APT #186238

ADVANCED REACTOR SAFEGUARDS

Flow-Enhanced In-Line Sensors for MSR Mass Accountancy

Assessment of Actinide Quantification Capabilities

PRESENTED BY

Colin E. Moore, William H. Doniger and Nathaniel C. Hoyt

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Sandia National Laboratories

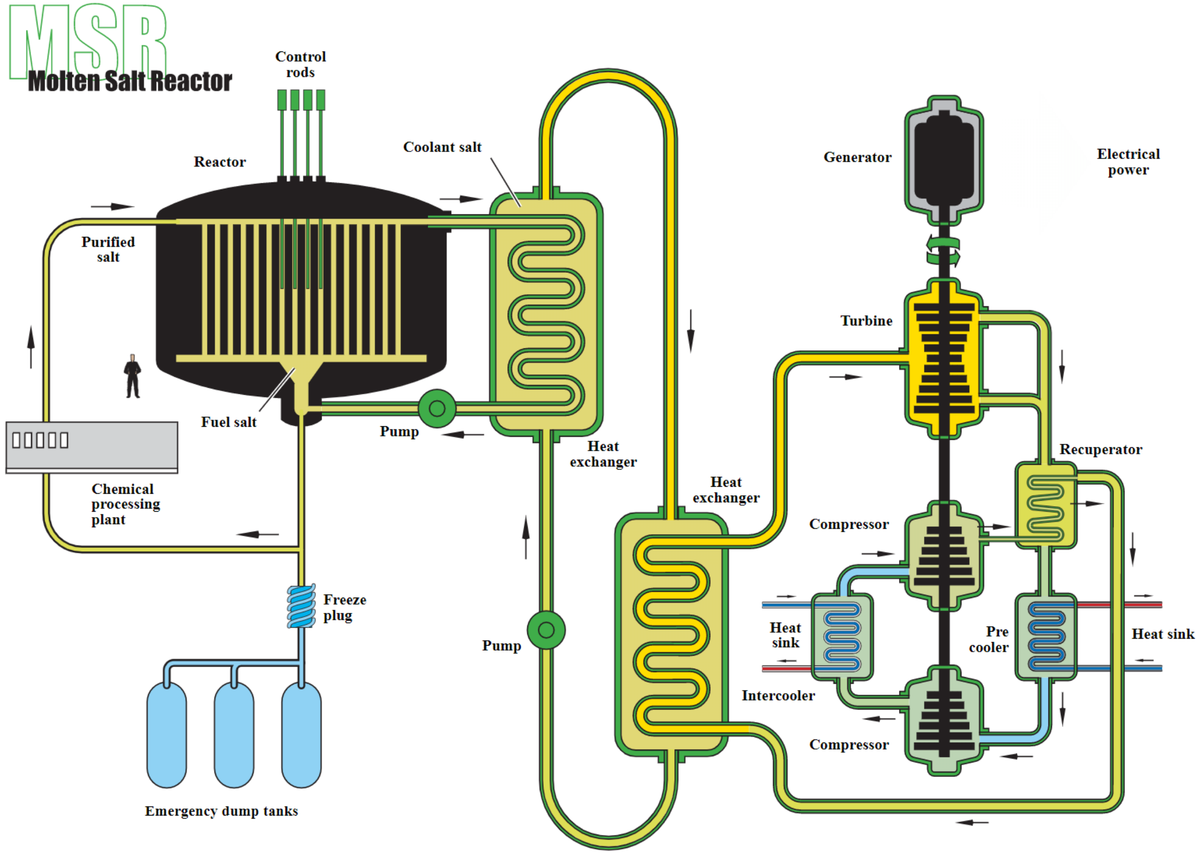
U.S. DEPARTMENT OF ENERGY

Safeguards and Process Monitoring for Molten Salt Reactors

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
- Rapid detection of concentration or salt level changes needed to identify diversion
- Operator readable sensor output necessary to detect anomalies

The goal of the Advanced Reactor Safeguards 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

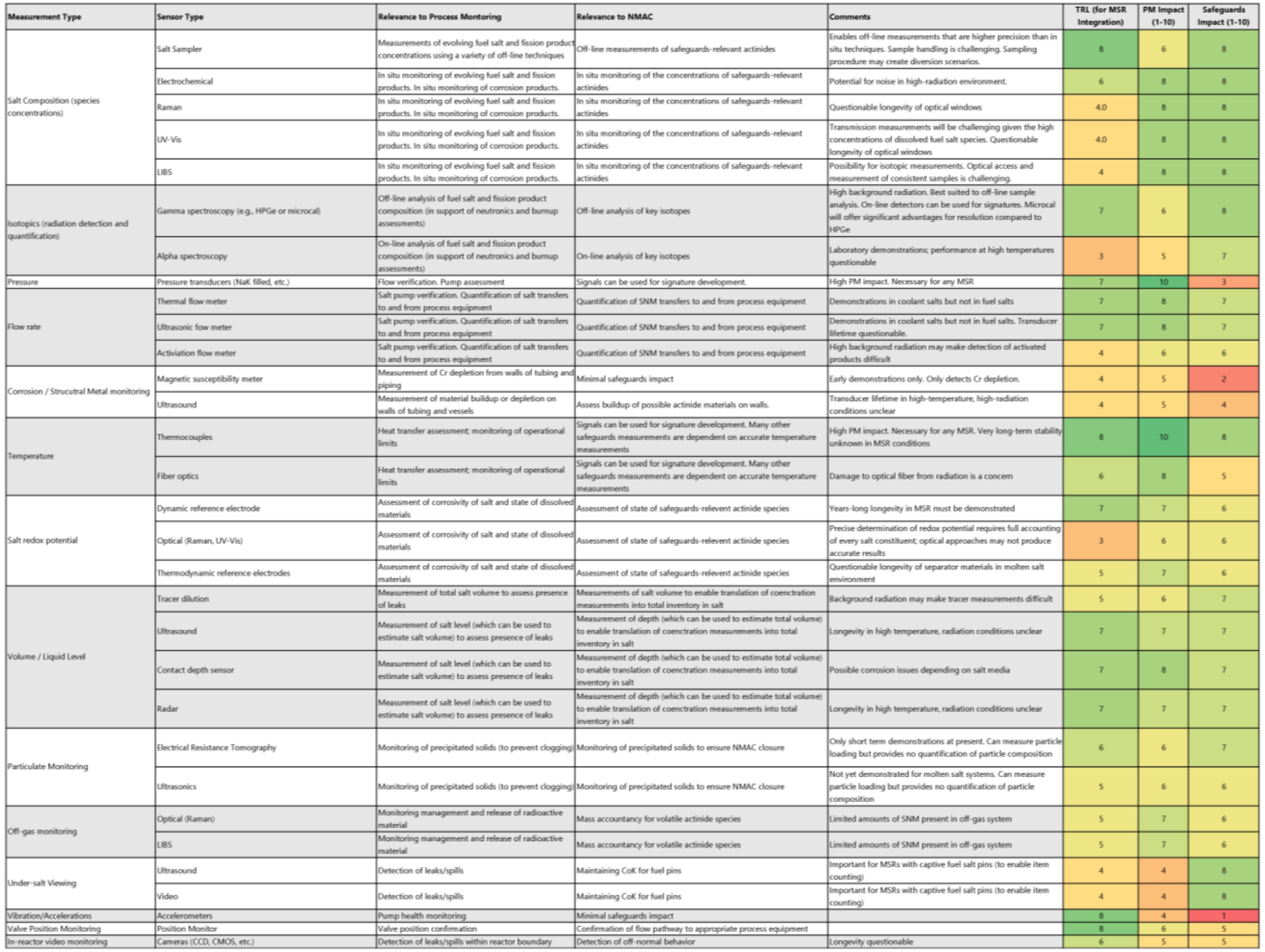
We have assessed MSR-relevant process monitoring and safeguards sensors to understand their technical maturity and potential for impact.

Examples of relevant measurements include:

- Salt composition
- Isotopics
- Salt volume
- Flow rates
- Redox state
- Particulates
- Off-gas
- etc.

Many crucial sensors are still at an insufficient technology readiness level to permit installation in an MSR

MSR Process Monitoring and Safeguards Instrumentation Assessment Sheet



Measurement Type	Sensor Type	Relevance to Process Montoring	Relevance to NMAC	Comments	TRL (for MSR Integration)	PM Impact (1-10)	Safeguards Impact (1-10)
Salt Composition (species concentrations)	Salt Sampler	Measurements of evolving fuel salt and fission product concentrations using a variety of off-line techniques	Off-line measurements of safeguards-relevant actinides	Enables off-line measurements that are higher precision than in situ techniques. Sample handling is challenging. Sampling procedure may create diversion scenarios.	8	6	8
	Electrochemical	In situ monitoring of evolving fuel salt and fission products. In situ monitoring of corrosion products.	In situ monitoring of the concentrations of safeguards-relevant actinides	Potential for noise in high-radiation environment.	6	8	8
	Raman	In situ monitoring of evolving fuel salt and fission products. In situ monitoring of corrosion products.	In situ monitoring of the concentrations of safeguards-relevant actinides	Questionable longevity of optical windows	4.0	8	8
	UV-Vis	In situ monitoring of evolving fuel salt and fission products. In situ monitoring of corrosion products.	In situ monitoring of the concentrations of safeguards-relevant actinides	Transmission measurements will be challenging given the high concentrations of dissolved fuel salt species. Questionable longevity of optical windows	4.0	8	8
	LIBS	In situ monitoring of evolving fuel salt and fission products. In situ monitoring of corrosion products.	In situ monitoring of the concentrations of safeguards-relevant actinides	Possibility for isotopic measurements. Optical access and measurement of consistent samples is challenging.	4	8	8
Isotopics (radiation detection and quantification)	Gamma spectroscopy (e.g., HPGe or microcal)	Off-line analysis of fuel salt and fission product composition (in support of neutronics and burnup assessments)	Off-line analysis of key isotopes	High background radiation. Best suited to off-line sample analysis. On-line detectors can be used for signatures. Microcal will offer significant advantages for resolution compared to HPGe	7	6	8
	Alpha spectroscopy	On-line analysis of fuel salt and fission product composition (in support of neutronics and burnup assessments)	On-line analysis of key isotopes	Laboratory demonstrations; performance at high temperatures questionable	3	5	7
Pressure	Pressure transducers (NaK filled, etc.)	Flow verification. Pump assessment	Signals can be used for signature development.	High PM impact. Necessary for any MSR	7	10	3
Flow rate	Thermal flow meter	Salt pump verification. Quantification of salt transfers to and from process equipment	Quantification of SNM transfers to and from process equipment	Demonstrations in coolant salts but not in fuel salts	7	8	7
	Ultrasonic fow meter	Salt pump verification. Quantification of salt transfers to and from process equipment	Quantification of SNM transfers to and from process equipment	Demonstrations in coolant salts but not in fuel salts. Transducer lifetime questionable.	7	8	7
	Activiation flow meter	Salt pump verification. Quantification of salt transfers to and from process equipment	Quantification of SNM transfers to and from process equipment	High background radiation may make detection of activated products difficult	4	6	6
Corrosion / Strucutral Metal monitoring	Magnetic susceptibility meter	Measurement of Cr depletion from walls of tubing and piping	Minimal safeguards impact	Early demonstrations only. Only detects Cr depletion.	4	5	2
	Ultrasound	Measurement of material buildup or depletion on walls of tubing and vessels	Assess buildup of possible actinide materials on walls.	Transducer lifetime in high-temperature, high-radiation conditions unclear	4	5	4
Temperature	Thermocouples	Heat transfer assessment; monitoring of operational limits	Signals can be used for signature development. Many other safeguards measurements are dependent on accurate temperature measurements	High PM impact. Necessary for any MSR. Very long-term stability unknown in MSR conditions	8	10	8
	Fiber optics	Heat transfer assessment; monitoring of operational limits	Signals can be used for signature development. Many other safeguards measurements are dependent on accurate temperature measurements	Damage to optical fiber from radiation is a concern	6	8	5
Salt redox potential	Dynamic reference electrode	Assessment of corrosivity of salt and state of dissolved materials	Assessment of state of safeguards-relevent actinide species	Years-long longevity in MSR must be demonstrated	7	7	6
	Optical (Raman, UV-Vis)	Assessment of corrosivity of salt and state of dissolved materials	Assessment of state of safeguards-relevent actinide species	Precise determination of redox potential requires full accounting of every salt constituent; optical approaches may not produce accurate results	3	6	6
	Thermodynamic reference electrodes	Assessment of corrosivity of salt and state of dissolved materials	Assessment of state of safeguards-relevent actinide species	Questionable longevity of separator materials in molten salt environment	5	7	6
Volume / Liquid Level	Tracer dilution	Measurement of total salt volume to assess presence of leaks	Measurements of salt volume to enable translation of coenctration measurements into total inventory in salt	Background radiation may make tracer measurements difficult	5	6	7
	Ultrasound	Measurement of salt level (which can be used to estimate salt volume) to assess presence of leaks	Measurement of depth (which can be used to estimate total volume) to enable translation of coenctration measurements into total inventory in salt	Longevity in high temperature, radiation conditions unclear	7	7	7
	Contact depth sensor	Measurement of salt level (which can be used to estimate salt volume) to assess presence of leaks	Measurement of depth (which can be used to estimate total volume) to enable translation of coenctration measurements into total inventory in salt	Possible corrosion issues depending on salt media	7	8	7
	Radar	Measurement of salt level (which can be used to estimate salt volume) to assess presence of leaks	Measurement of depth (which can be used to estimate total volume) to enable translation of coenctration measurements into total inventory in salt	Longevity in high temperature, radiation conditions unclear	7	7	7
Particulate Monitoring	Electrical Resistance Tomography	Monitoring of precipitated solids (to prevent clogging)	Monitoring of precipitated solids to ensure NMAC closure	Only short term demonstrations at present. Can measure particle loading but provides no quantification of particle composition	6	6	7
	Ultrasonics	Monitoring of precipitated solids (to prevent clogging)	Monitoring of precipitated solids to ensure NMAC closure	Not yet demonstrated for molten salt systems. Can measure particle loading but provides no quantification of particle composition	5	6	6
Off-gas monitoring	Optical (Raman)	Monitoring management and release of radioactive material	Mass accountancy for volatile actinide species	Limited amounts of SNM present in off-gas system	5	7	6
	LIBS	Monitoring management and release of radioactive material	Mass accountancy for volatile actinide species	Limited amounts of SNM present in off-gas system	5	7	6
Under-salt Viewing	Ultrasound	Detection of leaks/spills	Maintaining CoK for fuel pins	Important for MSRs with captive fuel salt pins (to enable item counting)	4	4	8
	Video	Detection of leaks/spills	Maintaining CoK for fuel pins	Important for MSRs with captive fuel salt pins (to enable item counting)	4	4	8
Vibration/Accelerations	Accelerometers	Pump health monitoring	Minimal safeguards impact		8	4	1
Valve Position Monitoring	Position Monitor	Valve position confirmation	Confirmation of flow pathway to appropriate process equipment		8	6	5
In-reactor video monitoring	Cameras (CCD, CMOS, etc.)	Detection of leaks/spills within reactor boundary	Detection of off-normal behavior	Longevity questionable	6	5	5

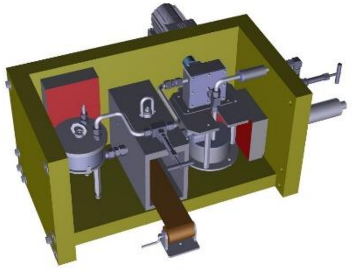
Introduction

Monitoring and Control of Molten Salt Systems

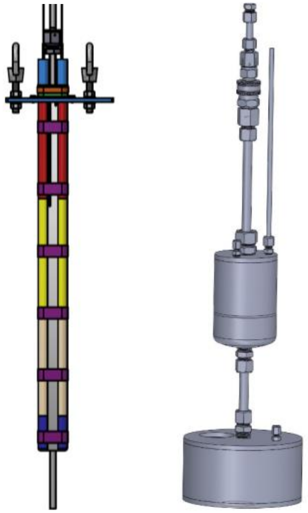
To address these gaps, Argonne has demonstrated monitoring for a variety of molten salt equipment including thermal convection loops, salt purification equipment, and process vessels. Deployable sensors for composition, redox state, particle concentrations, etc. have been created.

Electrochemical Monitoring of Salt Composition[1]

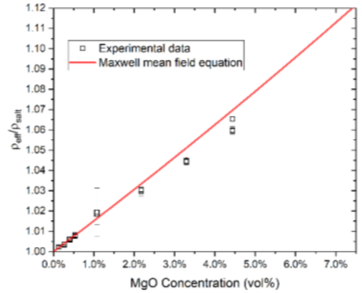
Windowless Optical Monitoring of Salt Composition[2]

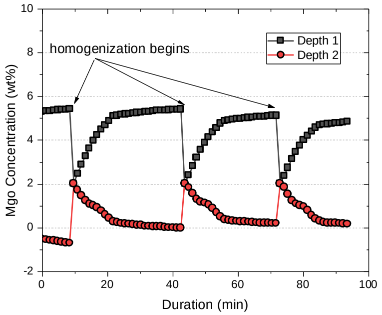


Automated Salt Sampling[2]



Monitoring of Precipitated Particles[3]





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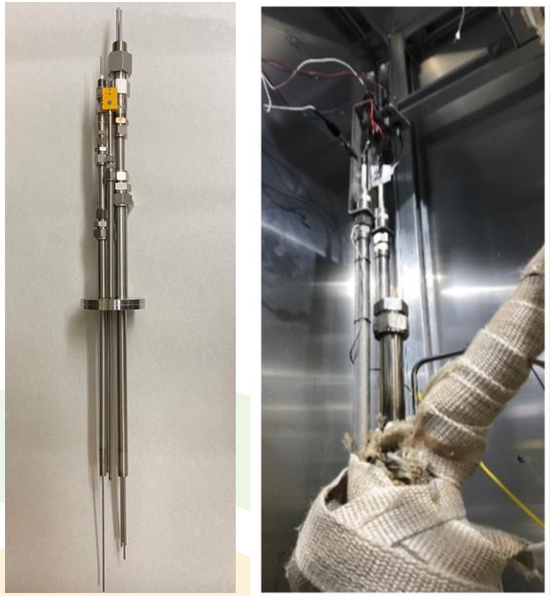
[1] $MgCl_2$-KCl-NaCl thermal convection loop run at ORNL (Bruce Pint)
[2] Funded by DOE NE MPACT [3] Funded by EERE-SETO

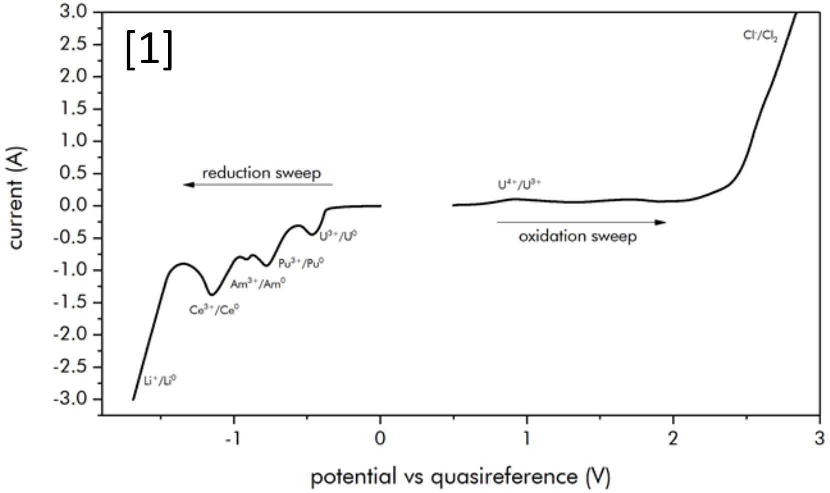
Electrochemical Sensors for MSRs

Molten Salt Monitoring

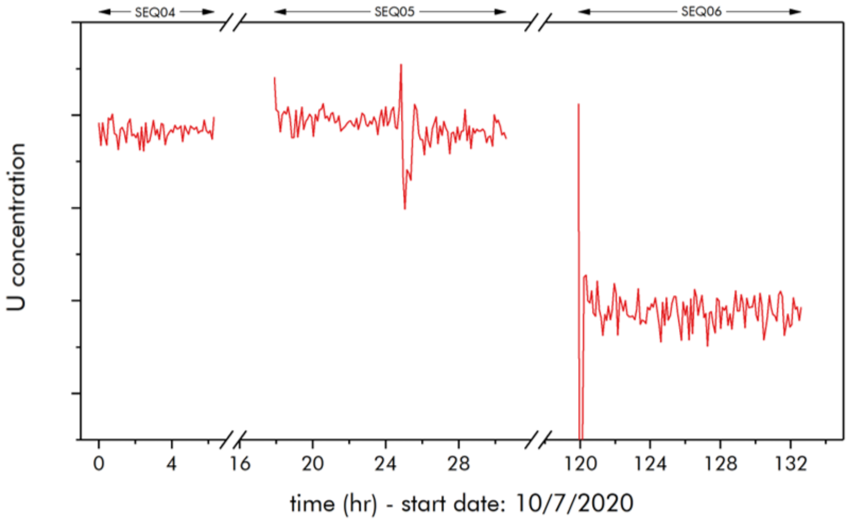
Argonne has operated electrochemical sensors for years-long durations in fuel reprocessing equipment and thermal convection loops. However, none of these previous probes were specifically designed be directly installed in flowing conditions.



Typical multielectrode array sensors for installation into flow loop vessels



Sensor measurement of actinide bearing salt



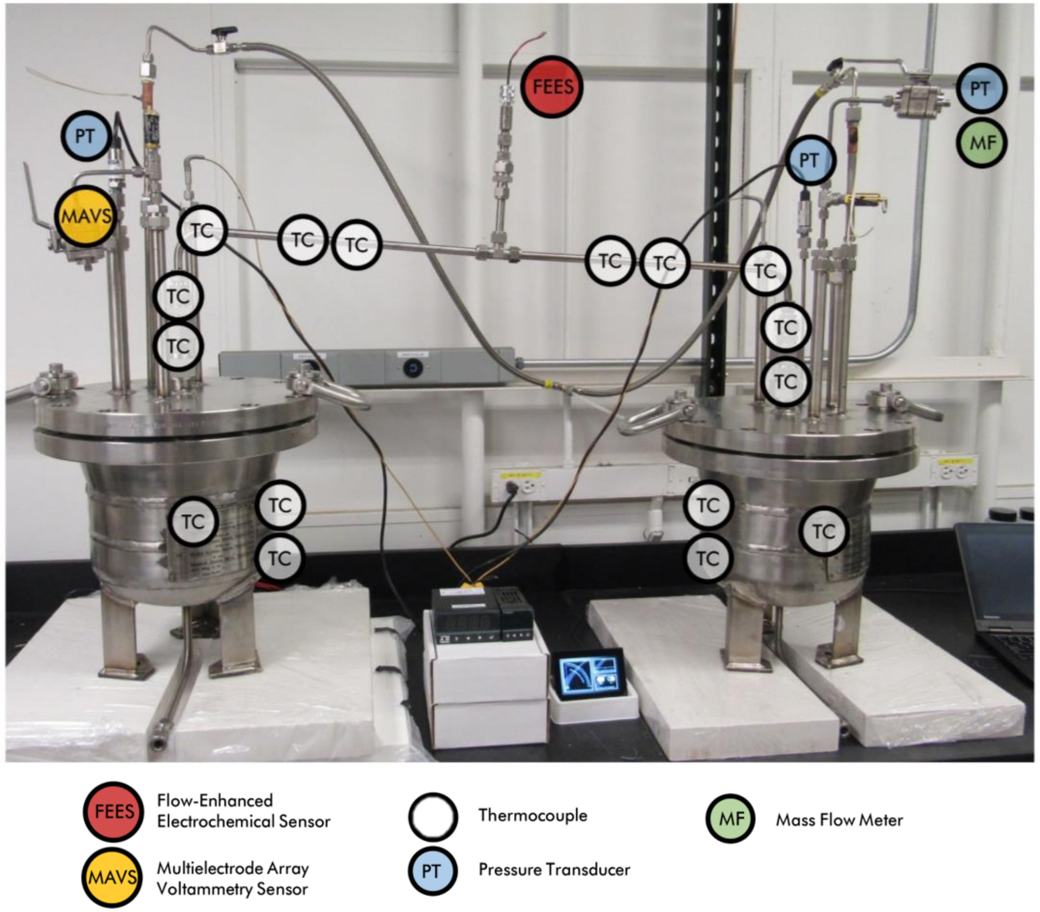
U concentration versus time during the salt addition

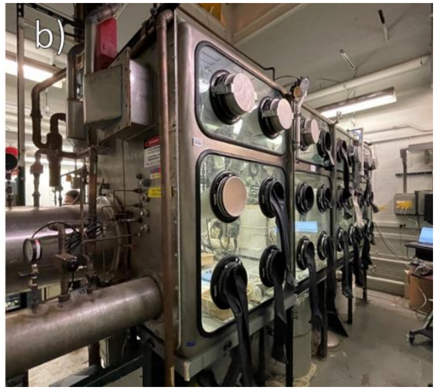
[1] B. Kersten, K. Hawthorne, M. Williamson, R. Akolkar, C.E. Duval, The Future of Nuclear Energy: Electrochemical Reprocessing of Fuel Takes Center Stage, Electrochem. Soc. Interface. 30 (2021) 45. https://doi.org/10.1149/2.F06213F.

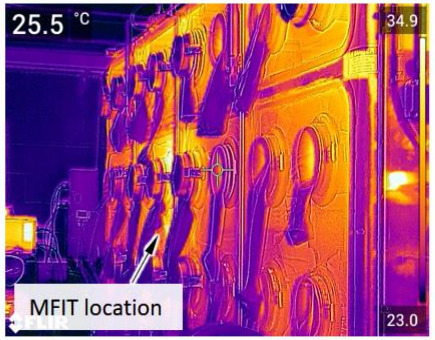
Modular Flow Instrumentation Testbed (MFIT)

A modular safeguards instrumentation testbed was constructed to develop and assess a variety of molten salt sensors in flowing conduits

- Enables rapid assessment of new sensor designs
    - Sensors installed in tanks and in the transfer line
- Supports radiological and non-radiological salts
- Supports a wide variety of instrumentation
- Permits rapid salt changes (chlorides, fluorides)
- Flow rates (0.01 to 1 L/s) and transfer line sizes (1/4″ to 1″) to achieve conditions representative of bypass lines, sampling lines, and flow conduits
- *Non-radiological operations: 3 months in total*
- *Radiological operations: >13 months in total*



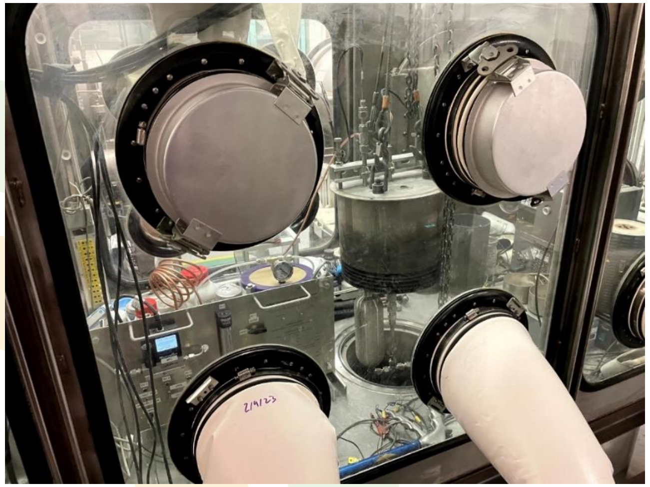




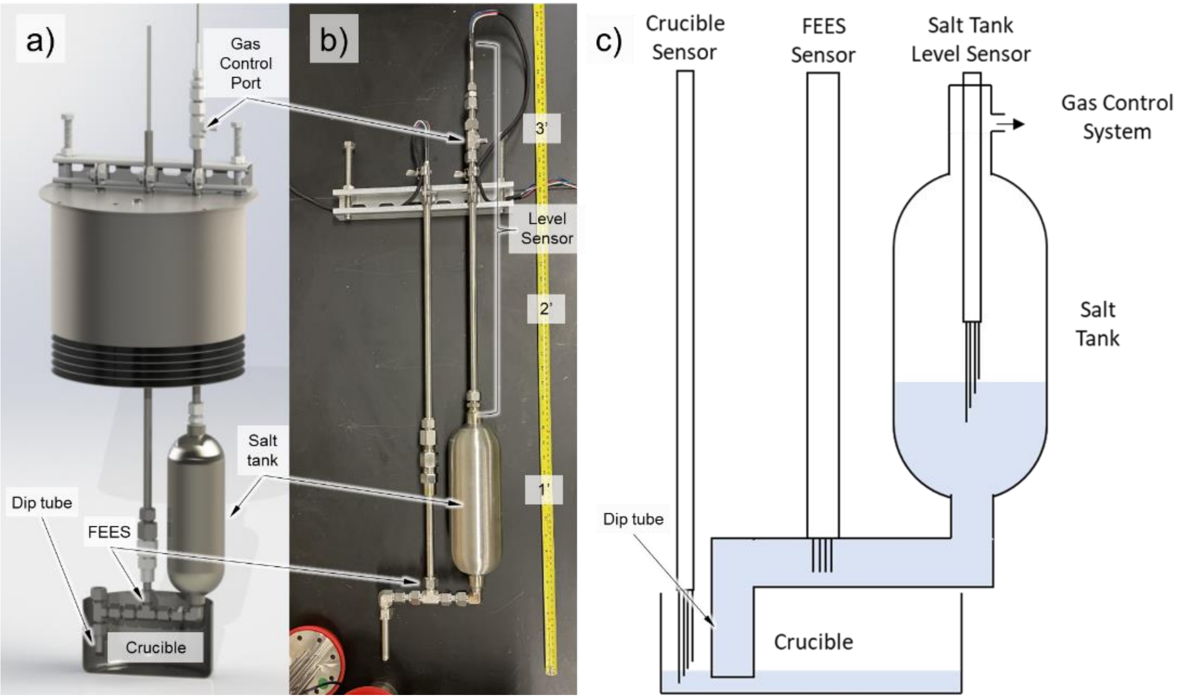
In-Well Mini-MFIT Flow System

A miniaturized in-well MFIT was also built to increase sensor development throughput

- Operated remotely using fully automated control panel
- Enables rapid assessment of new sensor designs:
  - Low flow rate (<2 SLPM) FEES sensors
  - Salt level and flow rate sensors.
  - Crucible (drain tank) chemistry sensors.
- Fits into furnace well for ease of disassembly/salt change



In-well Mini-MFIT flow system in operation



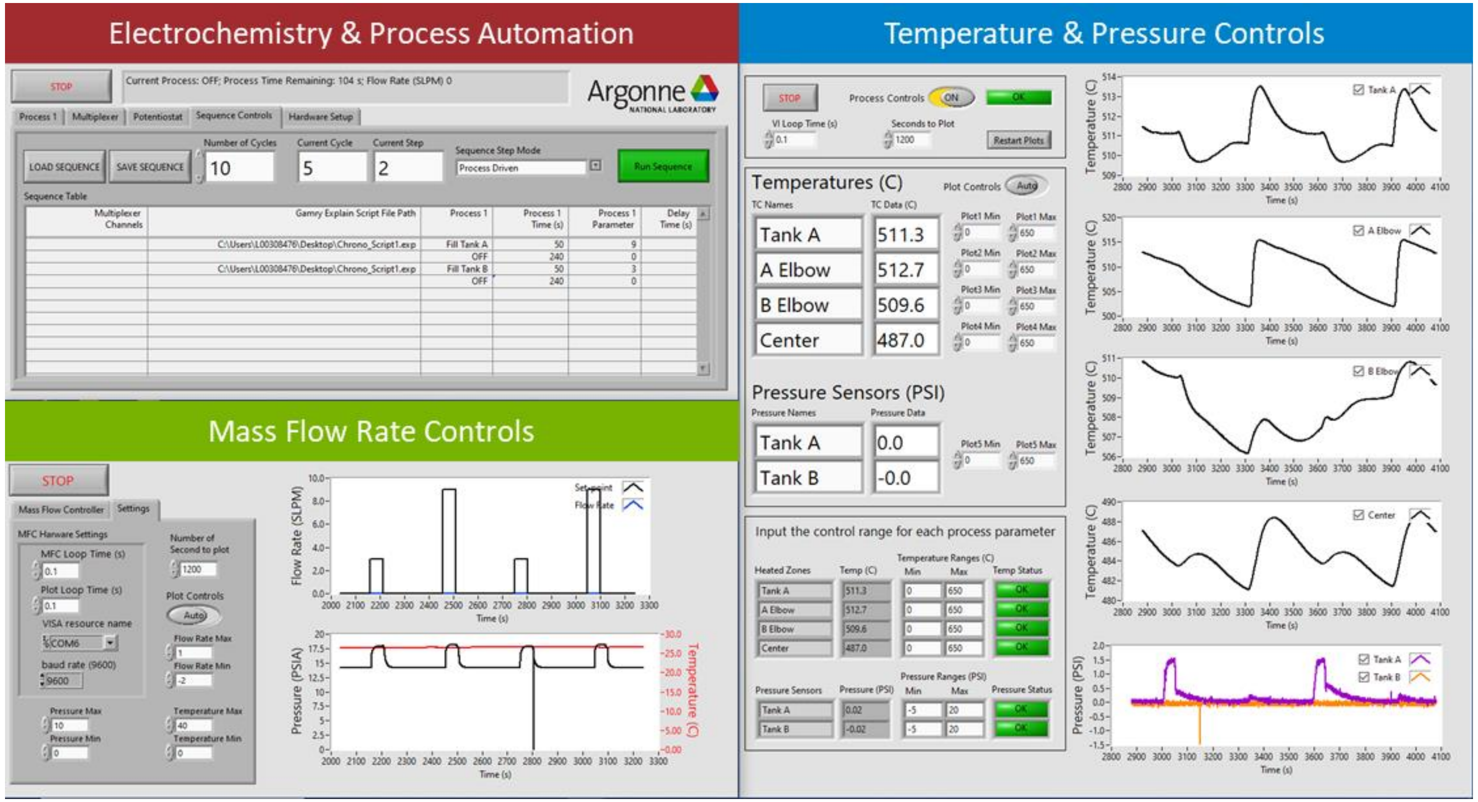
In-well Mini-MFIT flow system for safeguards sensor development

Automation of Measurements and Analysis

During FY22 and FY23, complete automation of the MFIT was completed

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

This safeguards sensor framework is being developed to enable complete multi-modal monitoring for molten salt systems



Current Process: OFF; Process Time Remaining: 104 s; Flow Rate (SLPM) 0

Number of Cycles: 10
Current Cycle: 5
Current Step: 2
Sequence Step Mode: Process Driven

Sequence Table

Multiplexer Channels	Gamry Explain Script File Path	Process 1	Process 1 Time (s)	Process 1 Parameter	Delay Time (s)
	C:\Users\L00308476\Desktop\Chrono_Script1.exp	Fill Tank A	50	9	
		OFF	240	0	
	C:\Users\L00308476\Desktop\Chrono_Script1.exp	Fill Tank B	50	3	
		OFF	240	0	

MFC Hanware Settings
MFC Loop Time (s): 0.1
Plot Loop Time (s): 0.1
VISA resource name: COM6
baud rate (9600): 9600
Number of Second to plot: 1200
Plot Controls: Auto
Flow Rate Max: 1
Flow Rate Min: -2
Pressure Max: 10
Pressure Min: 0
Temperature Max: 40
Temperature Min: 0

Process Controls: ON — OK
VI Loop Time (s): 0.1
Seconds to Plot: 1200

Temperatures (C) — Plot Controls: Auto

TC Names	TC Data (C)	Plot Min	Plot Max
Tank A	511.3	0	650
A Elbow	512.7	0	650
B Elbow	509.6	0	650
Center	487.0	0	650

Pressure Sensors (PSI)

Pressure Names	Pressure Data	Plot5 Min	Plot5 Max
Tank A	0.0	0	650
Tank B	-0.0		

Input the control range for each process parameter

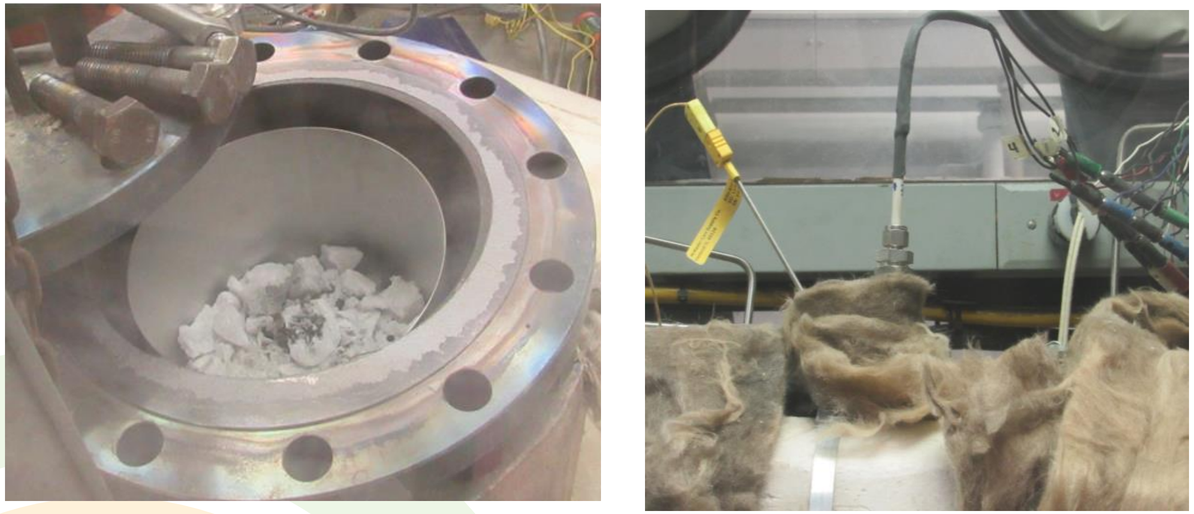
Heated Zones	Temp (C)	Temperature Ranges (C) Min	Max	Temp Status
Tank A	511.3	0	650	OK
A Elbow	512.7	0	650	OK
B Elbow	509.6	0	650	OK
Center	487.0	0	650	OK

Pressure Sensors	Pressure (PSI)	Pressure Ranges (PSI) Min	Max	Pressure Status
Tank A	0.02	-5	20	OK
Tank B	-0.02	-5	20	OK

Salt level & flow rate sensor digital read out

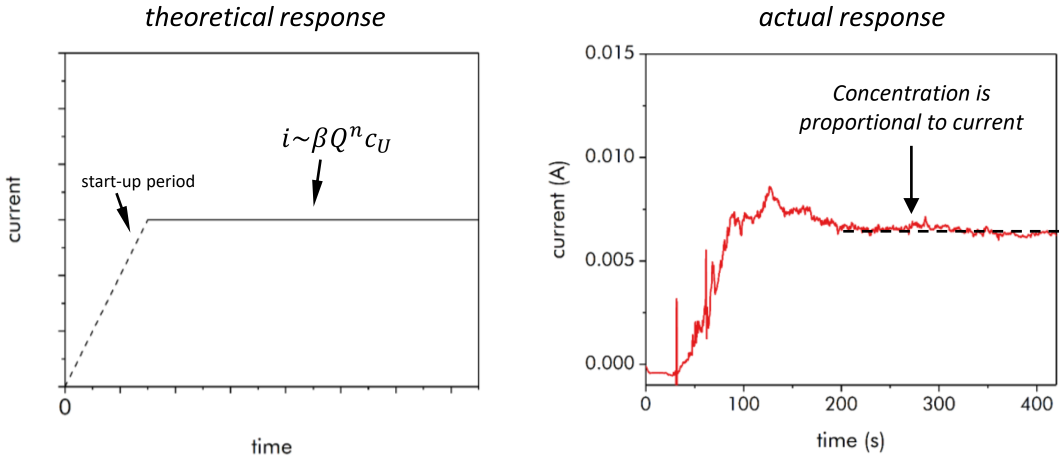
Actinide Measurements in Flowing Salts

Argonne conducted actinide measurement campaigns in FY22 and FY23. Experiments involved 4 kg of $MgCl_2$-KCl-NaCl-UCl_3 salt. FY23 experiments featured improved salt chemistry control and increased replicates of individual experiments.



Salt transfer tank (left) and flow-enhanced electrochemical sensor installed into transfer line (right)

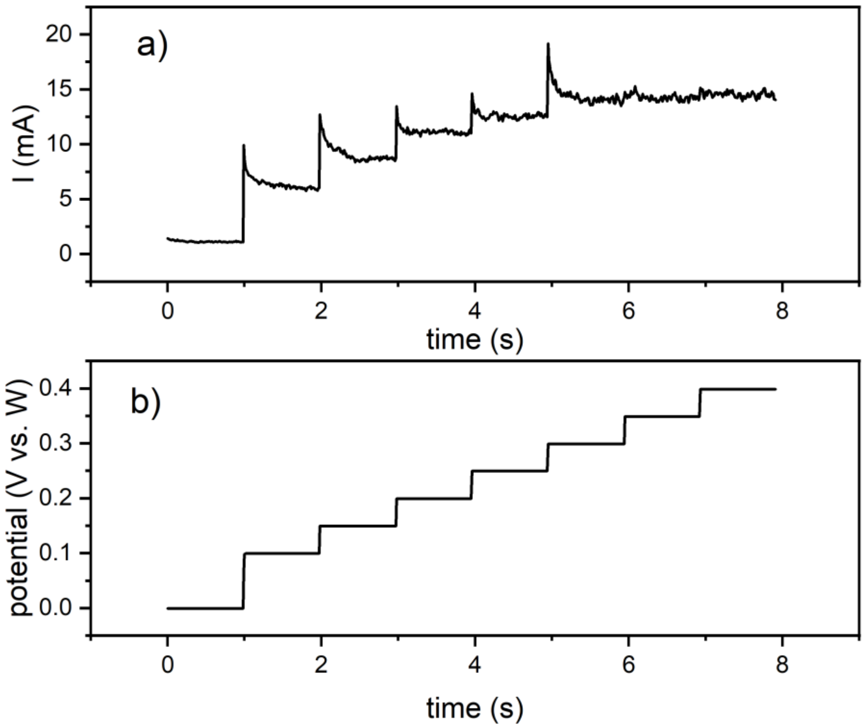
In-line sensor response to soluble-soluble reactions



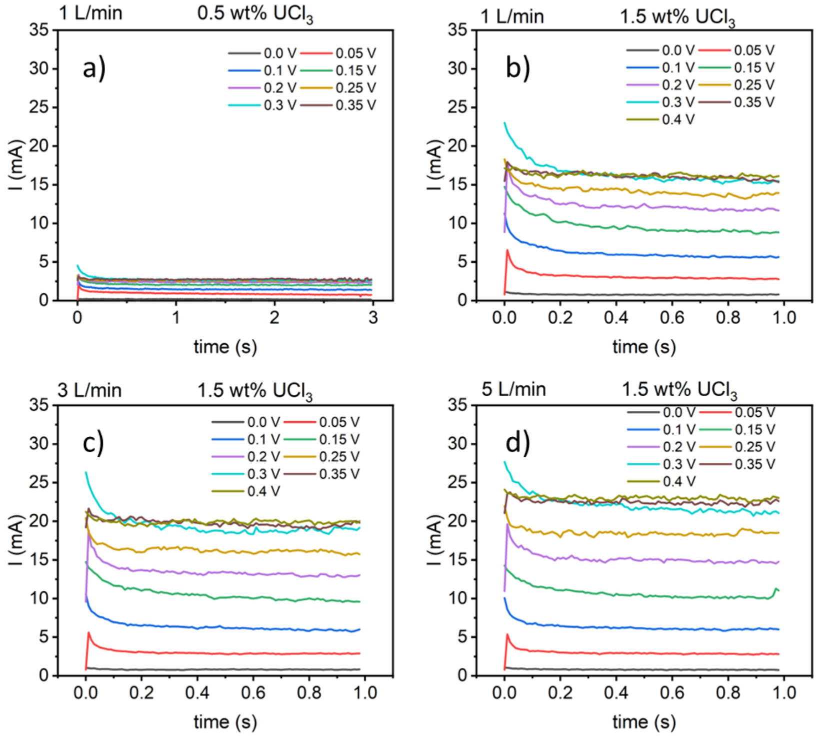
Theoretical (left) and actual (right) current response for soluble-soluble reaction

Actinide Measurements in Flowing Salts

The flowing conditions enable electrochemical approaches such as long-duration staircase voltammetry waveforms. These extended waveforms allow for discrimination and quantification of multiple soluble-soluble reactions



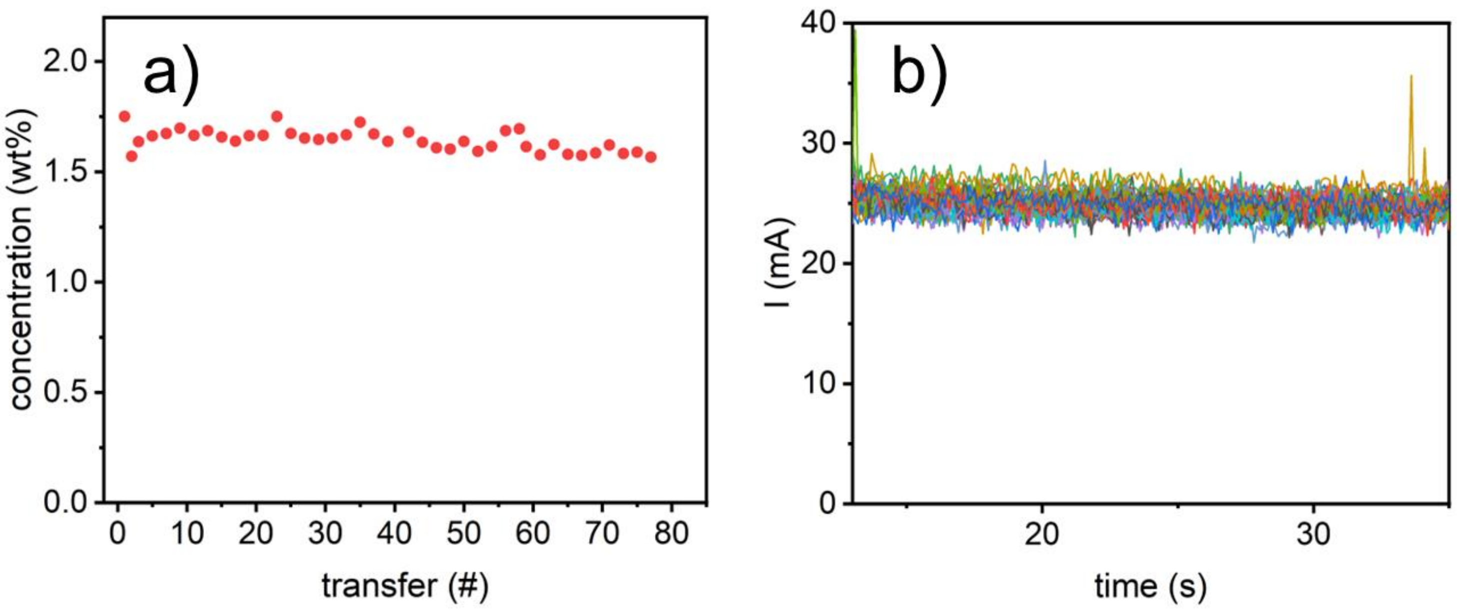
U^{3+}/U^{4+} current response to staggered potential holds during a single salt transfer.



Current response of multiple potential holds during a single flow experiment using the FEES. UCl_3 concentration was 0.5 wt% (a) and 1.5 wt% (b, c, and d)

Accelerated Measurements

- Repeatability of the automation system was tested with a series of repeated transfers and measurements
- Series of 80 transfers completed over the course of four days
- Low error associated with the measurements (*1.642±0.008 wt%)*
- Significant improvement in consistency of transfer intervals

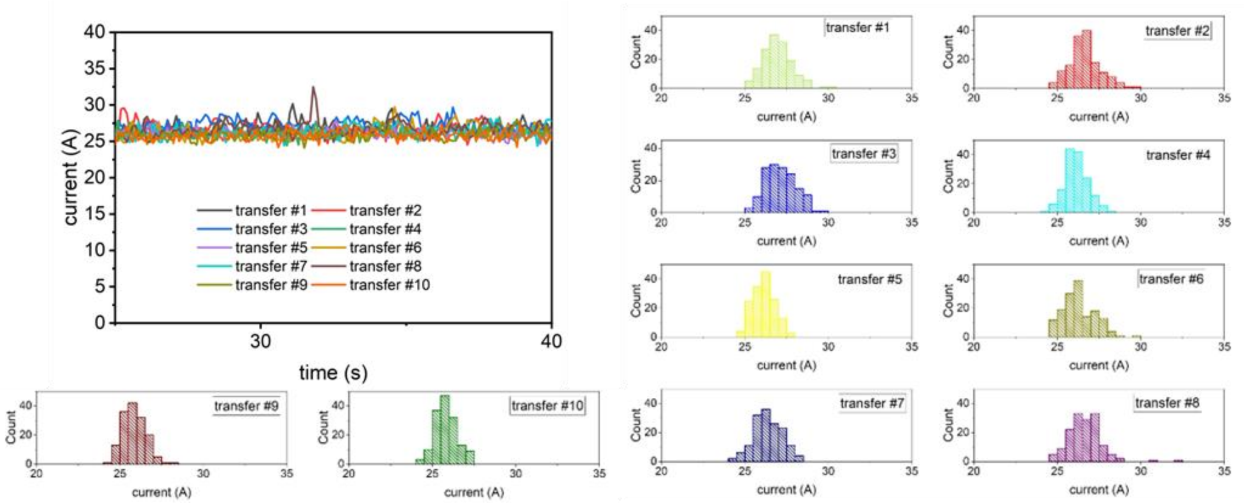


Repeated transfers using automated MFIT
Average UCl_3 concentration 1.642±0.008 wt%

Repeatability over Extended Testing

Sensor measurements were found to be highly repeatable across multiple salt transfers.

- Statistical analyses showed low standard deviation within single runs and a relative standard deviation of 0.54% vs 0.97% in FY22
- Measurements confirmed the robustness of the sensor design



	Transfer #1	Transfer #3	Transfer #6	Transfer #9
Mean Current (mA)	26.96	27.14	26.30	25.83
Standard Deviation (mA)	0.87	0.91	0.95	0.66
Confidence Interval (99.0%) (mA)	0.182	0.192	0.199	0.139

Metric	Value from Repeated Transfers
Mean Current (mA)	26.40 mA
Relative Standard Deviation	0.54%
Confidence Level (99.0%) (mA)	0.370 mA

Current Response to Flow Conditions

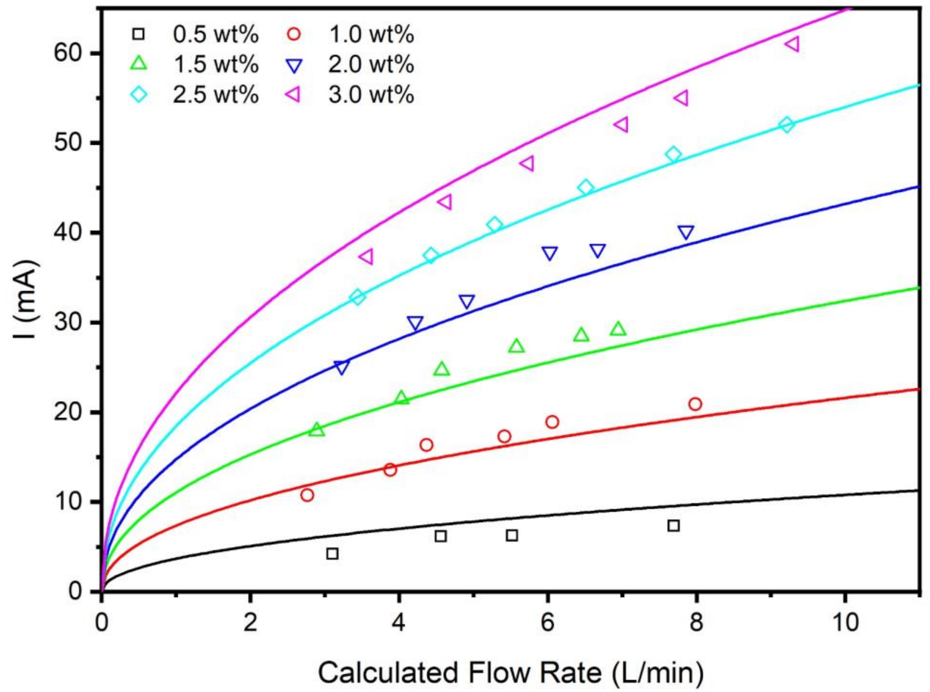
The sensor response with respect to flow rate has been found to vary in a manner consistent with standard mass transfer correlation (i.e., Sherwood numbers)

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

These Sherwood number correlations allows for accurate concentration measurements

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

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

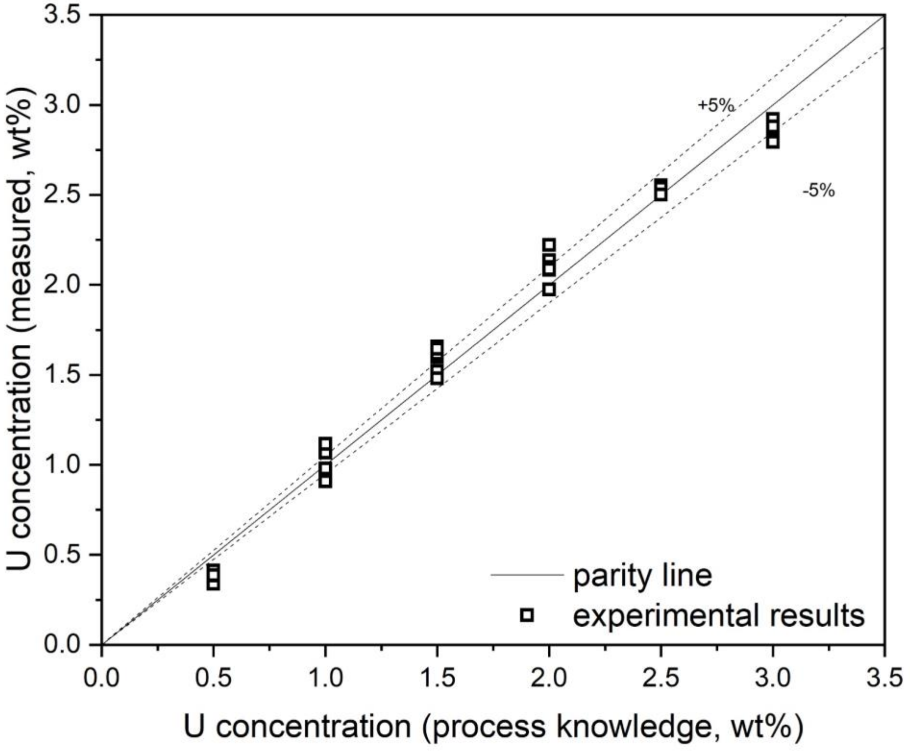


Constant potential measurements at various observed flow rates. Measurements taken at six UCl_3 *concentrations (0.5, 1.0, 1.5, , 2.0, 2.5 and 3.0 wt%) in* $MgCl_2$*-KCl-NaCl at 500 ℃.*

Concentration Measurements

Uranium concentration measurements have been found to closely follow the expected parity line.

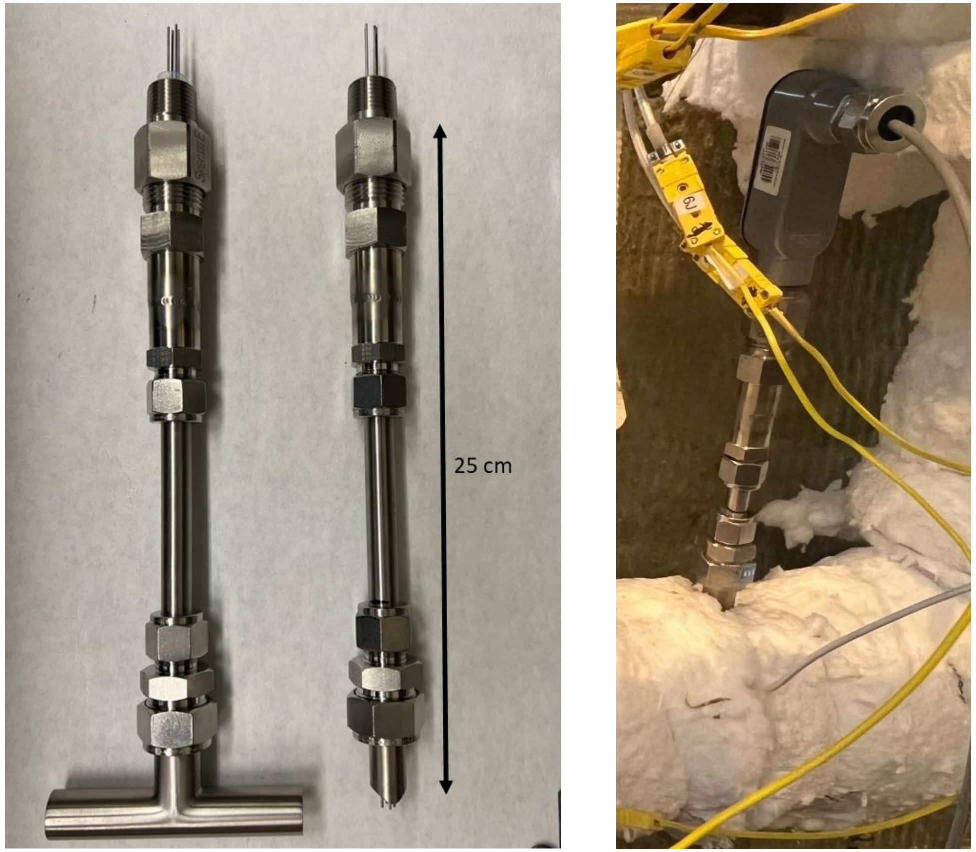
- Mean absolute relative error in measurements was 3.1% in FY23 compared to 5.6% in FY22
  - Most measurements were within ±5% of process knowledge
- Measurement precision was improved vs. FY22 results
- Low concentration measurements affected by residual impurities in salt
  - Reaction of impurities leading to UO_2 formation led to underpredictions



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

In-line Sensor Deployment

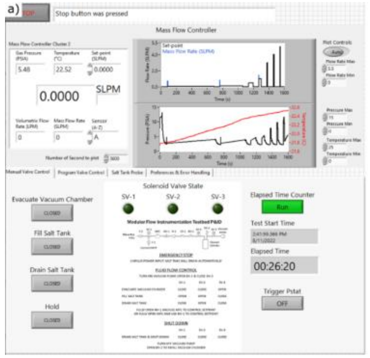
- Two FEES sensors installed at a partner institution’s flow loop
- Sensor design updates were made to enable safe FLiBe operations
  - Enable operation in fluoride salts
  - Improved sealing outside of glovebox environment
- Sensors installed at different points on flow circuit
  - Will study salt at same flow conditions but different temperatures
- Planned 1000 hour flowing test in FY24



FEES sensors deployed at industrial partner’s engineering scale forced convection FLiBe experiment (left). FEES sensor installed in industrial partner’s flow loop (right).

Conclusions

- During FY23, the MFIT was fully automated and additional safeguards-relevant measurement campaigns were carried out
  - Capabilities for simultaneous control over the flow system and multiple sensors
- In-line sensor accuracy improved
  - Mean absolute relative error in measurements was 3.1% in FY23 compared to 5.6% in FY22
  - Upgraded electrochemical sensors were shown to have good accuracy even across a wide range of flow conditions
  - New level sensor & flow rate measurement devices were developed in parallel using the Mini-MFIT system.
- High concentration UCl_3 measurements are planned for FY24



Stop button was pressed

Gas Pressure (PSIA): 5.48
Temperature (°C): 22.52
Set point (SLPM): 0.0000
0.0000 SLPM
Volumetric Flow Rate (LPM): 0
Mass Flow Rate (SLPM): 0
Sensor (A-Z): A
Elapsed Time: 00:26:20

Acknowledgements

Thanks to:

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Stefan Tosic