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ONLINE MONITORING OF MOLTEN SALT REACTORS

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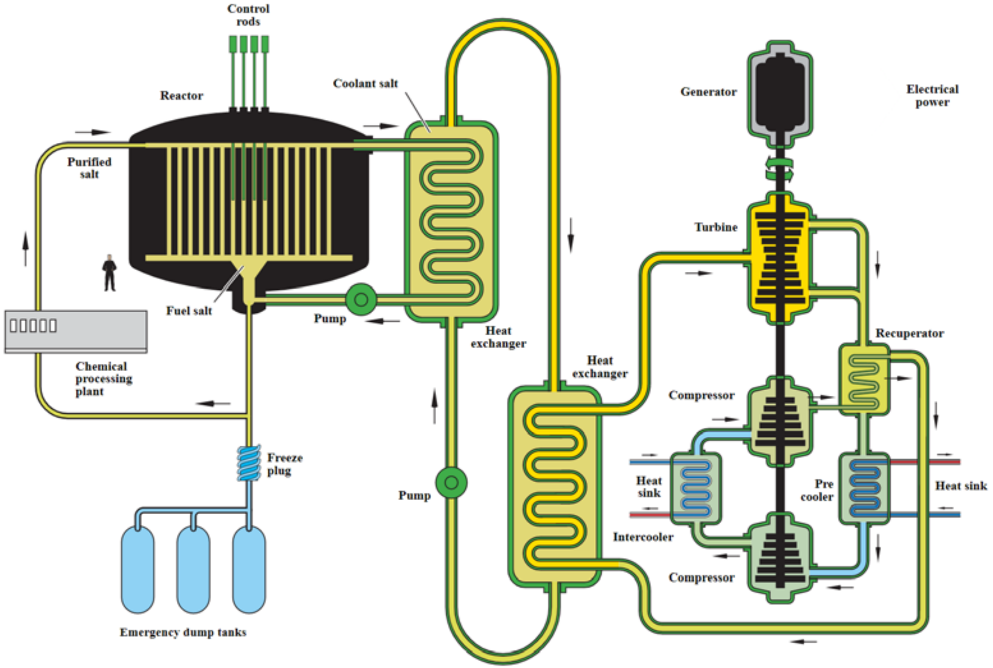
NRC Advanced Reactor Workshop 2019

INTRODUCTION

ONLINE MONITORING OF MSR CHEMISTRY

Chemical considerations within fuel salts and secondary salts demand high-fidelity process monitoring capabilities

- **Concentrations of reactants in core (neutronics)**
- **Fission product removal system (in situ processing)**
- **Noble metal deposition monitoring**
- **Structural corrosion monitoring**
- **Safeguards**



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

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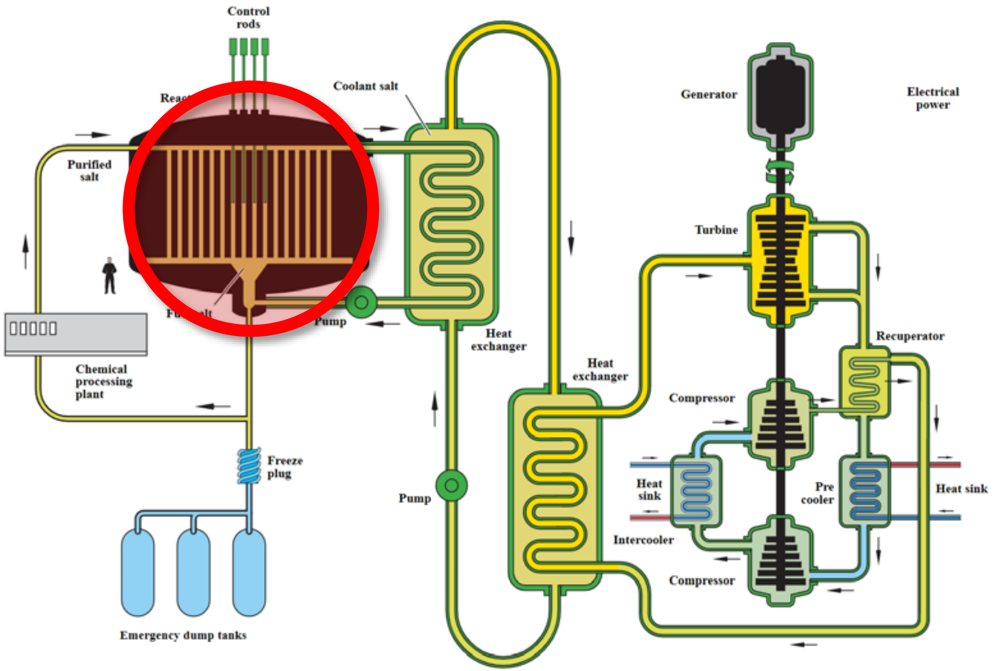

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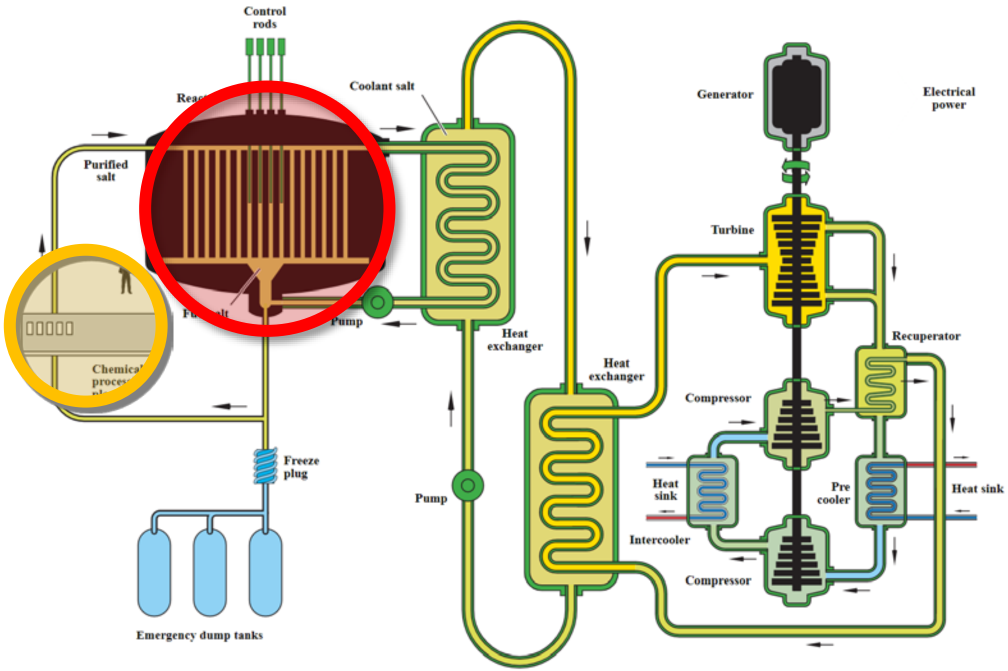

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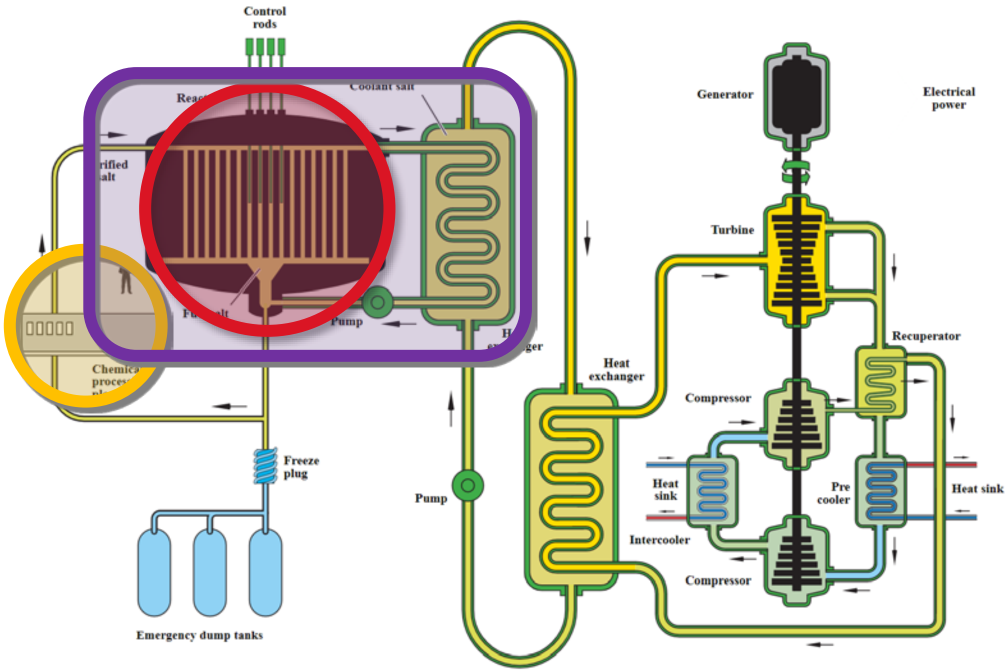

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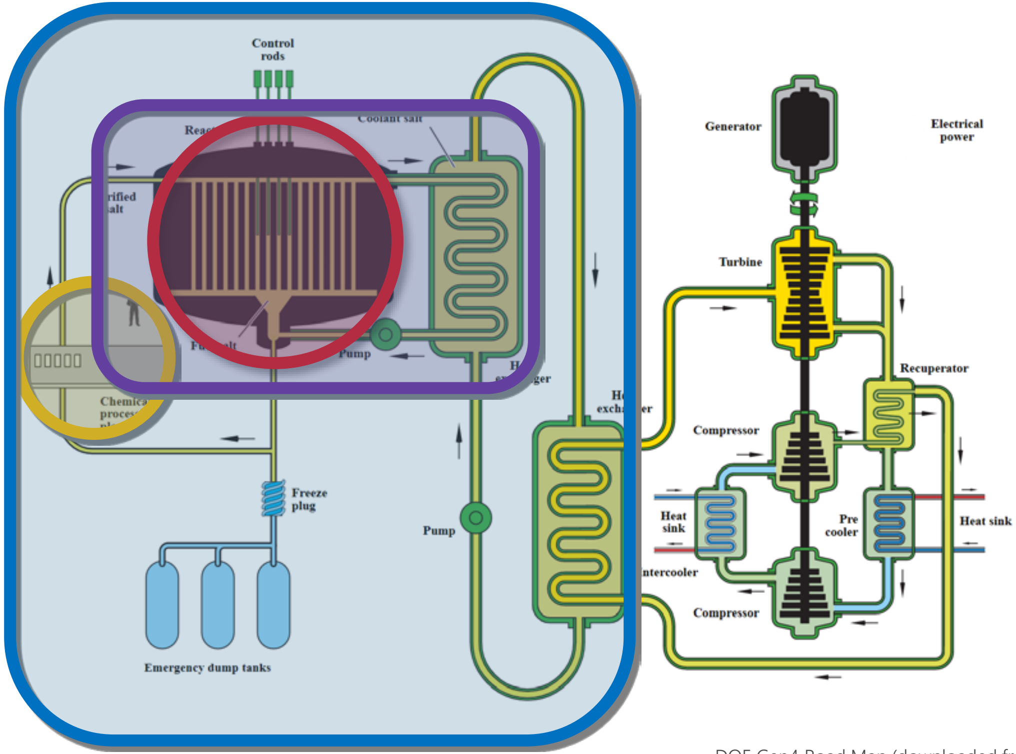

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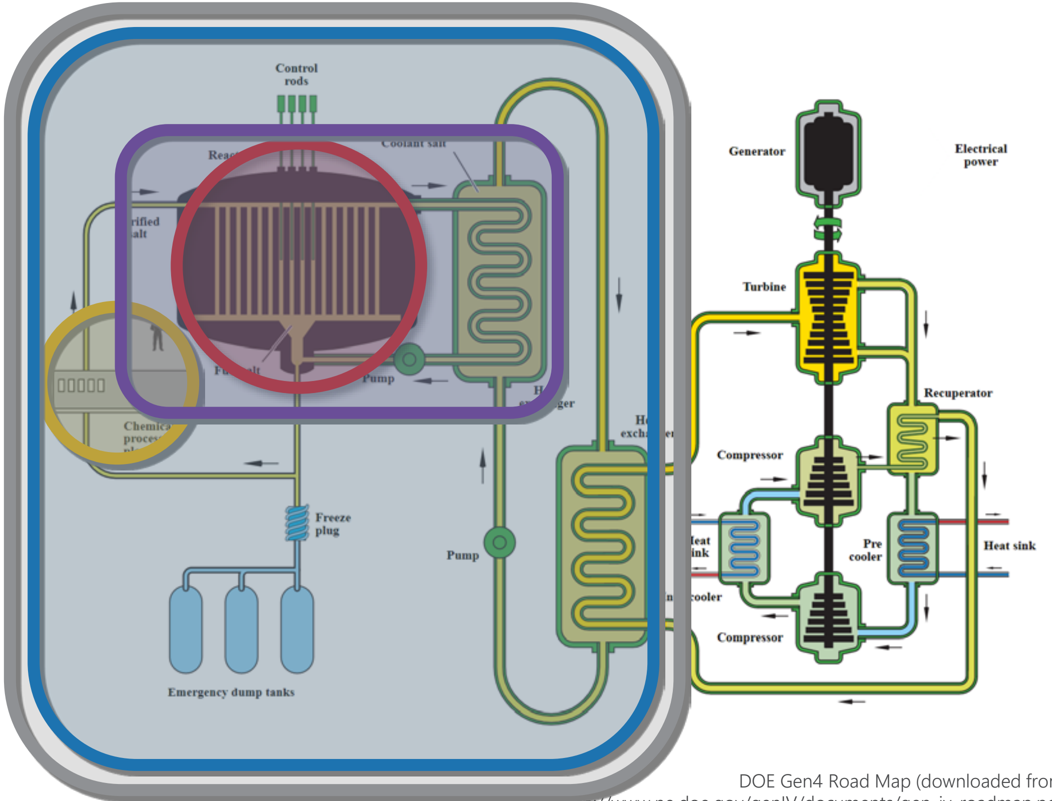

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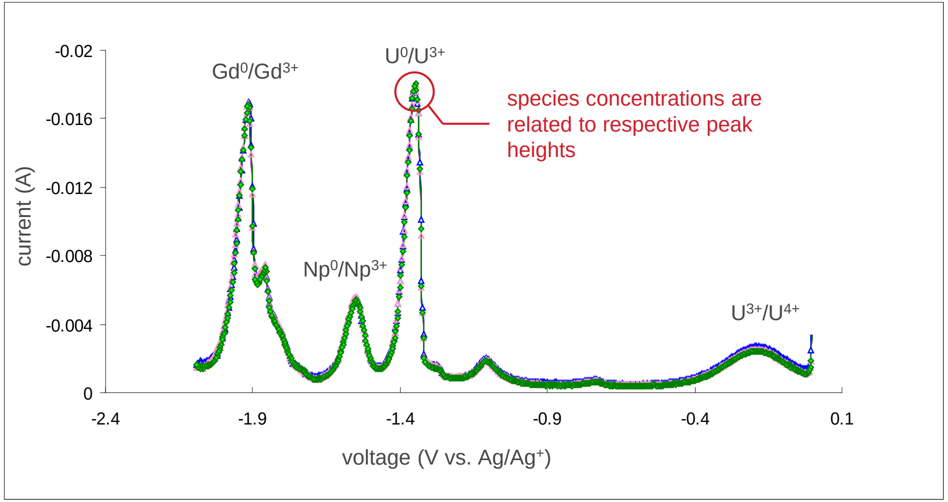
VOLTAMMETRY FOR IN-SITU PROCESS MONITORING

Voltammetric techniques can be used to monitor actinide concentrations in MSRs

- *Allows rapid, real-time measurements*
- *Equipment not affected by high radiation background*
- *Wetted materials are salt and temperature compatible*
- *Technique based on electrochemical properties and does not require use of standards*
- *Well-developed theory for voltammetric response for a given redox reaction*
- *Analyze for multiple components with single indicator electrode*
- *Multiple voltage perturbation waveforms and methods of analyzing resultant current are available*[1-5]

Concentrations and other salt characteristics determined from current response to voltage waveforms



Square-wave voltammogram for molten salt containing UCl_3, $NpCl_3$ and $GdCl_3$

[1]Hill, Perano, Osteryoung, *JES* **107** (8) 698 (1960)
[2]Mamantov, Manning, *Anal. Chem.* **38** (11) 1494 (1966)
[3]Tylka, et al. *JES* **162** (9) H625 (2015)
[4]Tylka, et al. *JES* **162** (12) H852 (2015)
[5]Hoyt, et al. *JES* **164** (2) H134 (2017)

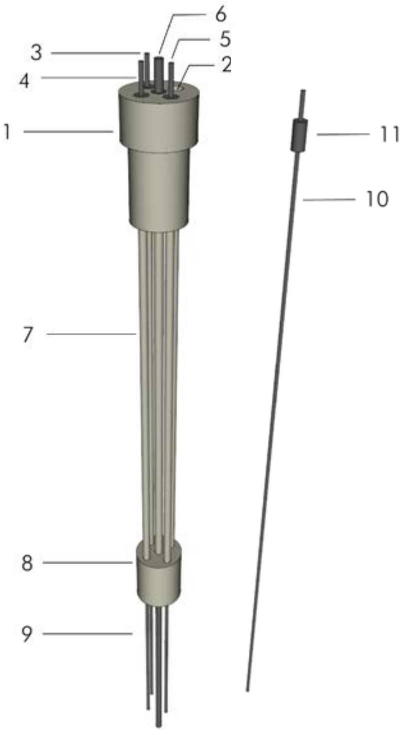
MULTIELECTRODE ARRAY SENSOR

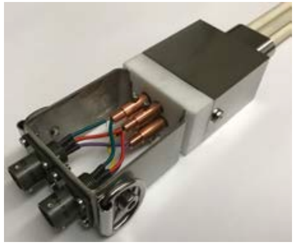
The multielectrode array provides a flexible platform for a wide range of voltammetry methods combined with quasi-reference and dynamic reference electrode measurements.

- *Salt redox potential*
- *Species concentrations*
- *Salt level*

Advantages

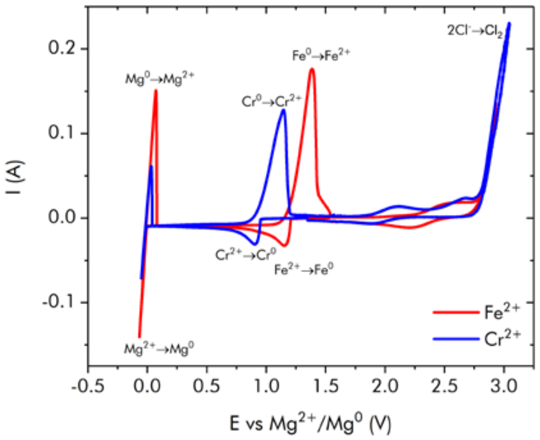
- Fast measurement rates
- No moving parts
- Wide potential range
- Long electrode service life
- Tolerant of thermal cycling



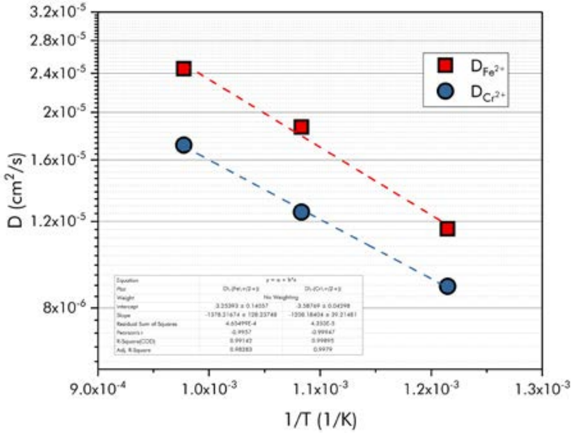


FUNDAMENTAL SALT PROPERTIES

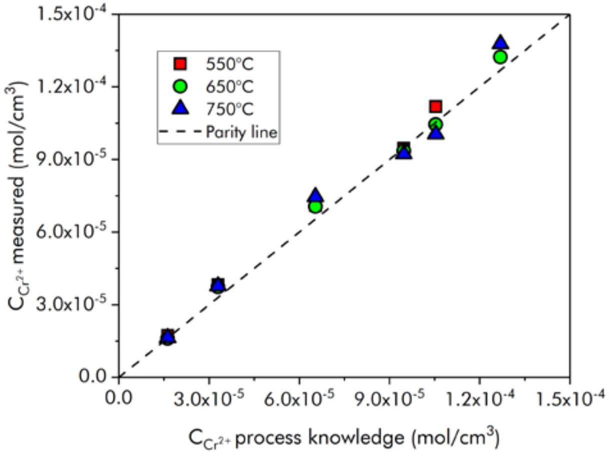
Fundamental salt properties including diffusion coefficients and kinetics parameters must be experimentally determined for each species of interest in a given salt across a complete range of temperatures.



Typical measurements during Cr^{2+} and Fe^{2+} property measurements testing



Experimentally determined diffusion coefficients for Cr^{2+} and Fe^{2+} versus temperature for $MgCl_2$-KCl-NaCl



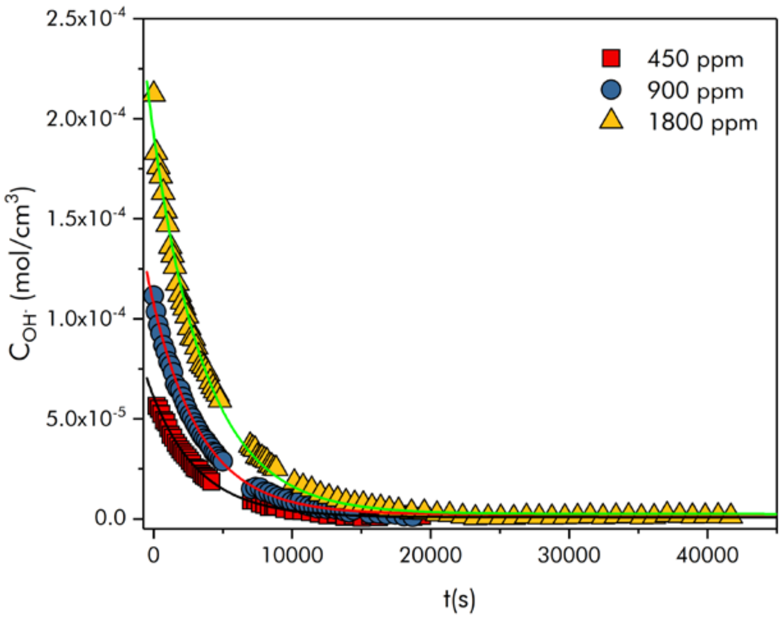
Parity plot comparing measured and known Cr^{2+} concentrations in $MgCl_2$-KCl-NaCl

FUNDAMENTAL SALT CHEMISTRY

Electroanalytical techniques and supporting salt properties have been established for a variety of species in several key salts

- Actinides
- Fission Products
- Corrosion Impurities
- Corrosion Products

Once suitable techniques have been developed, fundamental investigations of salt chemistry can be readily performed.

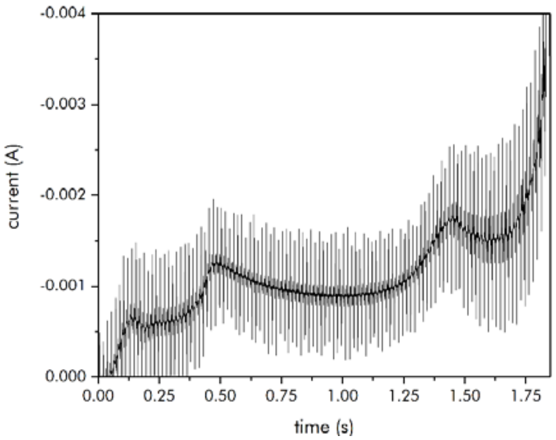


MgOHCl concentration versus time during decomposition reaction in $MgCl_2$-KCl-NaCl

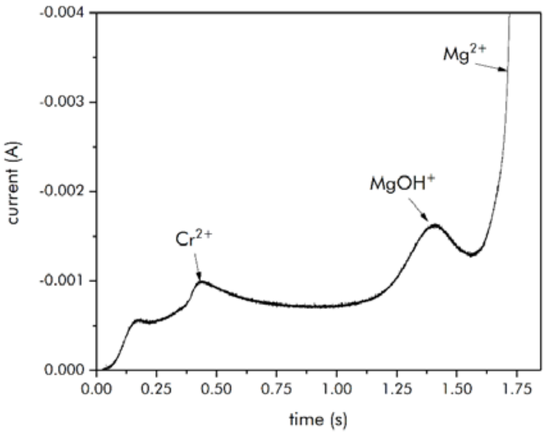
ELECTROANALYTICAL SENSOR CHALLENGES

Challenges exist for the use of electroanalytical sensors in real molten salt systems

- Electrical Noise
- Highly Concentrated Salts
- Non-ideal Electrochemical Behavior
- Materials Stability
- Seals
- Automation of Acquisition
- Automation of Analysis



Representative electroanalytical measurement in molten salt loop with significant interference from resistance heaters

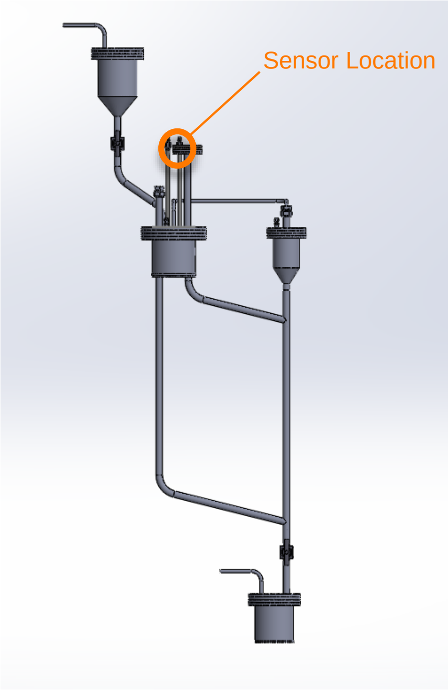


Representative electroanalytical measurement in molten salt loop with successful isolation of electrical noise

FLOW LOOP INTEGRATION

Versions of the sensors suitable for loop operations were constructed and installed into thermal convection loops (TCLs) at ORNL

- Materials compatibility tests conducted at maximum specified hot leg temperature (750 °C)
- Sensor provides long-term quantitative measurements of salt potential, metal ion corrosion products, and impurities

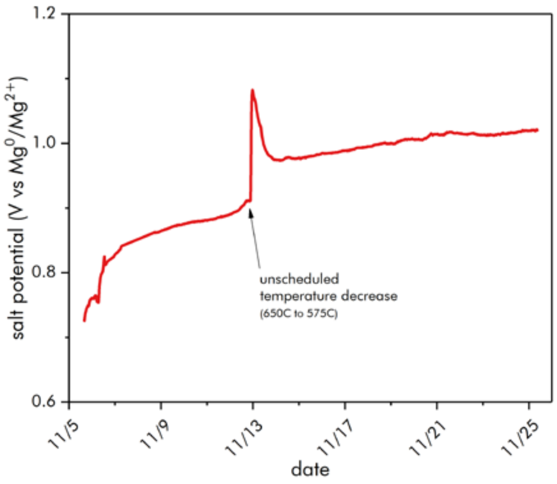


Rendering of TCL loop with indicated location of sensor installation[1]

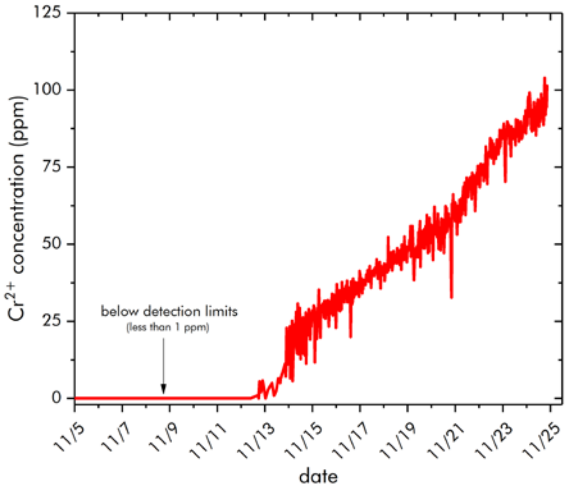
[1]HARP rendering courtesy of Bruce Pint (ORNL)

FLOW LOOP INTEGRATION

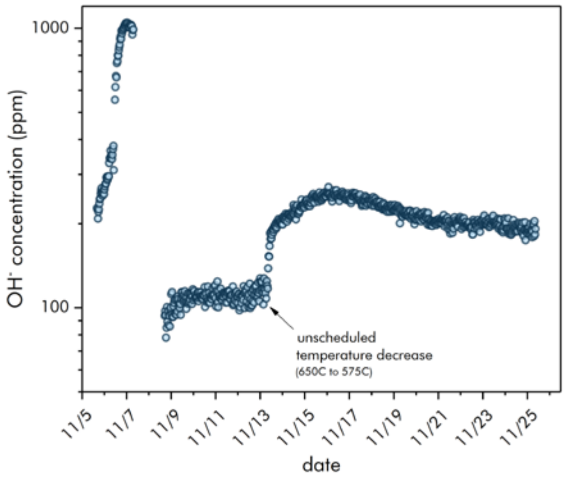
The sensor has been providing measurements throughout the >650 hour test. Principal measurements include salt potential, Cr^{2+} concentration, MgOHCl concentration, H^{+} concentration, and the salt depth.



Salt redox potential versus time during TCL loop operations



Cr^{2+} concentration versus time during TCL loop operations

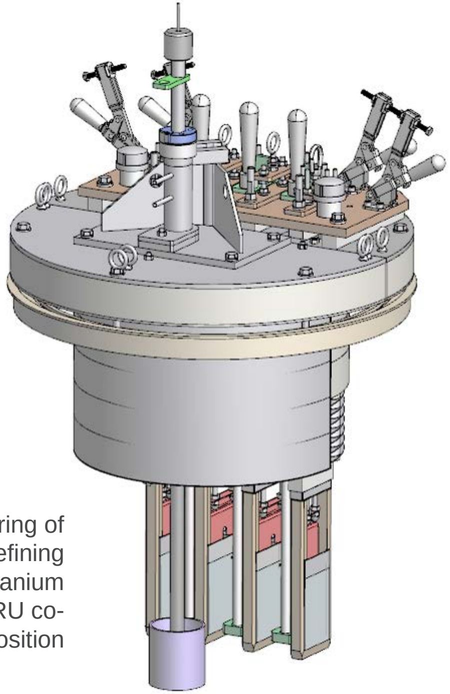


MgOHCl concentration versus time during TCL loop operations

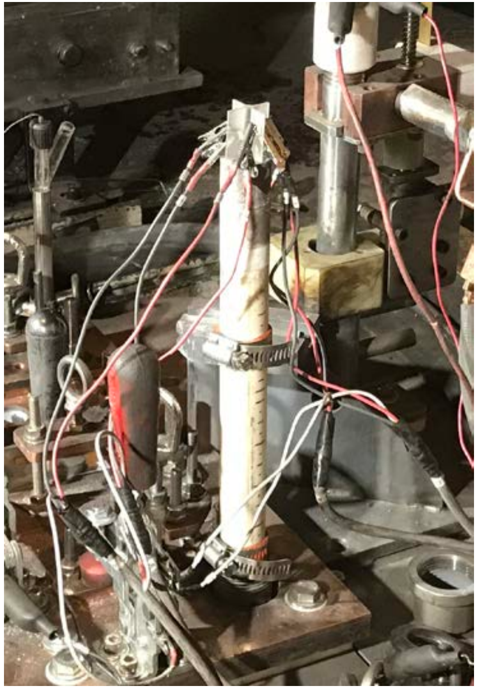
SENSOR PERFORMANCE ASSESSMENT

A 100 day trial sequence was conducted to assess the long-term stability, accuracy, uncertainty, and longevity of the sensors in a molten salt electrorefiner.

The experimental sequence included electroanalytical measurements and in situ electrochemical procedures to maintain electrode surfaces.



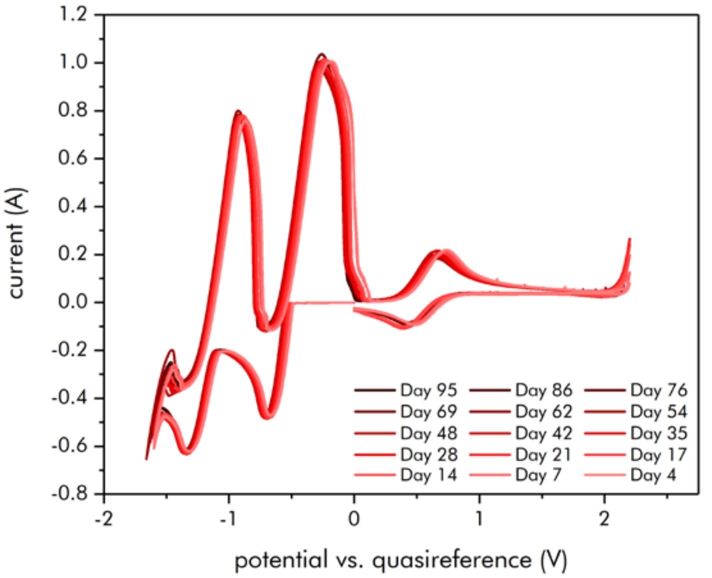
Rendering of electrorefining system for uranium and U/TRU co-deposition



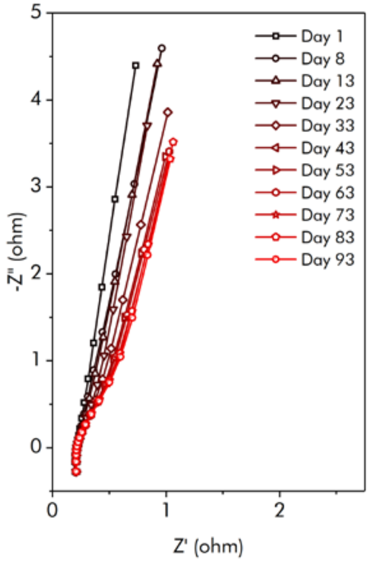
VOLTAMMETRY DURING LONG-DURATION TESTING

With proper procedures, long-duration service life tests demonstrated highly repeatable electroanalytical measurements over the 100 day testing period (and well beyond).

With proper electrochemical conditioning, in situ monitoring of the electrode health showed no film formation or material degradation.



Electroanalytical measurements taken over 100 day service life test in the pilot-scale electrorefiner (500 mV/s, with indicated immersion times)

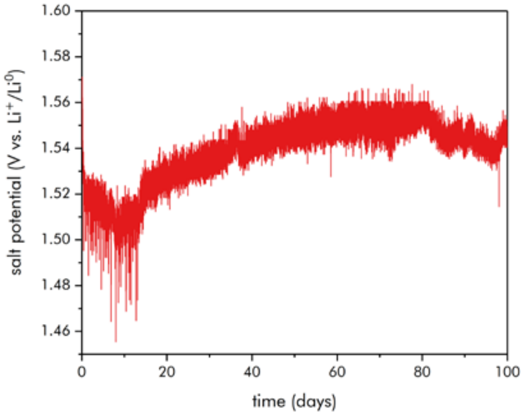


EIS Nyquist plots for electrode health monitoring (20 mV perturbation, 100 kHz to 100 Hz)

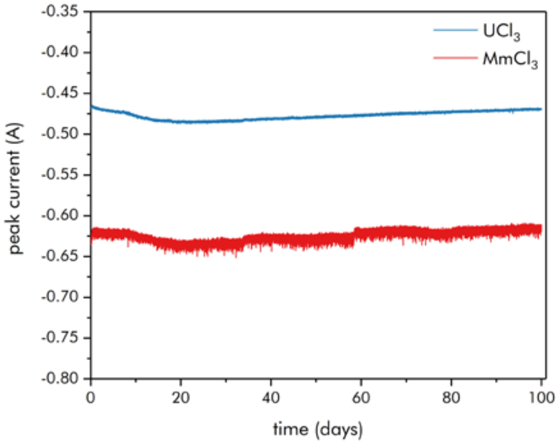
CONCENTRATIONS DURING LONG-DURATION TESTING

Measurements of the salt potential were consistent over the entire 100 day duration (mean absolute deviation less than 15 mV over entire test).

Measurements of the UCl_3 and $CeCl_3$ concentrations were also consistent over the entire test (relative standard deviation over the entire test of 1.08% and 1.10% for UCl_3 and $CeCl_3$ respectively; 0.13% and 0.60% on a daily basis)



Salt potential versus time during long-duration test as measured by quasireference using Li^+/Li^0 as an internal standard



Species concentrations versus time during long-duration test as measured by quasireference using Li^+/Li^0 as an internal standard

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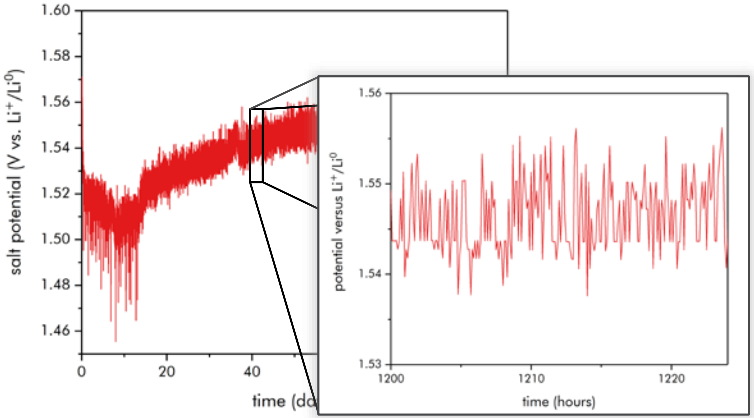

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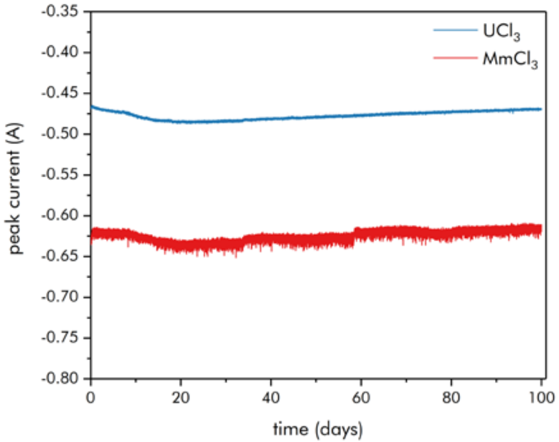

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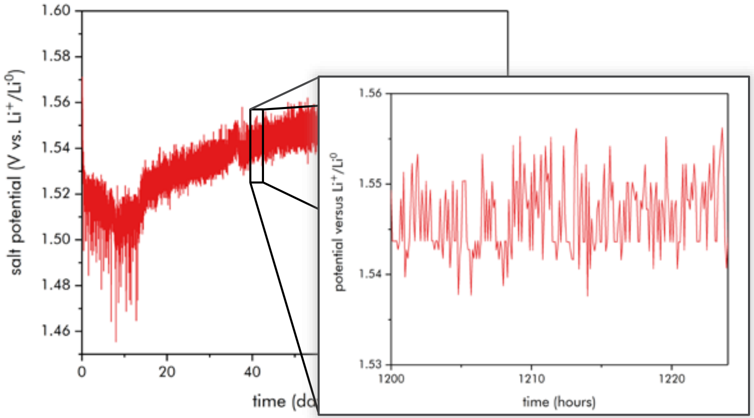

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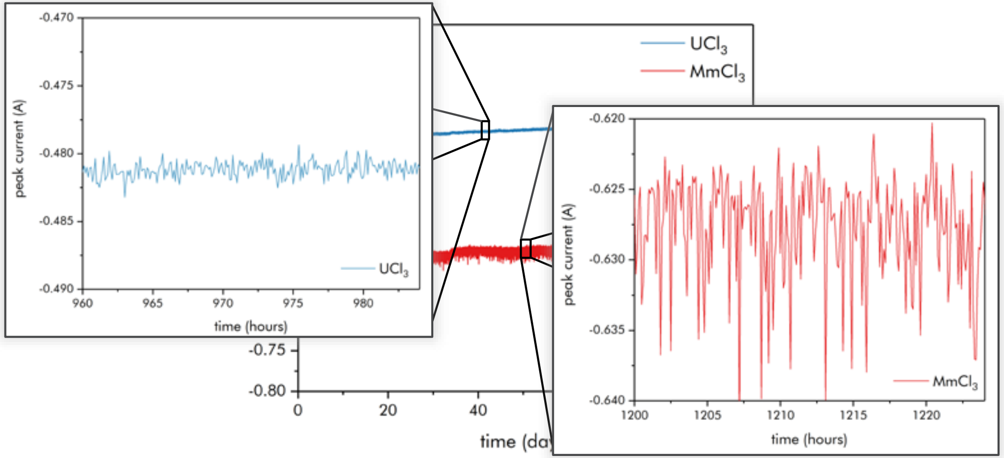

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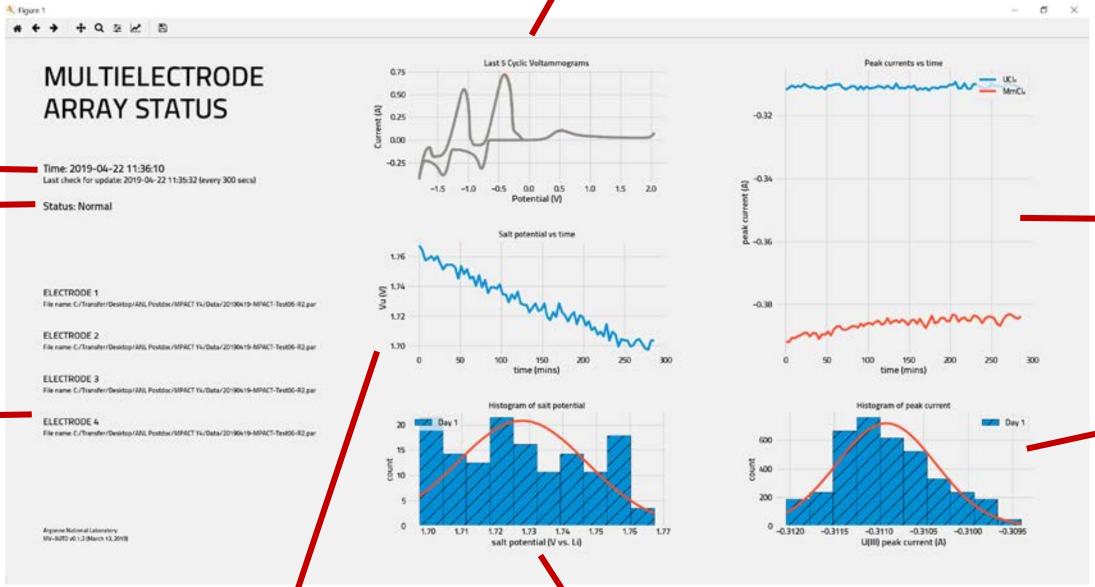
AUTOMATED ACQUISITION AND ANALYSIS



raw electroanalytical signals

experiment duration and most recent update time

species concentrations versus time

system status

histogram of daily concentration measurements

electrode status

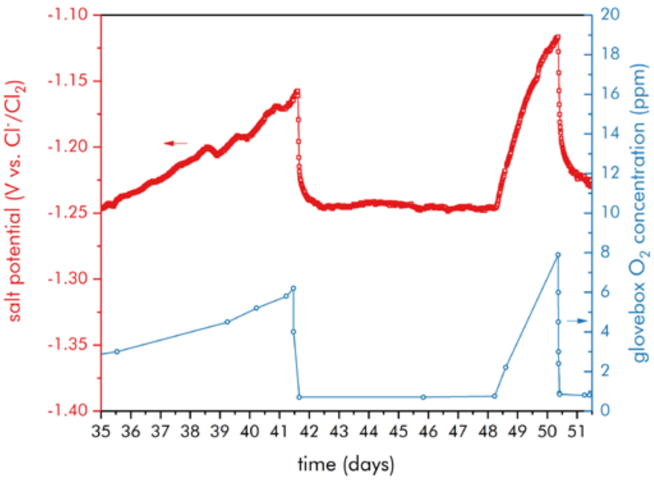
salt potential versus time

histogram of daily potential measurements

AIR INGRESSION MONITORING

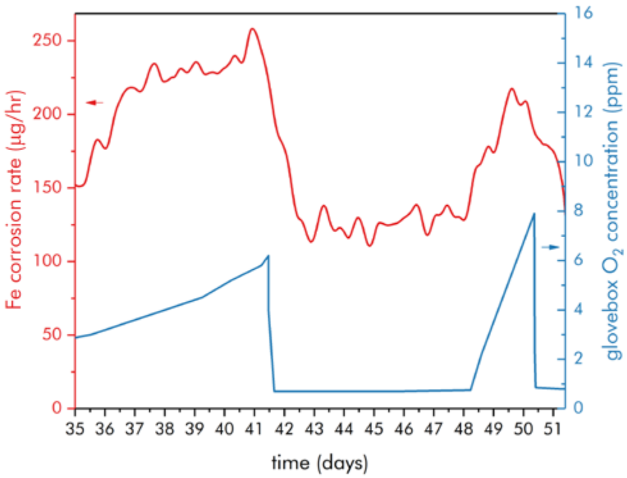
- A variety of realistic scenarios including air ingression tests have been performed to demonstrate the ability of the sensor to indicate off-normal conditions
  - Changes in the salt potential were immediately detected as impurities entered the salt
  - Increased corrosion rates could be calculated from the measurements and were highly correlated to the condition of the atmosphere

SALT REDOX POTENTIAL



Salt potential and glovebox O_2 concentration versus time

CORROSION RATES



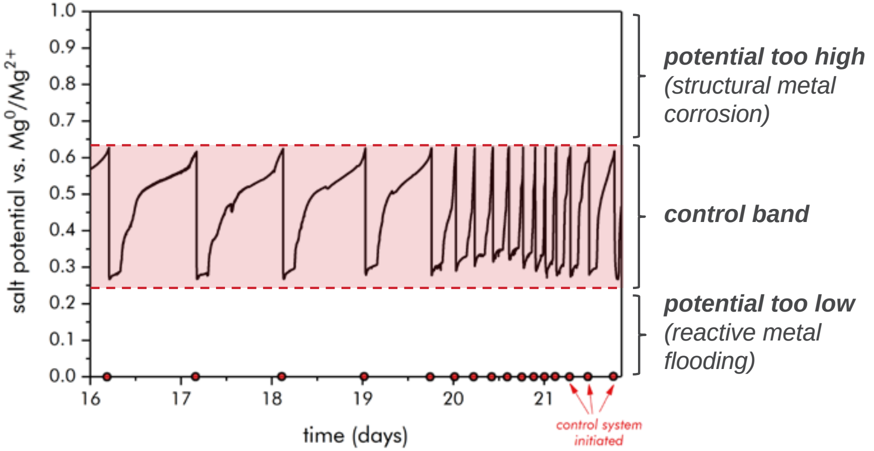
Fe corrosion rate and glovebox O_2 concentration versus time

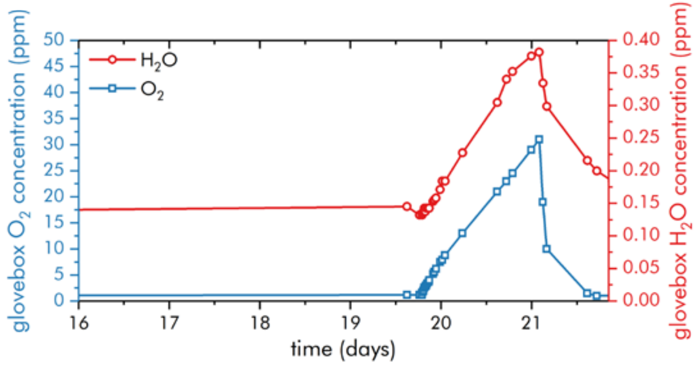
CORROSION MONITORING AND CONTROL

Operation of the salt monitoring capabilities can be used in tandem with corrosion control capabilities to maintain the salt in a healthy state

The salt redox potential was properly controlled during a trial 20+ day trial that included air ingression testing

- The rate of actuation of the corrosion control system increased in response to impurities in the glovebox atmosphere
- No corrosion products were detected by the voltammetry sensor during the course of the test





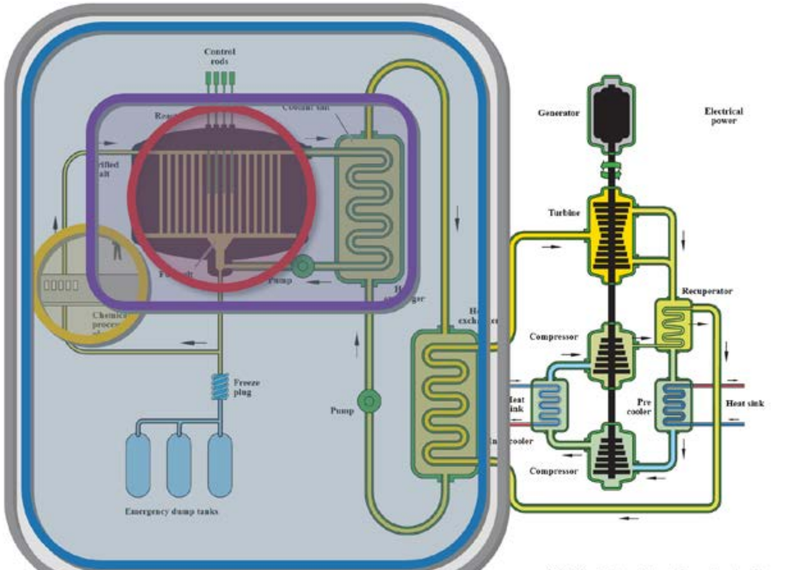
SENSOR FUSION

Electrochemical sensors provide a wide array of information, but there are some chemical measurements they cannot observe.

- Solids
- Off-gas
- Etc.

A variety of sensor technologies are under development across the national laboratory complex to close these gaps.

Fusion of all these sensing capabilities will provide a full picture of the MSR chemistry.



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One example of a complementary technology for corrosion monitoring are the eddy current corrosion sensors under development at ORNL.

Measurement Physics

- Eddy currents develop in corrosion zone of pipe wall as magnetic flux passes through

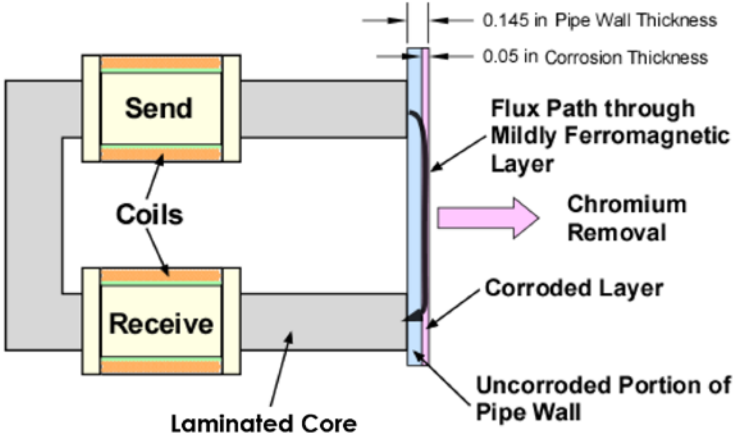
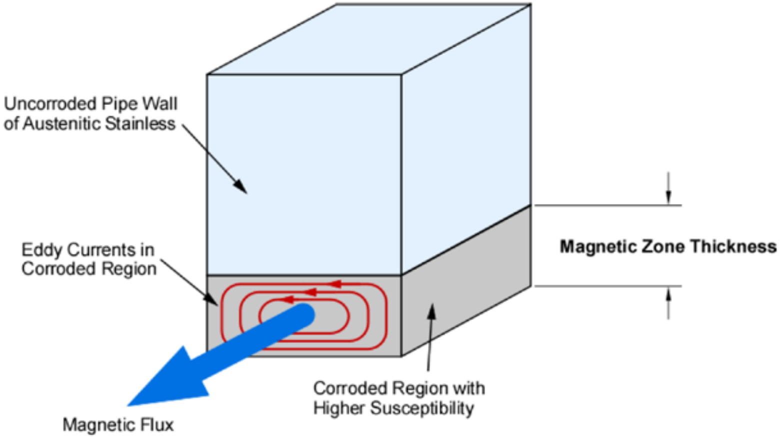
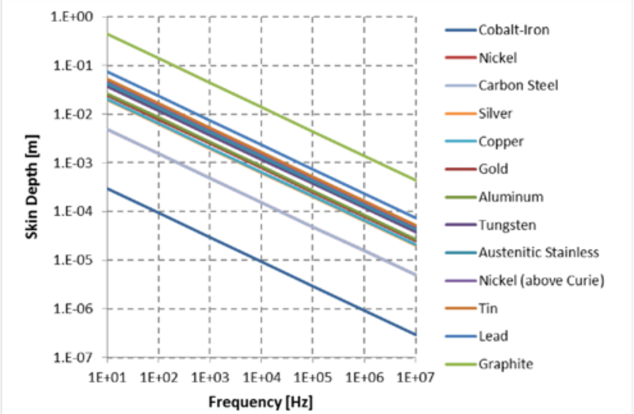


Illustration of flux path in corrosion zone of pipe wall

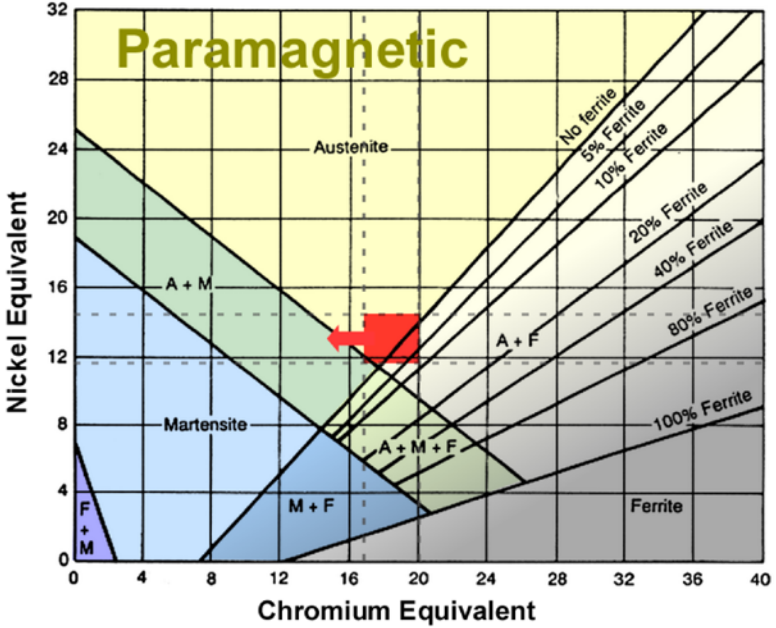


Eddy currents develop in corrosion zone of pipe wall



Comparison of material skin depth vs frequency

Measurement Physics



Schaeffler Diagram for predicting phase characteristic of stainless steel as a function of nickel and chromium[1]

- Magnetic properties of stainless steel associated with crystalline structure and compositions, austenite, martensite, and ferrite
- 304 stainless steel lies just at boundary of austenite
- As chromium is lost – 304 moves left into martensite region (magnetic)

[1] P. Guiraldeng and O. H. Duparc. The Genesis of the Schaeer Diagram in the History of Stainless Steel. Metallurgical Research and Technology, 114(613), 2017.

Measurement Physics / FY18 Prototype

- Initial low-temperature prototype
  - Built from modified power transformer
  - Concept proven using six corroded cube specimens
  - Minimal gap between sensor and sample ensures best performance
  - Samples show anisotropic properties
  - Implemented improvements to next testbed
  - Upper operating temperature limit of sensor: 120°C

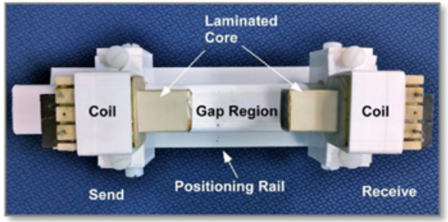


Image of low-temperature experimental test appartaus[2]

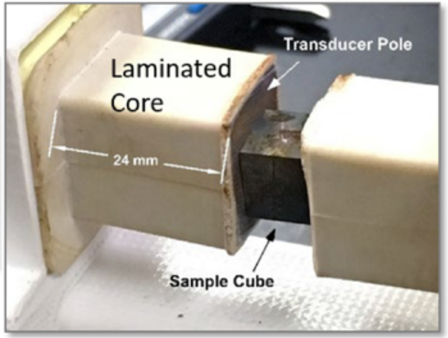
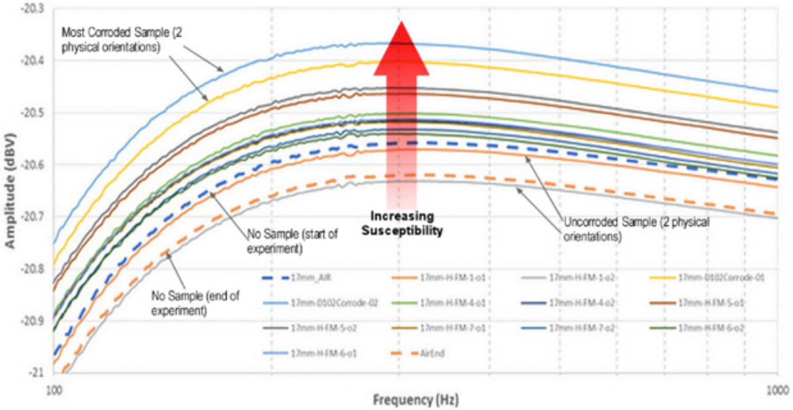


Image of low-temperature test with sample cube[2]



Testing results showing an increase in susceptibility as corrosion level increases with each test specimen

[2] David E. Holcomb, Roger A. Kisner, F. Kyle Reed, James Bates, and James R. Keiser. Development of an In-Situ Corrosion Monitor for Molten Salt Reactors. *Proceedings of NPIC&HMIT*, 2019.

TPOC: N. Dianne Bull Ezell, bullnd@ornl.gov

High-Temperature Sensor Design

- Transducer
  - Core lamination: HyperCo 50 Alloy
    - 70 laminations
  - Insulator: Boron Nitride
    - Sprayed on (thin layer)
    - Can use other materials for radiation concerns
  - Bobbins: Alumina
    - Insulator between lamination and wire
    - Minimize airgap
  - Coil wire: ceramic coated magnet wire

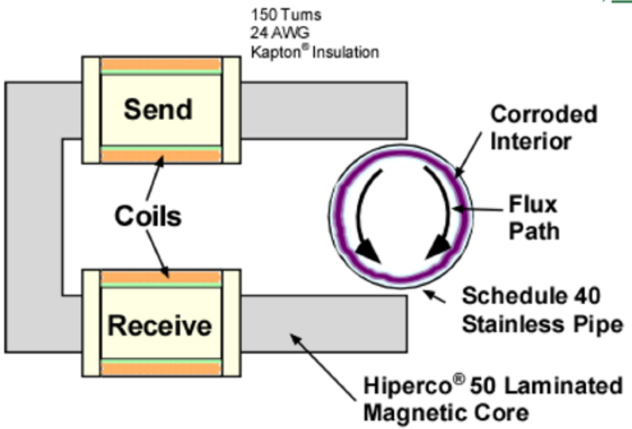


Illustration of corrosion monitoring sensor

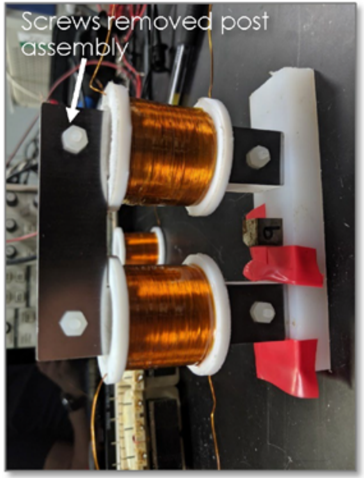
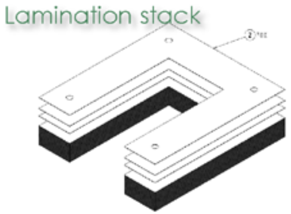


Image of prototype high-temperature corrosion monitoring sensor



CONCLUSIONS AND FUTURE WORK

Robust electroanalytical sensors have been demonstrated for durations longer than a year and a half. They provide high stability, longevity, and accuracy combined with very low uncertainty.

Future work will be directed toward:

- Application of the sensor to additional nuclear-relevant fluoride and chloride salts
- Shakedown testing in noisy EMI environments
- Standardization of sensor construction
- Forced convection studies

Sensor fusion will provide process monitoring capabilities for reactor control, safeguards, material accountancy, and corrosion control applications

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