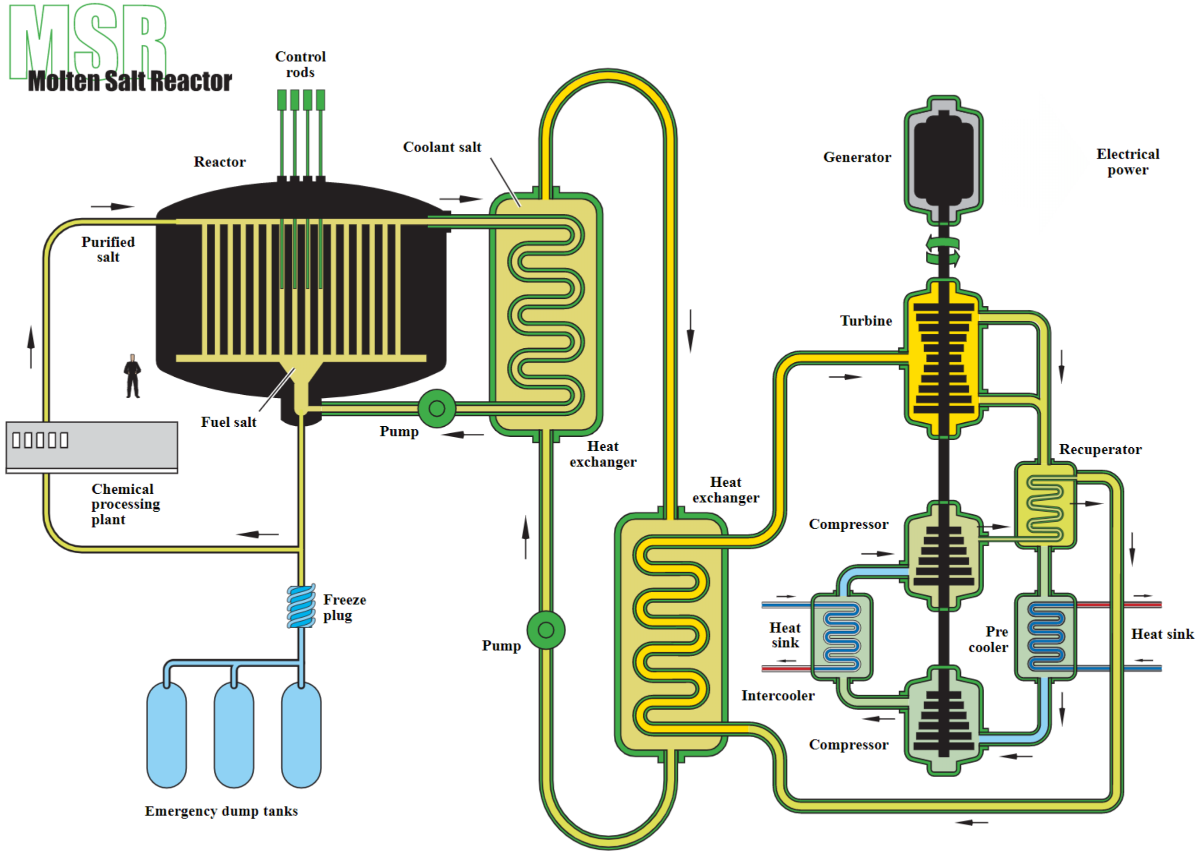
Argonne NATIONAL LABORATORY | U.S. DEPARTMENT OF ENERGY

Safeguards and Process Monitoring for Molten Salt Reactors

Online materials accountancy of fuel salts containing dissolved actinides within MSRs is a safeguards challenge.

- High temperatures and corrosive salts require robust and accurate sensors.
- Rapid detection of concentration or salt level changes needed to identify diversion.
- Outputs with high stability and low uncertainty necessary to detect anomalies.

The goal of our Advanced Reactor Safeguards & Security project is to develop technologies that will enable MSR vendors to meet broad NRC licensing challenges for materials accountancy.

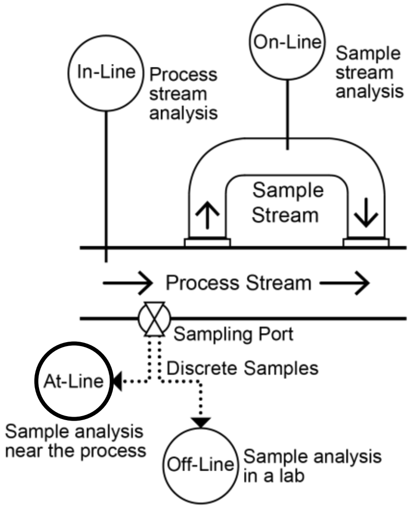


DOE Gen4 Road Map (downloaded from: http://www.ne.doe.gov/genIV/documents/gen_iv_roadmap.pdf)

Safeguards and Process Monitoring for Molten Salt Reactors

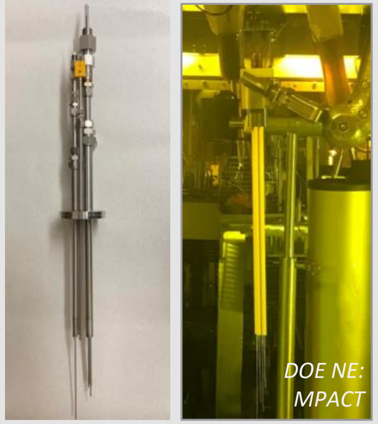
Key monitoring capabilities needed for MSRs:

- Salt composition
- Isotopics
- Salt level
- Flow rates
- Redox state
- Particulates
- Density
- Off-gas



Hoyt et al. JNMM (*2021*)

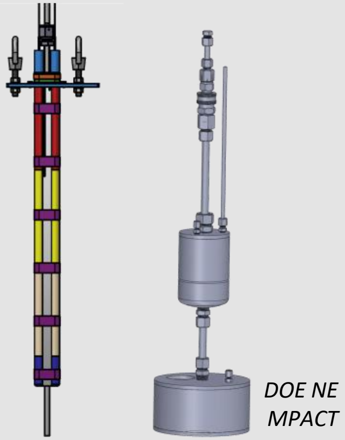
Argonne has demonstrated a variety of monitoring technologies to enable safe operations and material accountancy for nuclear-relevant systems. Deployable sensors for salt composition, redox state, particle concentrations, flow rates, etc. have been created.



Electrochemical Monitoring of Salt Composition

Windowless Optical Monitoring of Composition

Particulate Monitoring

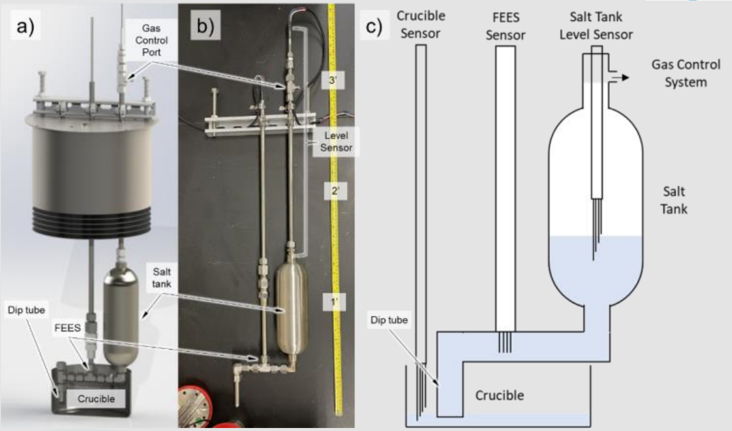


Automated Salt Sampling

Molten Salt Testbeds

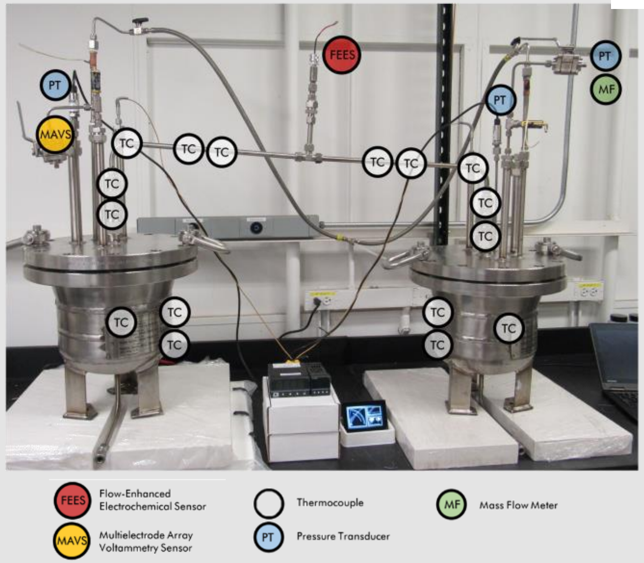
Modular Flow Instrumentation Testbeds (MFIT)

Mini-MFIT for Coolant Salts



- Flow rates: 0.01 to 2.0 L/s
- Salt level sensor for making flow rate determinations.

MFIT for Fuel-Bearing Salts



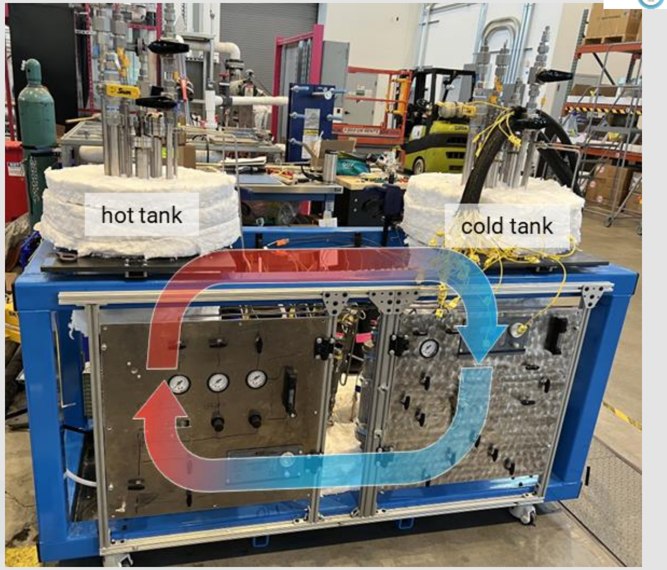
- Flow rates: 1.0 to 10 L/s
- Radiological operations: >13 months of active operations in total

Secondary Effects Loop

- Engineering-scale flow loop with suite of monitoring and control capabilities *(coming online soon…)*

Partnerships with Industry

Kairos STL-03

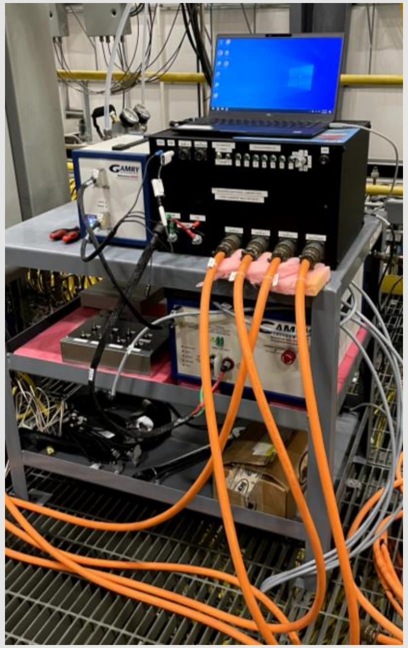


Kairos Power's Engineering-scale flow Salt Test Loop-3 with suite of corrosion monitoring and control tools

Kairos Engineering Test Unit 1

funded by GAIN

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



Kairos Power's Engineering Test Unit 1 and electrochemical sensor instrumentation

Activities for ARSS

Technology Development

- Development of flow-enhanced electro-chemical sensors
- Integration of multimodal monitoring capabilities via ILEX software

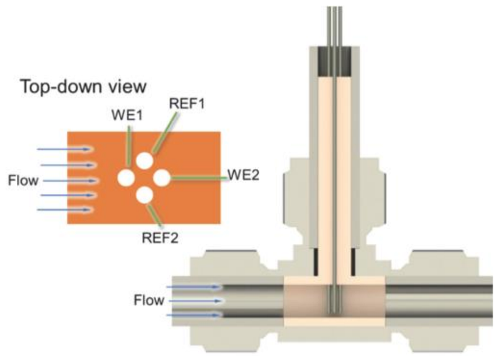
Safeguards Scenarios / MC&A Demonstrations

- Development of modular testbeds for technology and safeguards demos
- Integration of salt purification equipment for end-to-end testing campaign

Deployment to Industrial Partners

- Operation of FEES sensors in FLiBe loop at Kairos
- Planned operations in thermal convection loops at TerraPower

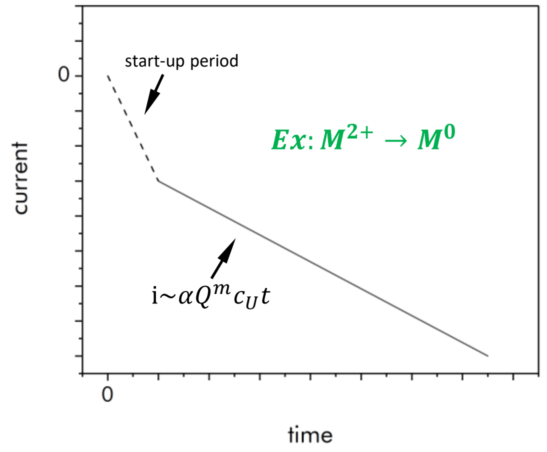
Flow-Enhanced Electrochemical Sensors for Molten Salts



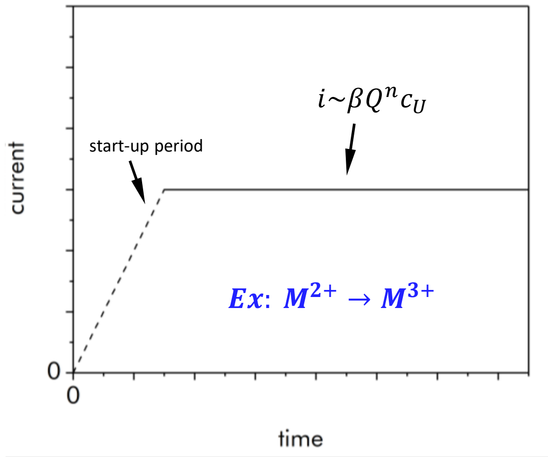
Flow enhanced electrochemical sensor (FEES) design for in-line salt chemistry measurement

In flowing conditions:

- There is competition between the rate of mass transport to an electrode and the electrochemical consumption of the species.
- Applying a constant voltage signal to an electrode results in characteristic current responses for soluble-soluble and soluble-insoluble reactions.



Theoretical linear current response for soluble-insoluble reaction induced by applied negative potential



Theoretical constant current response for soluble-soluble reaction induced by applied positive potential

In-line FEES Operations in Flowing Actinide Salts

The FEES sensor response with respect to flow rate is consistent with the theoretical standard mass transfer correlation (i.e., Sherwood numbers)

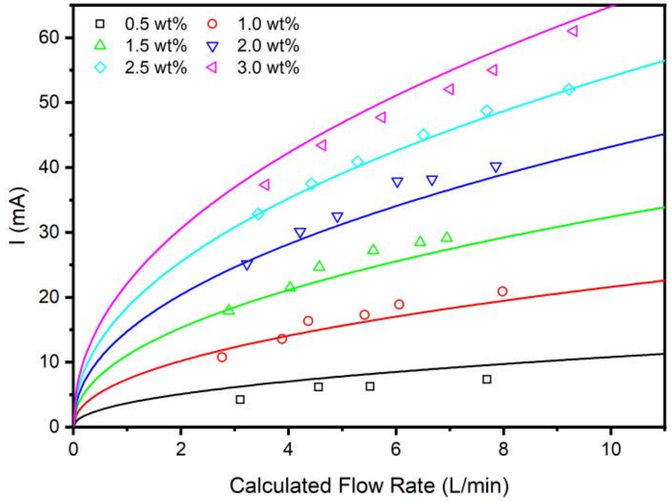
$$Sh = kRe^{m}Sc^{1/3}$$

These Sherwood number correlations allows for accurate concentration measurements.

$$i = \beta Q^{n} \Delta C$$

$$\beta = \frac{(\pi/4)^{1-m} d D_i z F k Sc^{1/3}}{\rho} \left(\frac{\rho}{\mu d_0}\right)^{m}$$

MFIT for fuel-bearing salts (top),
As-received $MgCl_2$-KCl-NaCl (bottom left),
$MgCl_2$-KCl-NaCl with 2.0 wt% UCl_3 (bottom right).



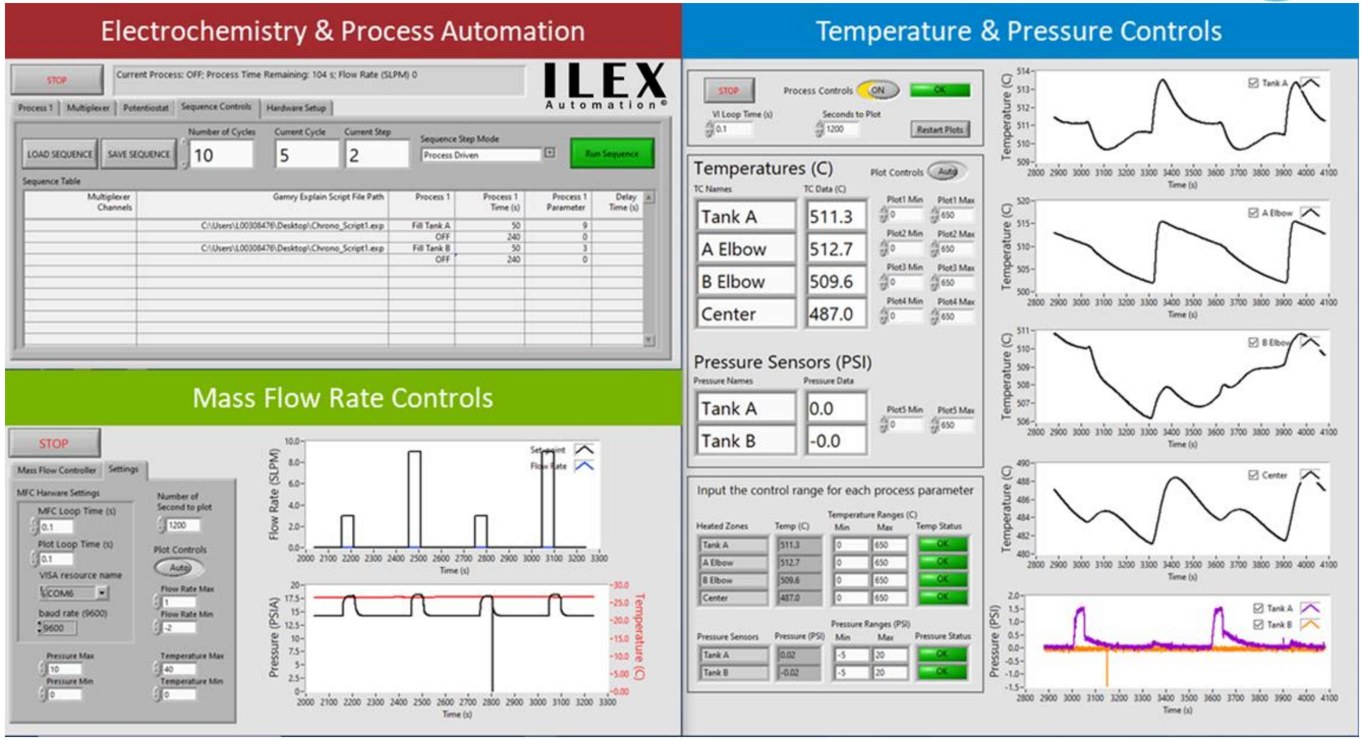
Constant potential measurements at various observed flow rates. Measurements taken at six UCl_3 concentrations (0.5, 1.0, 1.5, , 2.0, 2.5 and 3.0 wt%) in $MgCl_2$-KCl-NaCl at 500 ℃.

Automation of Measurements and Analysis

ILEX Automation© software is a versatile safeguards sensor framework developed to enable complete multi-modal monitoring for molten salt systems.

- Automated salt transfers and sensor data acquisition.
- Real time display of system parameters (T, P, etc.)
- Remote-operation improves safety and accelerates sensor assessments

Software has been deployed at industrial partners to facilitate remote operation of electrochemical sensors.



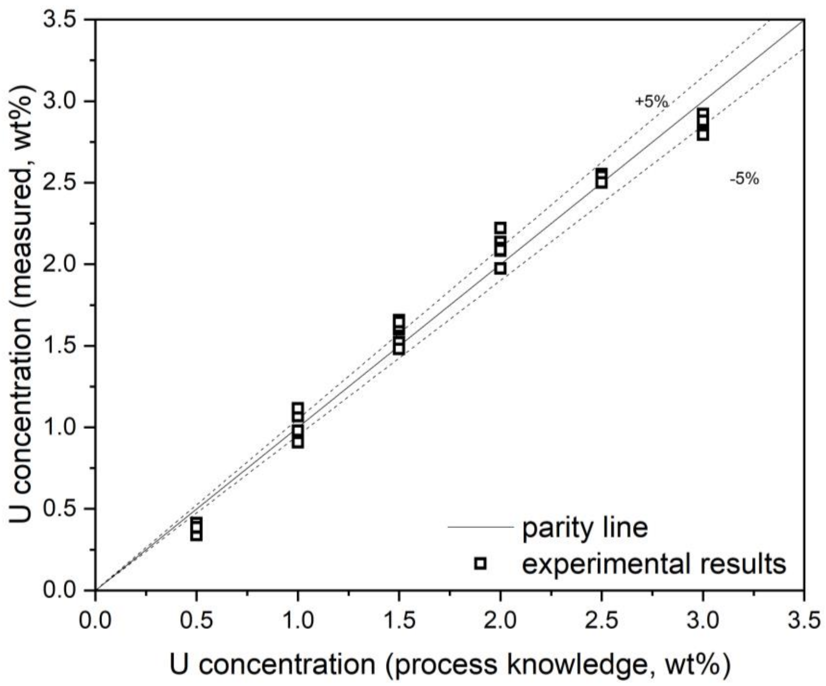
ILEX Automation© software salt level & flow rate sensor digital read out

Actinide Concentration Measurements in Flowing Salt Conditions

With the addition of full automation, uranium concentration measurements have been found to closely follow the expected parity line.

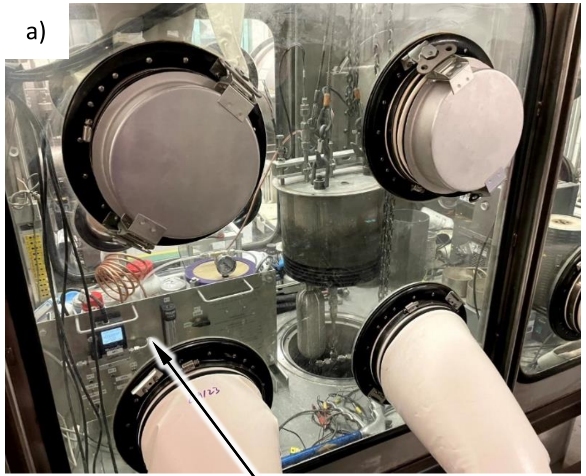
- Mean absolute relative error in measurements was 3.1% with full automation compared to 5.6% without
- Some of the disparity likely resulted from uncertainty in flow rate measurements
- Low concentration measurements likely affected by residual impurities in salt
  - Reaction of impurities leading to UO_2 formation led to underpredictions

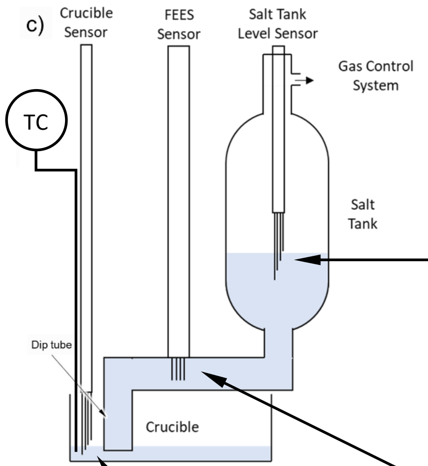
Improved particle quantification and flow rate measurements could improve the results further



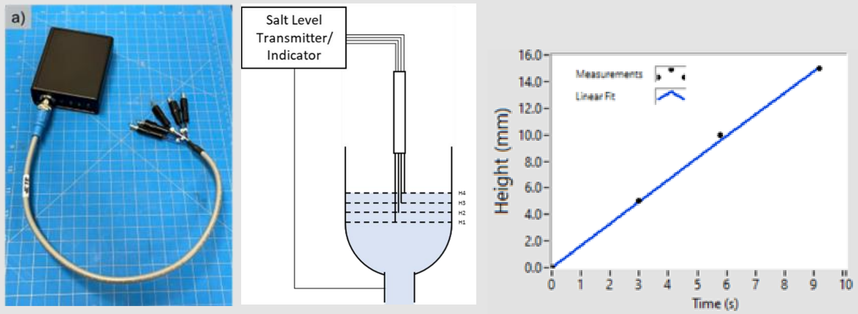
U concentration measured with flow sensor vs. U concentration from process knowledge. Dotted lines are parity ±5%.

Multimodal Monitoring Developments with the Mini-MFIT

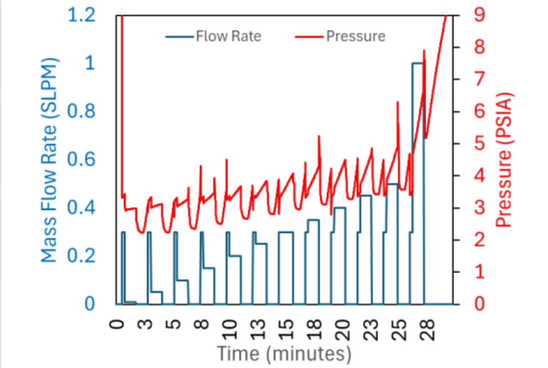




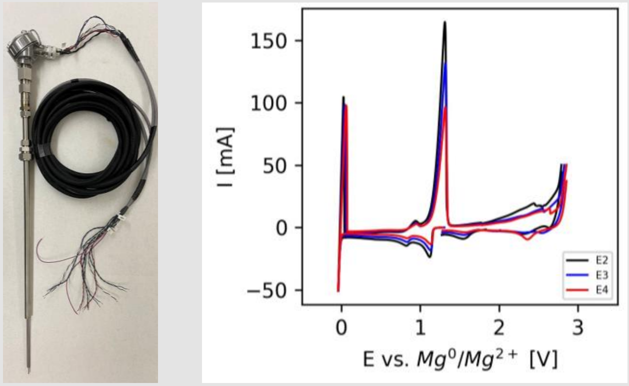
Salt tank level and flow rate sensor



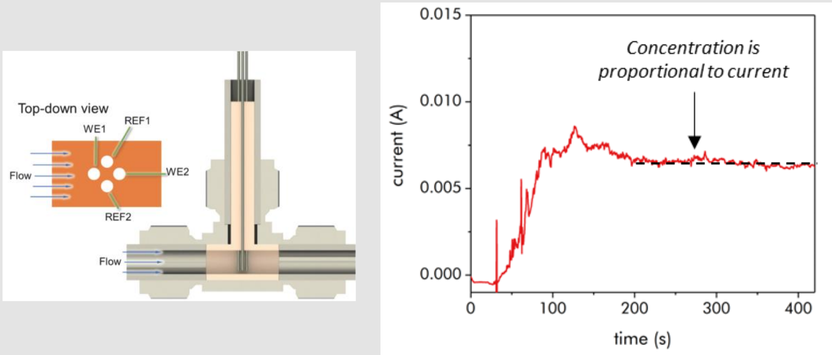
Automated vacuum system for flow control



Stationary salt chemistry measurement

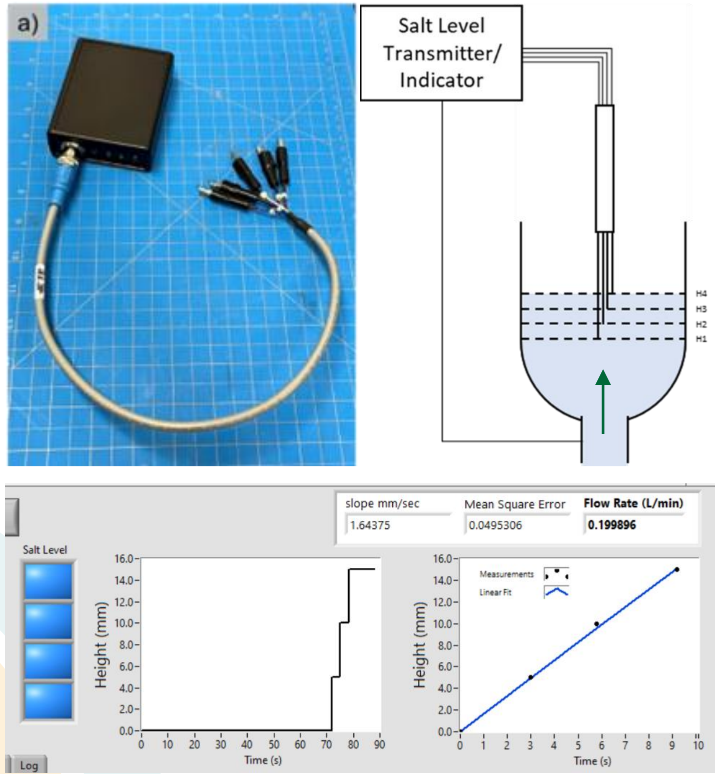


In-line FEES flowing salt chemistry measurements

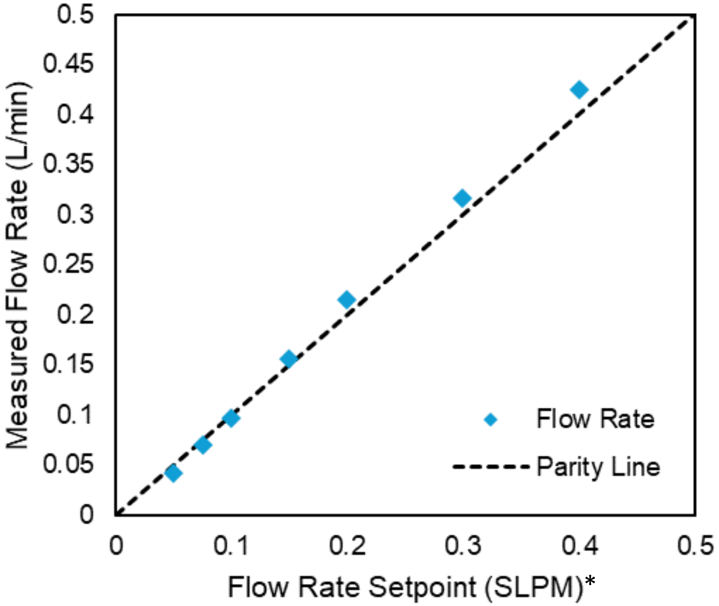


Improved Flow Rate Verification

- The salt tank level sensor records flow rates that are close to the gas control system setpoint albeit with deviations of a few percent.
- Provides improved verification of salt flow rate for FEES sensor development.



Mini-MFIT salt tank level & flow rate sensor



Salt tank level sensor flow rate measurements of NaCl-KCl-$MgCl_2$ at 500 ˚C.

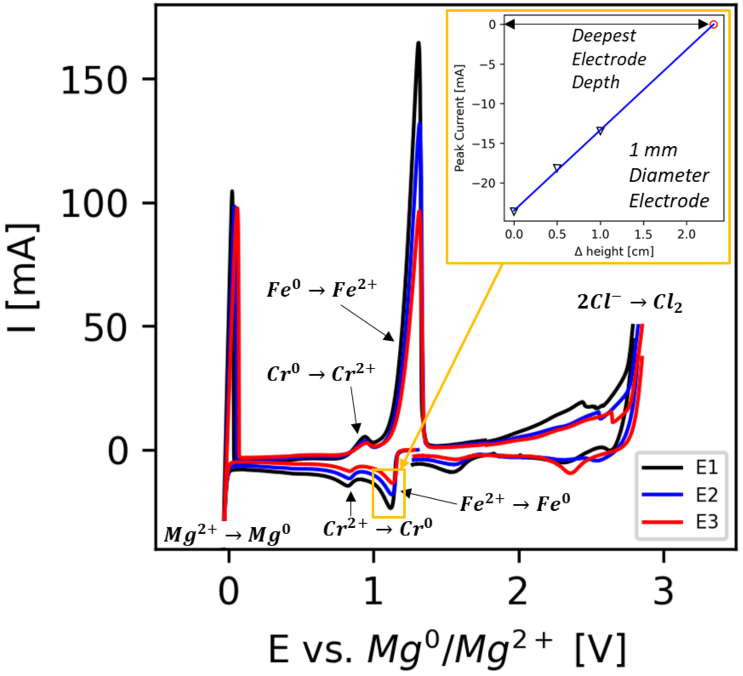
*Standard Liters Per Minute (SLPM)

Mini-MFIT In-line Sensor Measurements in Flowing Salt Conditions

Results are still pending from this FY24 measurement campaign, but we are expecting multimodal approaches to enable further improvements in FEES accuracy.

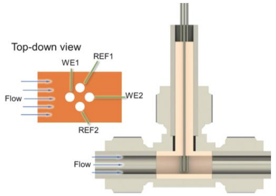
Static In-line Measurements

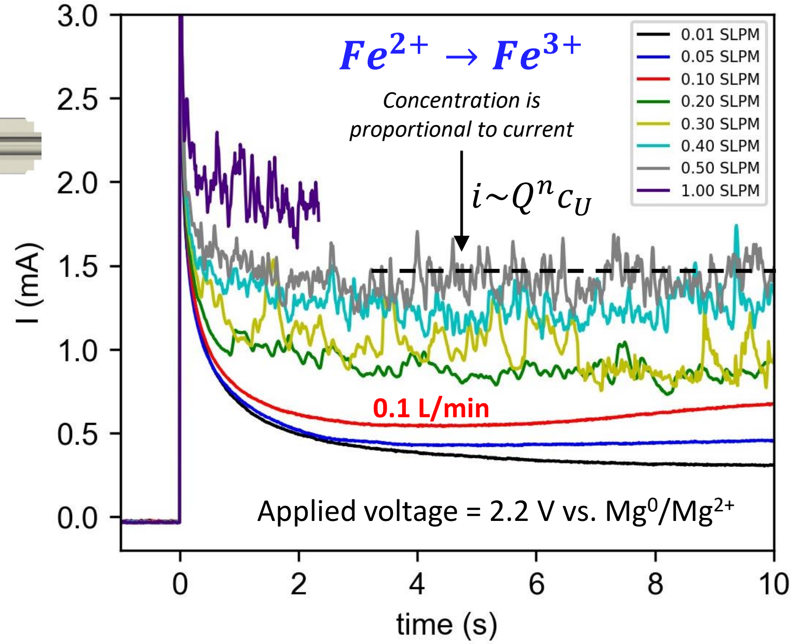
Stationary salt electrochemical sensor



Linear Sweep Voltammogram of stationary NaCl-KCl-$MgCl_2$ with corrosion products at 500 °C.

On-line FEES Measurements



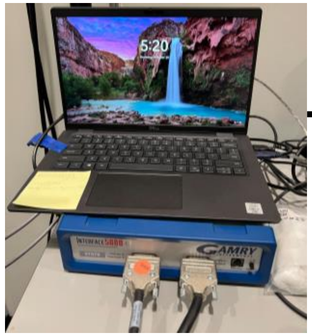


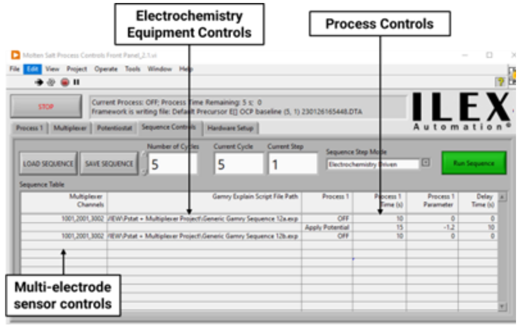
Current response to an oxidizing voltage in flowing NaCl-KCl-$MgCl_2$ with corrosion products at 500 °C.

Deployments to Industrial Partners

This research is partially funded by
DOE Contract No. DE-AC02-06CH11357

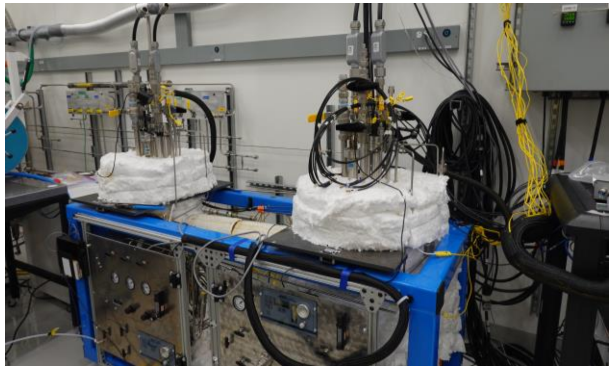
- In-line electrochemical sensors have been deployed in Kairos Power's STL-03
- STL-03 is a forced convection loop containing 15 kg of FLiBe salt
- Argonne has conducted electrochemical measurements utilizing remotely operated instrumentation (potentiostats and custom multiplexer)
- ILEX Automation software enables semi-autonomous control of multiple distributed electrochemical sensors





Electrochemical instrumentation and ILEX Automation© software for remotely operation of STL-03 sensors

ANL's 12-channel Multiplexer



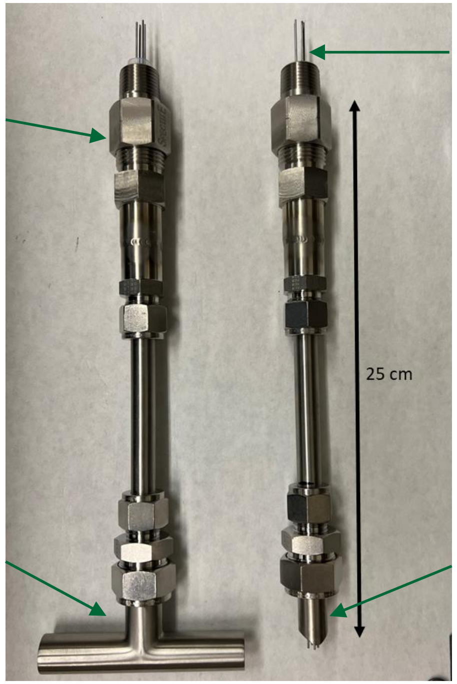
STL-03 Distributed Electrochemical Sensors

Kairos Power S-Lab

Note: Electrochemical monitoring is not explicitly needed for safeguards purposes in Kairos' FHRs as their reactors only use the salt as a coolant

Industrial scale systems engineering challenges for In-line electrochemical sensor design

- The design must be adaptable to the process stream flow path geometry
  - Adaptable to a tube rather than a compression fitting tee
  - Precision welding enables more efficient use of ceramic insulators
  - The machined sensor maintains the internal radius of the process stream
- Seals must be dependable and handle higher pressures
  - < 1×10^{-6} standard cubic centimeters/sec H_2 leak rate at 1 atm
- Sensors must be easy to install and maintain



In-line electrochemical sensors design for the Kairos Power's STL-03 FLiBe experiment.

In-line electrochemical sensors have operated for over 900 hours of salt exposure in the Kairos Power STL-03

The robust sensors endured numerous heating cycles which occurred during initial loop testing

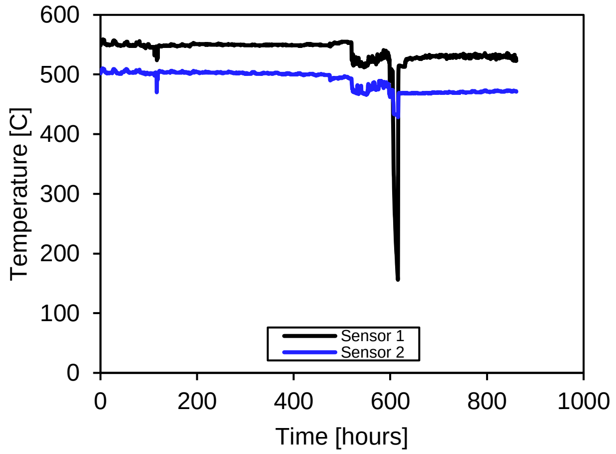
- No leaks or damage to sensors observed

Flow measurements were conducted periodically during steady state loop operation with natural convection and forced flow circulation.

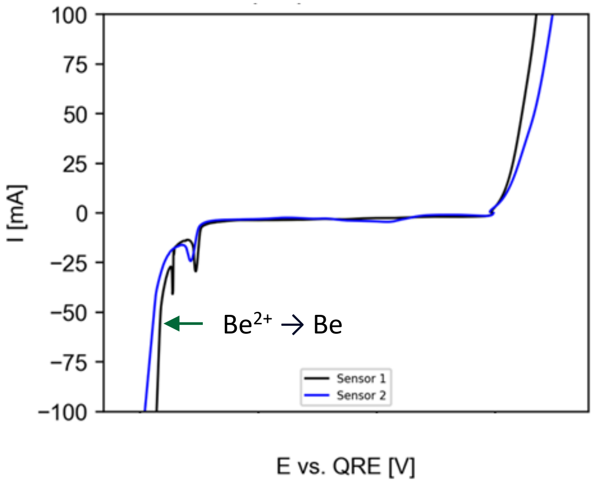
The chemistry of the FLiBe salt was very stable during operations.

- Minimal changes to salt redox potential and dissolved metal ion concentrations

Results from the in-line sensors were consistent with other sensors installed in the STL-03.



Temperatures near the in-line electrochemical sensors



In-line electrochemical sensor voltammetry measurements of circulating FLiBe salt.

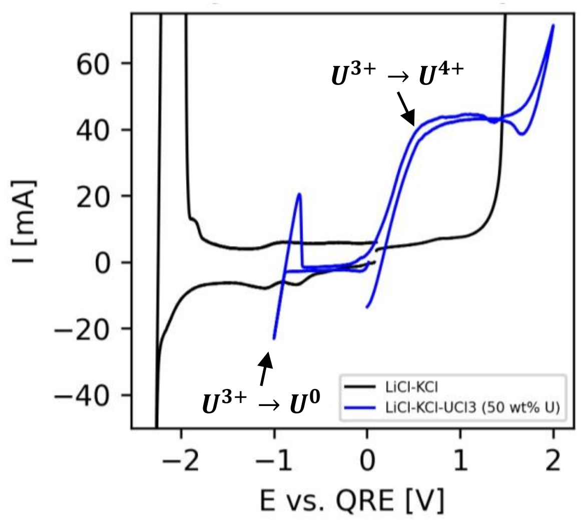
Forthcoming FY24 Activities

Objective 1 – Test and optimize electrochemical sensors in very high-concentration salts that are encountered in molten salt reactors.

a. Completion of updates to enable sensor operations at the very high actinide concentrations.

b. Measurements in very high-concentration flowing salts

c. Large-batch synthesis run for UCl_3-based fuel salt including integrated monitoring



Preliminary studies of high-concentration salt containing 50 wt% U

Objective 2 – Continue sensor deployment activities in collaboration with partner institutions.

a. Ongoing experimentation at Kairos Power, LLC

b. Deployment of sensors at Terra Power, LLC

ANL plans to deploy echem sensors to TerraPower molten salt loops
(pending completion of legal paperwork)

Conclusions

- In-line flow enhanced electrochemical sensors have been investigated in fuel-bearing and non-fuel-bearing salts over a range of salt flow conditions.
  - Full automation led to improved results in FY23
  - For FY24 we are pursuing multimodal approaches to improve results further
- In-line sensors have successfully operated in Kairos Power's STL-03 for over 900 hours of salt exposure
  - Deployments to other partners are planned for FY24
- Additional safeguards scenarios will be tested this year as additional multimodal and high-concentration monitoring capabilities come online