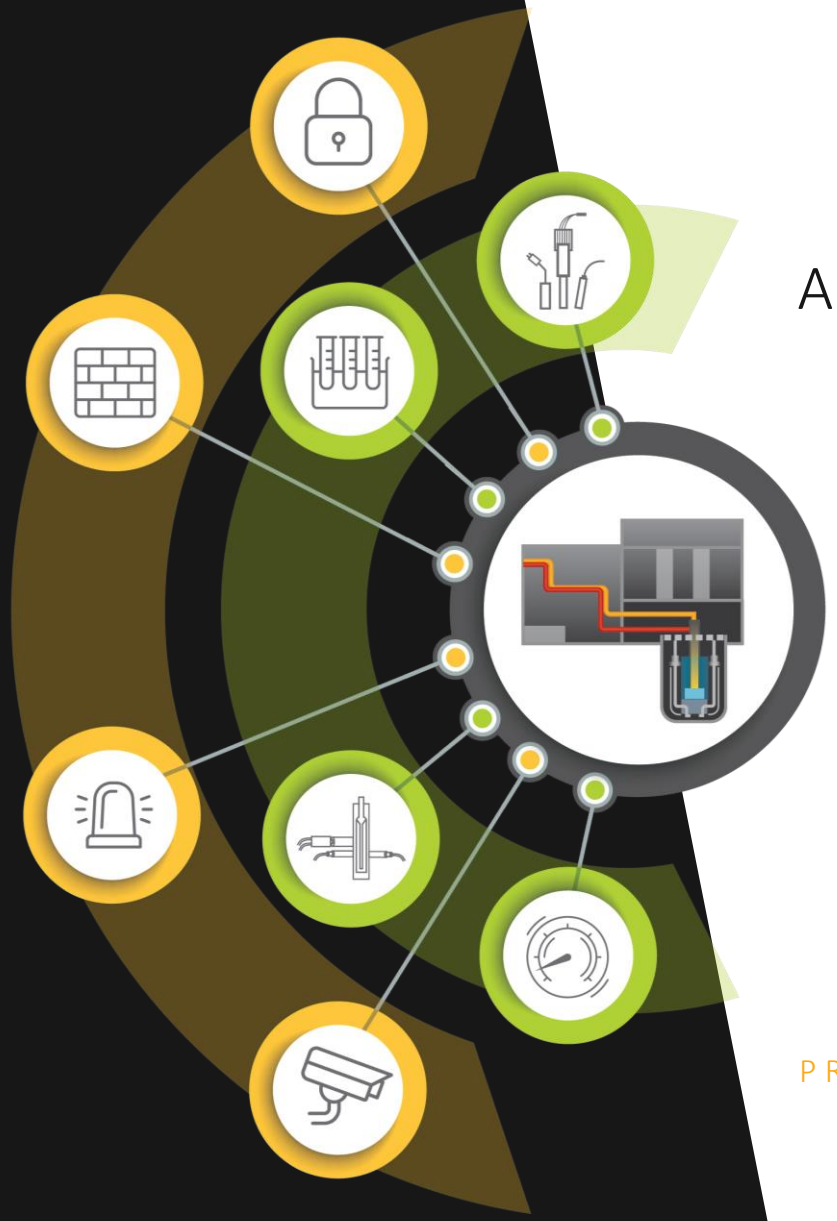

ADVANCED REACTOR SAFEGUARDS

Flow Enhanced Electrochemical Sensors for Molten Salt Reactors

PRESENTED BY

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Argonne NATIONAL LABORATORY

U.S. DEPARTMENT OF ENERGY

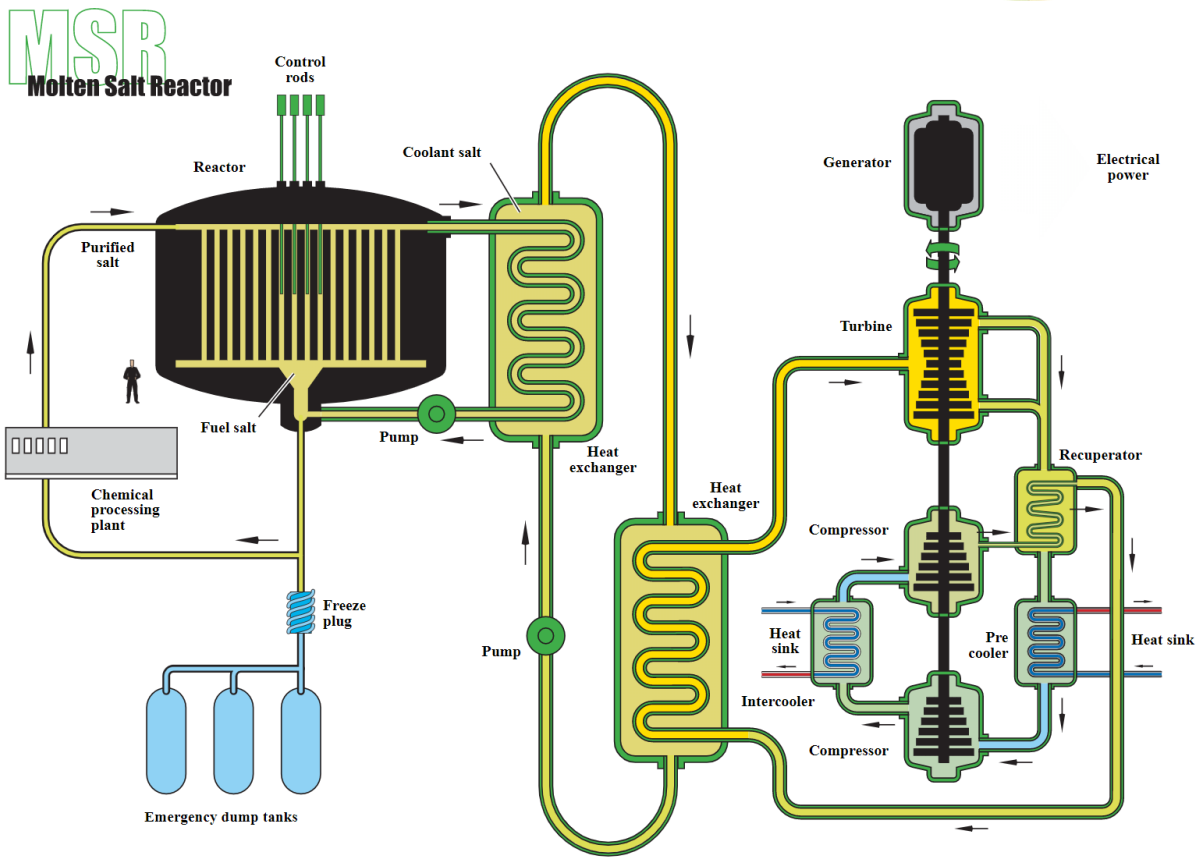
Introduction

Safeguards and Process Monitoring for MSRs

The dissolved actinides within fuel salts make MSRs a challenge for safeguards

- High temperatures and corrosive salts make it difficult to design sensors with sufficient longevity, stability, and accuracy
- Simple flush-out accountancy is difficult to implement
- Actinides may be present in a variety of chemical/oxidation states (e.g. UF_3, UF_4)
- Fission products and corrosion products may plate out in various regions of the loop

The ultimate goal of this project is to provide MSR vendors the sensors needed to meet broad NRC licensing challenges for materials accountancy, criticality safety, and corrosion monitoring.



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

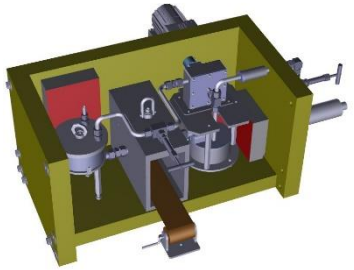
Introduction

Monitoring and Control of Molten Salt Systems

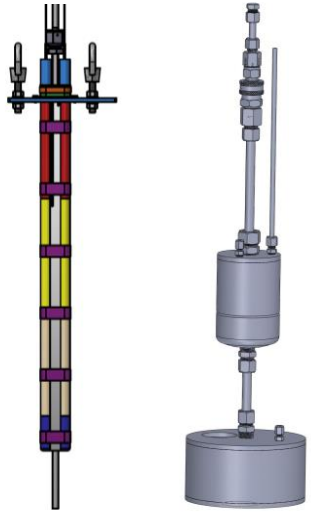
Argonne has demonstrated monitoring for a variety of molten salt equipment including thermal convection loops, salt purification equipment, and process vessels. Deployable sensors for composition, redox state, particle concentrations, etc. have been created.

Electrochemical Monitoring of Salt Composition[1]

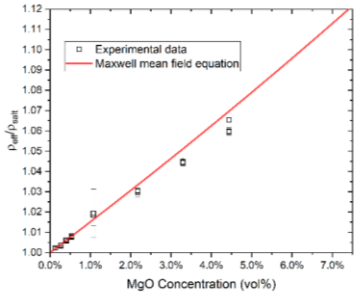
Windowless Optical Monitoring of Salt Composition[2]

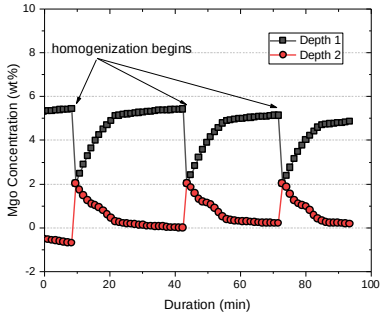


Automated Salt Sampling[2]



Monitoring of Precipitated Particles[3]





[1]$MgCl_2$-KCl-NaCl thermal convection loop run at ORNL (Bruce Pint)
[2]Funded by DOE NE MPACT [3]Funded by EERE-SETO

Electrochemical Sensors for Flowing Systems

Standard electrochemical sensors need to be installed in quiescent regions or use shrouds

- Unwanted flow velocities around the electrodes can distort the measurements

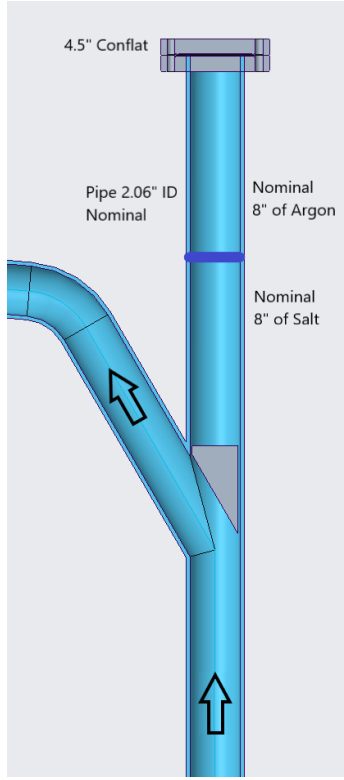
Hydrodynamic electrochemical sensors can be installed directly in the flow

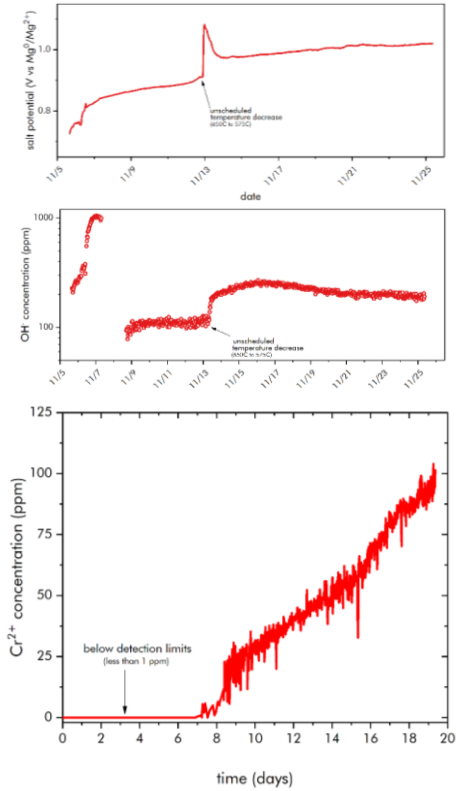
- Requires control/knowledge of the flowstream

Direct insertion into the flow has a number of advantages

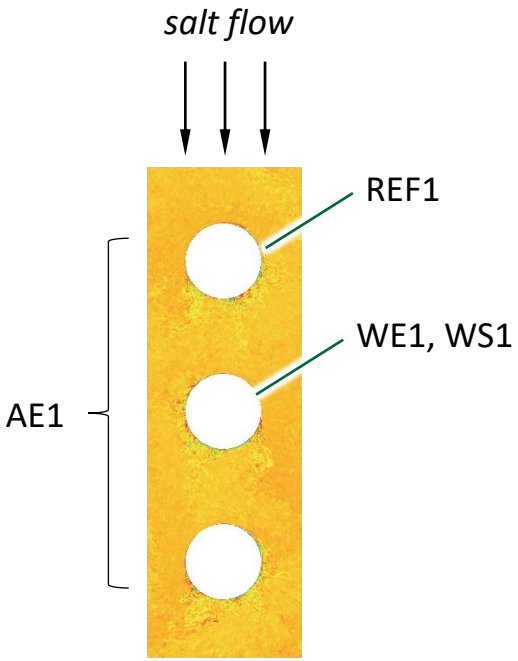
- Faster response
- Smaller footprint
- No headspace required

Traditional Installation Location and Typical Results





Direct Insertion into Flow

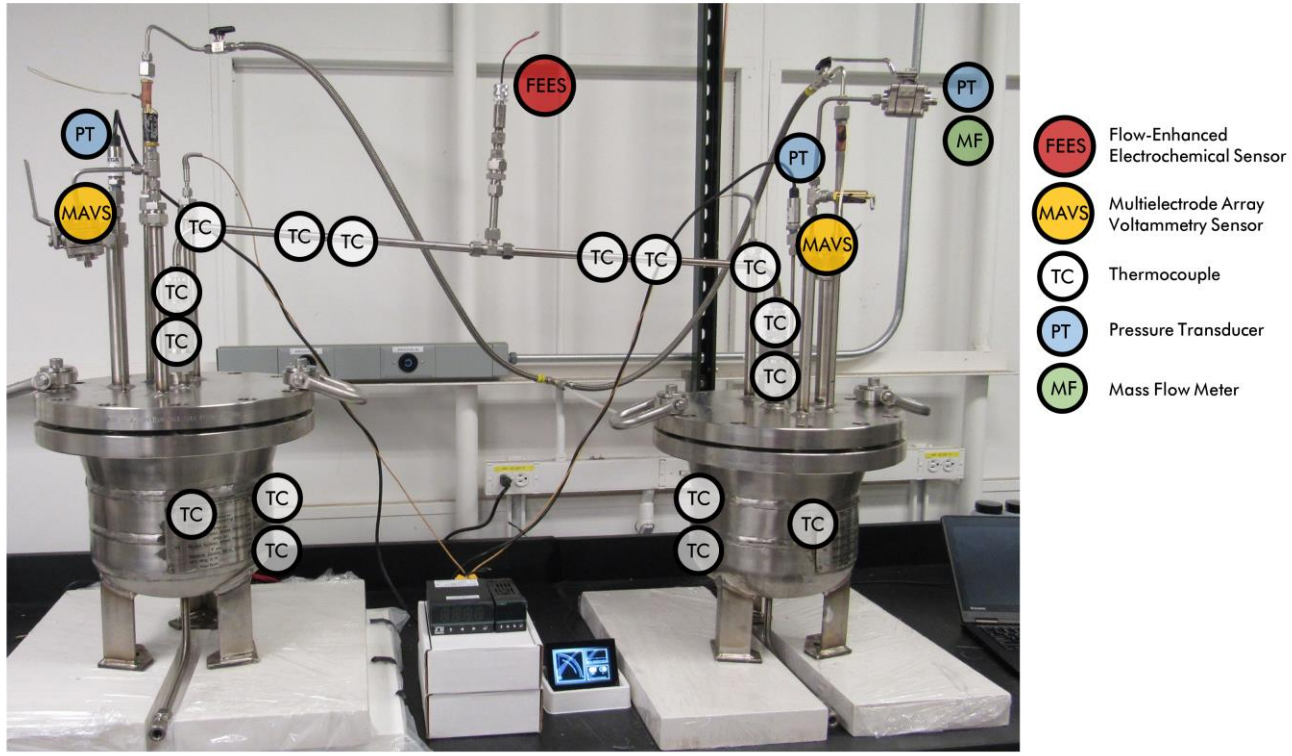


[1]Tee-junction figure courtesy Kevin Robb (ORNL)

Modular Flow Instrumentation Testbed (MFIT)

A modular instrumentation testbed has been created in order to operate and assess the flow enhanced electrochemical sensors

- Enables rapid assessment of new sensor designs
- Supports radiological and non-radiological salts
- Supports a wide variety of instrumentation
- Allows system disassembly without complete shutdown
- Permits rapid salt changes (chlorides, fluorides)
- Wide range of flow rates and transfer line sizes to achieve conditions representative of bypass lines, sampling lines, and flow conduits



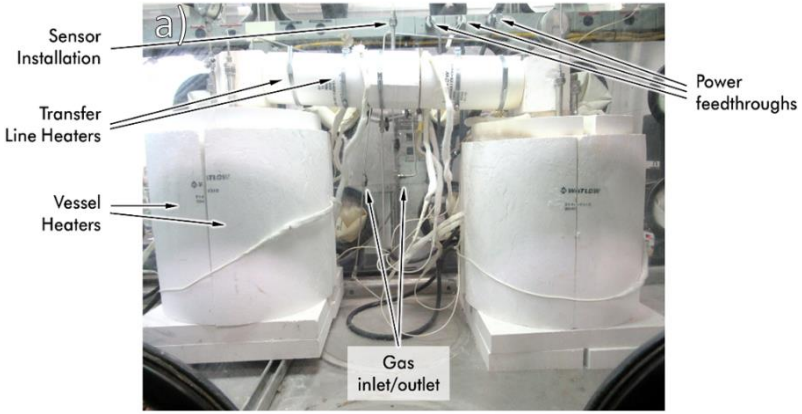
Modular Flow Instrumentation Testbed (MFIT)

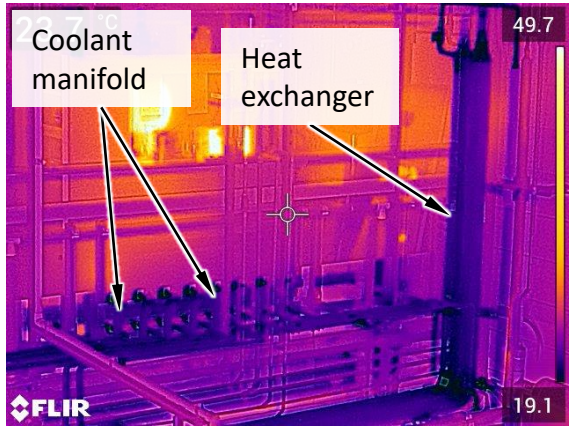
The MFIT was brought online in September 2021.

Installation within a glovebox required extensive modifications

- Cooling system to address thermal load
- New electrical system to support furnaces

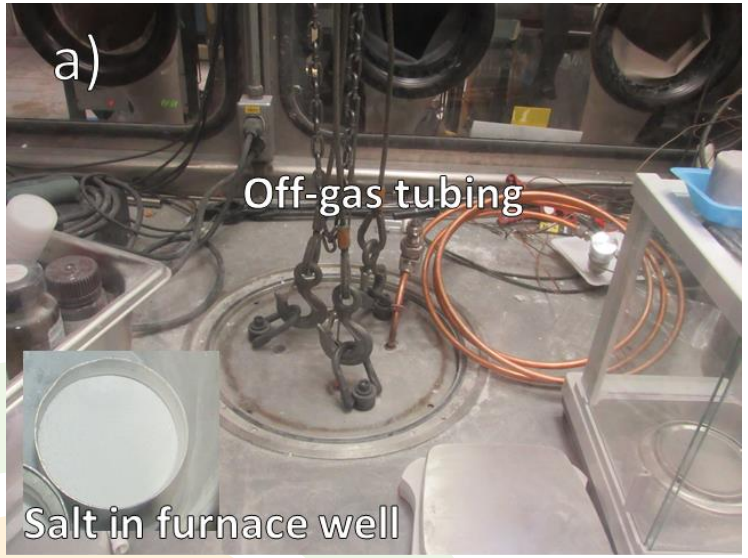
Since being brought online, the system has been used extensively to performed hundreds of salt transfer tests using radiological and non-radiological salts.

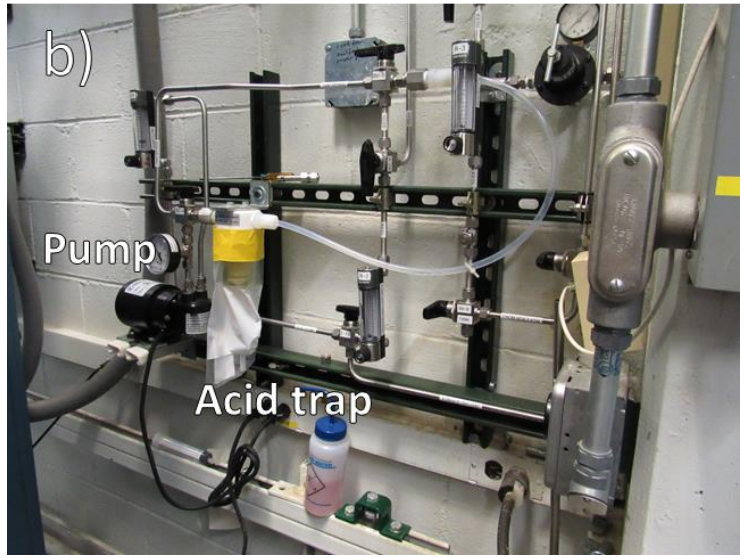




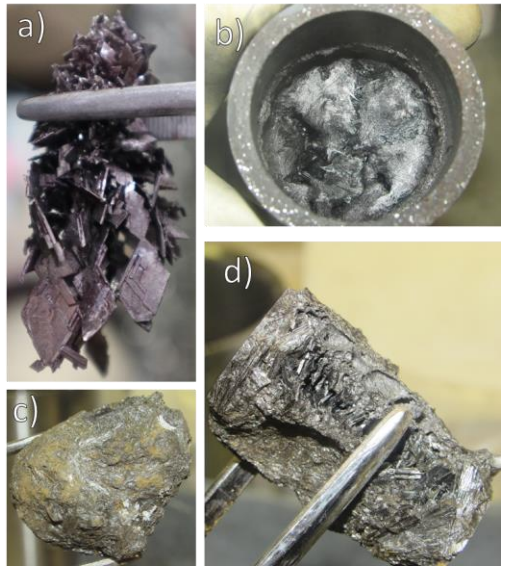
Salt Production and Purification

Large quantities of MSR-relevant fuel salt has been created for operations of the flow system. The purification process involves reactive metal contacting, filtration, liquid metal contacting, and distillation.





Salt purification system (left) and off-gas system (right) used for $MgCl_2$-KCl-NaCl-UCl_3 production

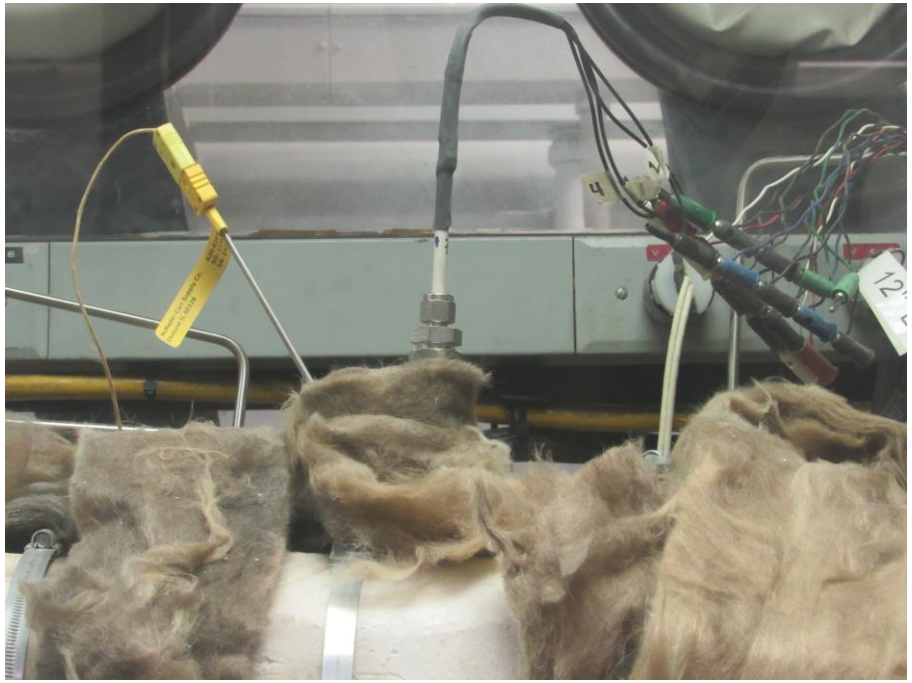


Synthesis steps for $MgCl_2$-KCl-NaCl-UCl_3

Salt Loading and Sensor Operations

The MFIT is typically operated with 5-10 kg of salt. Flow rates range from 0.25 to 5.0 L/min — resulting in transfers lasting ~10 seconds up to several minutes.

Salt loading operation

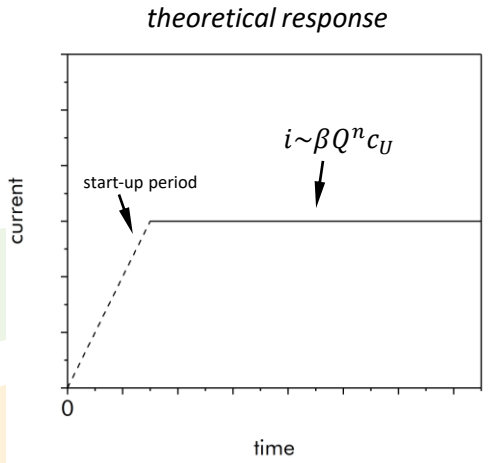


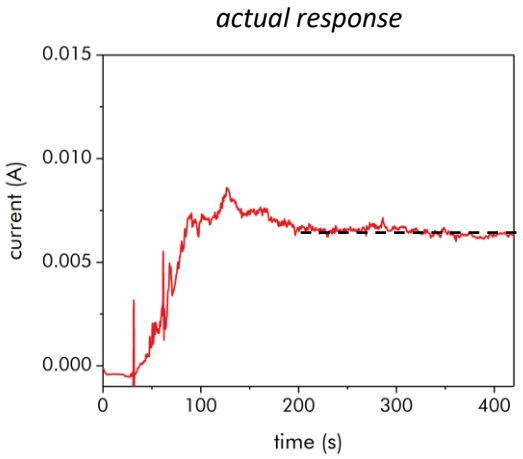
Installed flow-enhanced electrochemical sensor

Sensor Response Under Flow Conditions

By applying positive potentials, soluble-soluble reactions such as $Cr^{2+} \rightarrow Cr^{3+} + e^-$ and $U^{3+} \rightarrow U^{4+} + e^-$ be induced at the electrode surface. By applying negative potentials, soluble-insoluble reactions can be induced instead. The trend of the current response differs accordingly.

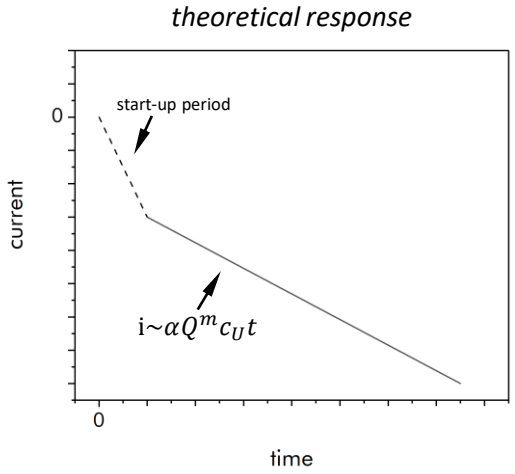
Soluble-soluble reaction

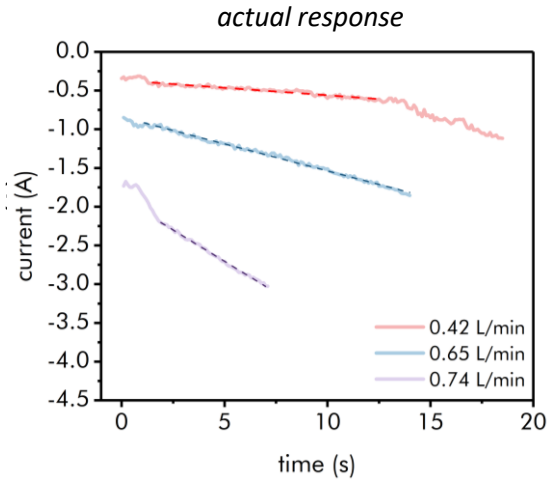




Current response for soluble-soluble reaction

Soluble-insoluble reaction

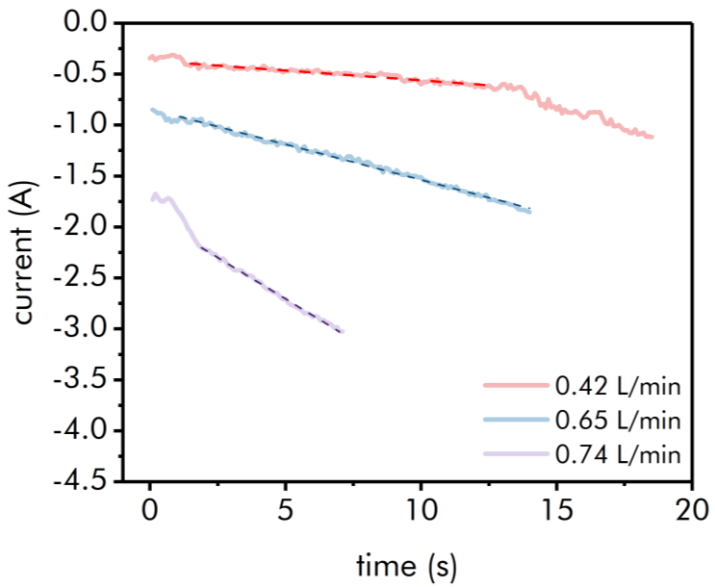




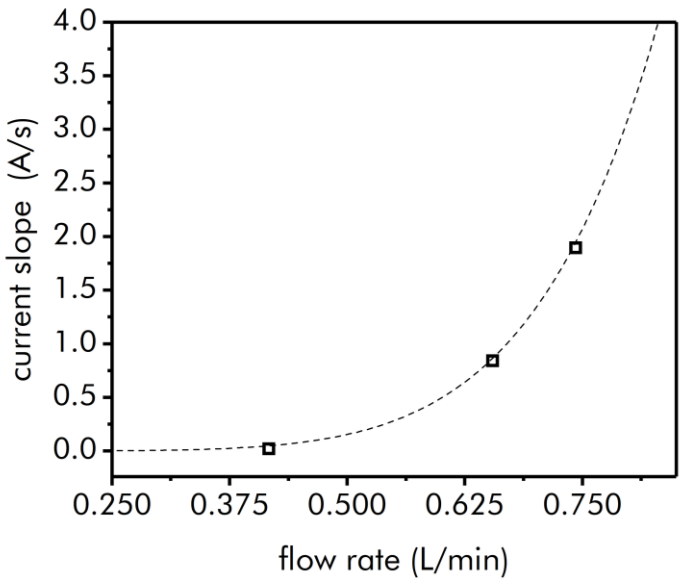
Current response for soluble-insoluble (deposition) reaction

Performance for Soluble-Insoluble Operations

The current response for soluble-insoluble operations followed expected trends for flow rate dependence, and the sensor's Sherwood number parameters could be extracted.



Steady state Cr^{2+} reduction current from potentiostatic hold during hydrodynamic conditions at different flow rates



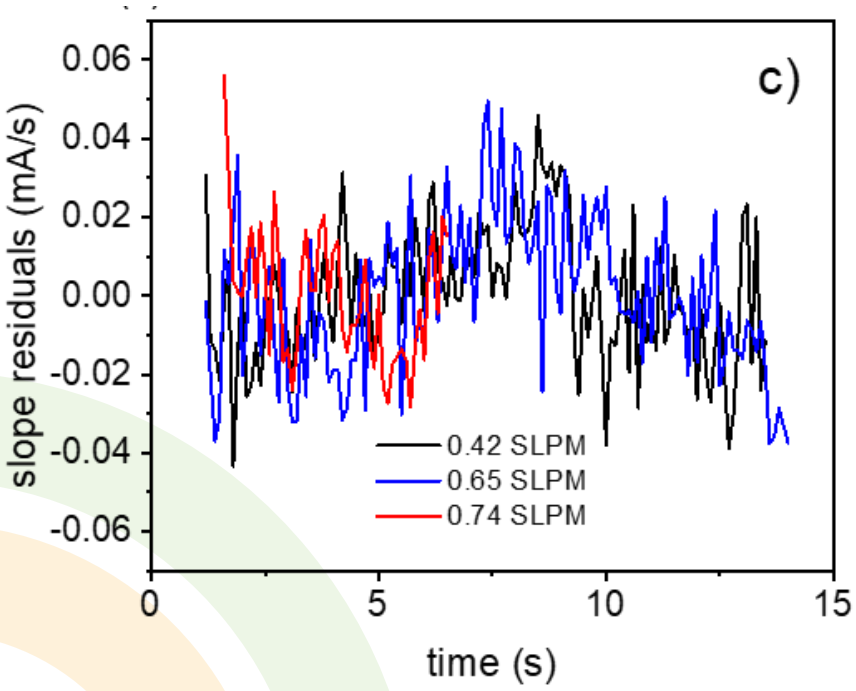
Reduction current slope vs. salt flowrate

Sherwood Number Parameter	FEES Correlation
k	3.12×10^{-14}
m	3.07

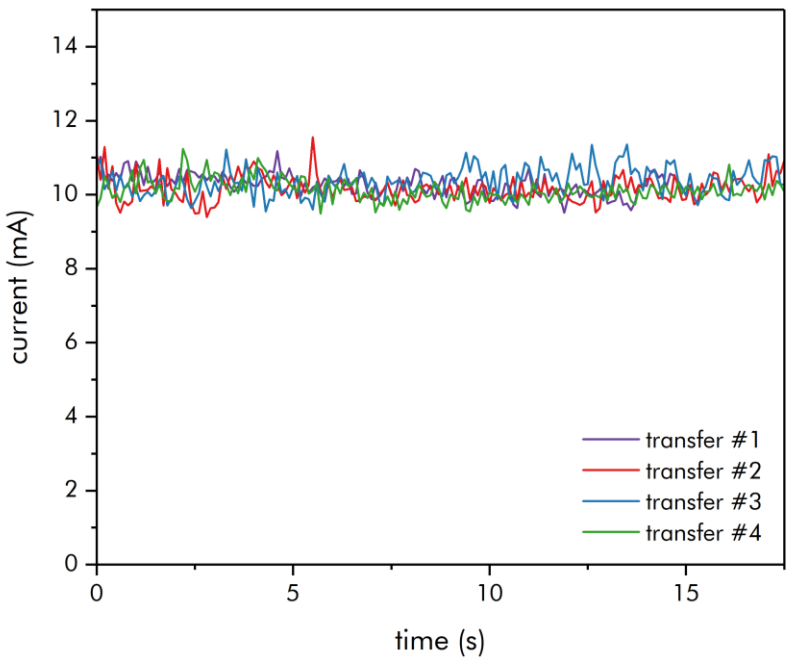
$$\left.\frac{di}{dt}\right|_{initial} = k^2\left(\frac{\pi mzFh}{M}\right)\left(\frac{DSc^{1/3}\Delta C}{d_0}\right)^2\left(\frac{\rho_{salt}d_0U}{\mu_{salt}}\right)^m$$

Statistical Assessment

Preliminary statistical assessments have been performed for the sensors under flowing conditions for soluble-soluble and soluble-insoluble reactions.



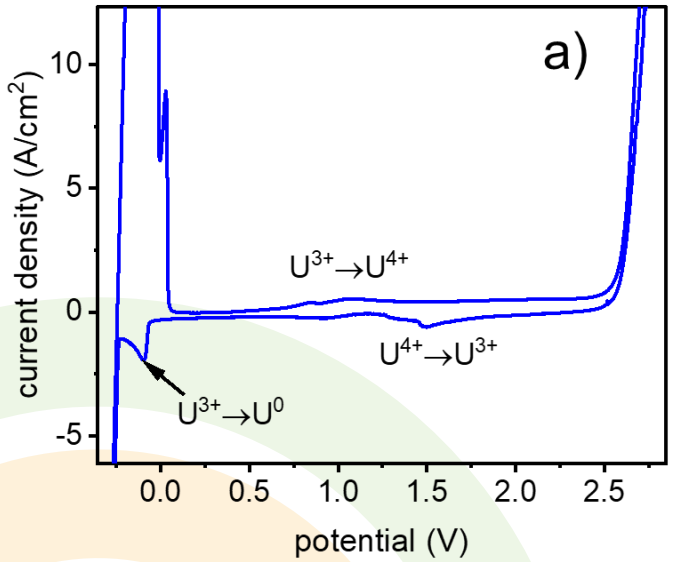
Residuals from linear fit to soluble-insoluble current responses



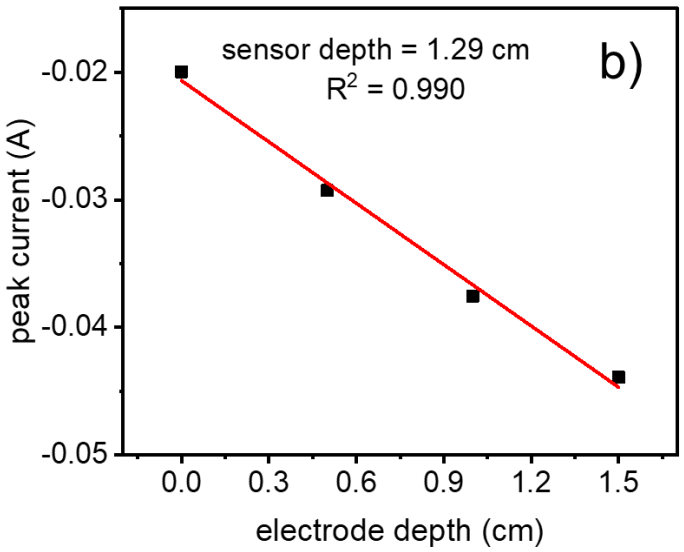
Soluble-soluble current response for repeated transfers ($MgCl_2$-KCl-NaCl-UCl_3)

Multimodal Sensors / Data Fusion

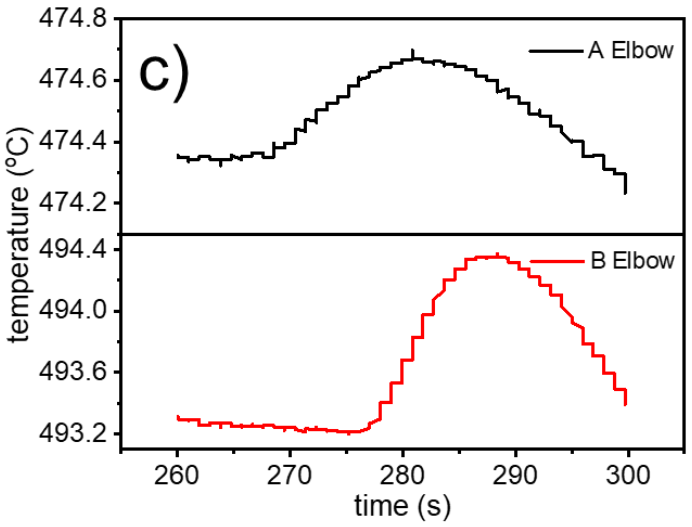
Concentration measurements from the tank sensors can be used to cross check values from the transfer line sensor. Combined data from other sensors installed in the MFIT can also be used to improve measurements.



Cyclic voltammogram of UCl_3 in $MgCl_2$-KCl-NaCl salt at 500 mV/s



UCl_3 peak height vs. electrode depth used to calculate the sensor depth in the salt



Cross correlation of thermocouple signals can be used to cross-check volume flow measurements

Conclusions

- The Modular Flow Instrumentation Testbed is operational and enabling development of the flow-enhanced electrochemical sensors
- The electrochemical sensor response is consistent with theoretical trends
- Testing with additional safeguards relevant sensors is underway to enable measurement cross-checks, validation, and eventual sensor fusion
- Additional sensor design and testing work will continue throughout FY22, culminating in a full assessment of sensor performance using MSR-relevant radiological salts

Future Work

FY22 Goals

- Complete sensor testing with radiological salts
- Assess performance of the flow-enhanced sensors with respect to mass accountancy requirements
- Perform cross-checking using sensors installed in the MFIT tanks

M2 Milestone

- **Description:** A test campaign will be conducted to provide a complete assessment of the sensors' ability to meet NMAC requirements for molten salt reactors
- **Deliverable Title:** Feasibility Assessment of the Flow-Enhanced Sensors for Actinide Quantification in MSRs
- **Due:** 9/30/2022

Acknowledgements

Thanks to:

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Stefan Tosic