ADVANCED REACTOR SAFEGUARDS

Flow Enhanced Electrochemical Sensors for Molten Salt Reactors

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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 Composition¹

Windowless Optical Monitoring of Salt Composition²

Automated Salt Sampling²

Monitoring of Precipitated Particles³

¹MgCl₂-KCl-NaCl thermal convection loop run at ORNL (Bruce Pint)
²Funded by DOE NE MPACT
³Funded 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

*Tee-junction figure courtesy Kevin Robb (ORNL)*
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 MgCl₂-KCl-NaCl-UCl₃ production

Synthesis steps for MgCl₂-KCl-NaCl-UCl₃
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.
By applying positive potentials, soluble-soluble reactions such as $\text{Cr}^{2+} \rightarrow \text{Cr}^{3+} + e^-$ and $\text{U}^{3+} \rightarrow \text{U}^{4+} + e^-$ 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.

Sensor Response Under Flow Conditions

**Soluble-soluble reaction**

**Soluble-insoluble reaction**

Current response for soluble-soluble 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.

![Graph showing current response to different flow rates](image)

Steady state Cr²⁺ reduction current from potentiostatic hold during hydrodynamic conditions at different flow rates

![Graph showing current slope vs. salt flowrate](image)

Reduction current slope vs. salt flowrate

<table>
<thead>
<tr>
<th>Sherwood Number Parameter</th>
<th>FEES Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$</td>
<td>$3.12 \times 10^{-14}$</td>
</tr>
<tr>
<td>$m$</td>
<td>$3.07$</td>
</tr>
</tbody>
</table>

\[
\frac{dl}{dt}_{initial} = k^2 \left( \frac{\pi mzFh}{M} \right) \left( \frac{DSc^{1/3} \Delta C}{d_0} \right)^2 \left( \frac{\rho_{salt}d_0U}{\mu_{salt}} \right)^m
\]
Preliminary statistical assessments have been performed for the sensors under flowing conditions for soluble-soluble and soluble-insoluble reactions.
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
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