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# Method for Redox Control with Continuous Electrochemical Measurements in MSRs

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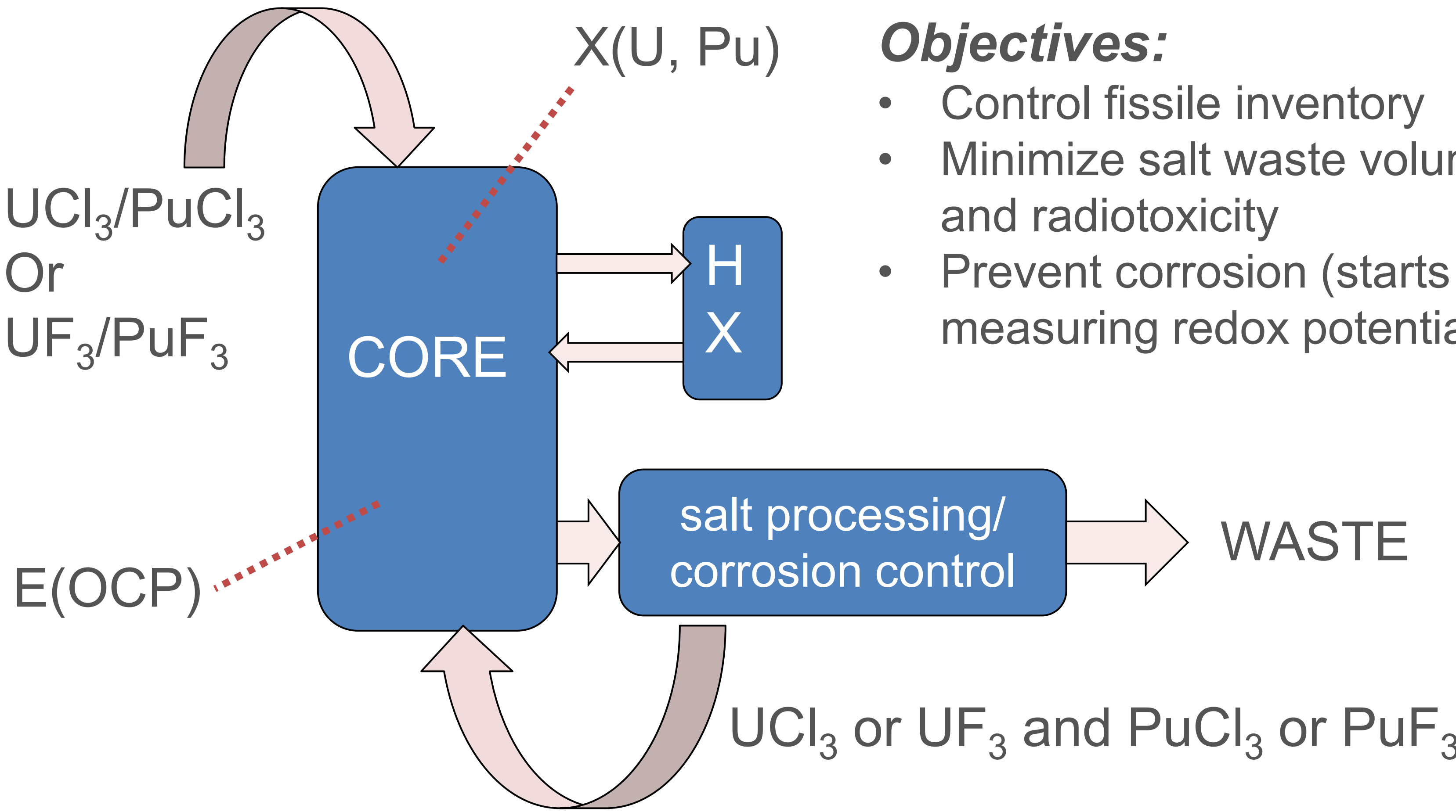
Nuclear Pyrometallurgy Laboratory

# Optimized Chemistry Control of Fuel Salt

***Objectives:***

- Control fissile inventory
- Minimize salt waste volume and radiotoxicity
- Prevent corrosion (starts with measuring redox potential)



# Reactions that increase Redox Potential

## Hydrolysis

$$H_2O + 2Cl^- \rightarrow 2HCl + O^{2-}$$

$$H_2O + Cl^- \rightarrow HCl + OH^-$$

$$H_2O + 2F^- \rightarrow 2\text{HF} + O^{2-}$$

$$H_2O + F^- \rightarrow \text{HF} + OH^-$$

## Salt Irradiation

$$^6LiF + n \rightarrow {}^4He + TF$$

$$UF_4 + n \rightarrow MF_x + yF_2$$

$$UCl_3 + n \rightarrow MCl_x + yCl_2$$

HCl/HF can cause oxidation or increase salt redox potential

HF/TF, $F_2$, and $Cl_2$ are all corrosive towards metals

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# Redox Buffer Options

These are our options

$$Zn + 2HCl = ZnCl_2 + H_2$$
$$Zr + 4HCl = ZrCl_4 + 2H_2$$
$$Mn + 2HCl = MnCl_2 + H_2$$
$$Ti + 2HCl = TiCl_2 + H_2$$

We also need a continuous, real time sensor to measure redox potential

## Chloride Series

| Element | Chloride Properties (500 C) | |
|---|---|---|
| | ΔG (kJ/mole) | Eo (V) vs. Ag/AgCl |
| Mo(III) | -172.2 | 0.302 |
| Ag(I) | -86.5 | 0.000 |
| Ni(II) | -188.3 | -0.079 |
| U(IV) | -789.9 | -0.053 |
| Co(II) | -206.3 | -0.172 |
| Sn(II) | -226.3 | -0.276 |
| Fe(II) | -243.4 | -0.365 |
| Pb(II) | -245.8 | -0.377 |
| Cd(II) | -270.8 | -0.507 |
| Cr(II) | -298.3 | -0.649 |
| Zn(II) | -303.6 | -0.677 |
| Al(III) | -540.0 | -0.969 |
| Pu(IV) | -739.7 | -1.020 |
| Mn(II) | -378.7 | -1.066 |
| Ti(II) | -389.4 | -1.121 |
| Zr(IV) | -780.9 | -1.127 |
| U(III) | -698.3 | -1.516 |
| Th(IV) | -957.2 | -1.584 |
| Np(III) | -729.0 | -1.622 |
| Cm(III) | -767.0 | -1.753 |
| Mg(II) | -516.7 | -1.781 |
| Pu(III) | -786.9 | -1.822 |
| Am(III) | -795.3 | -1.851 |
| Y(III) | -817.1 | -1.926 |
| Gd(III) | -818.5 | -1.931 |
| Nd(III) | -852.7 | -2.049 |
| Ce(III) | -861.5 | -2.080 |
| Pr(III) | -866.0 | -2.095 |
| La(III) | -880.9 | -2.147 |
| Ca(II) | -675.4 | -2.603 |
| Na(I) | -357.9 | -2.813 |
| Li(I) | -344.8 | -2.677 |
| Sr(II) | -706.8 | -2.766 |
| Rb(I) | -361.4 | -2.849 |
| K(I) | -362.6 | -2.861 |
| Cs(I) | -366.6 | -2.903 |
| Ba(II) | -733.2 | -2.903 |

Increasing resistance to corrosion

Structure

Fuel

Base salt

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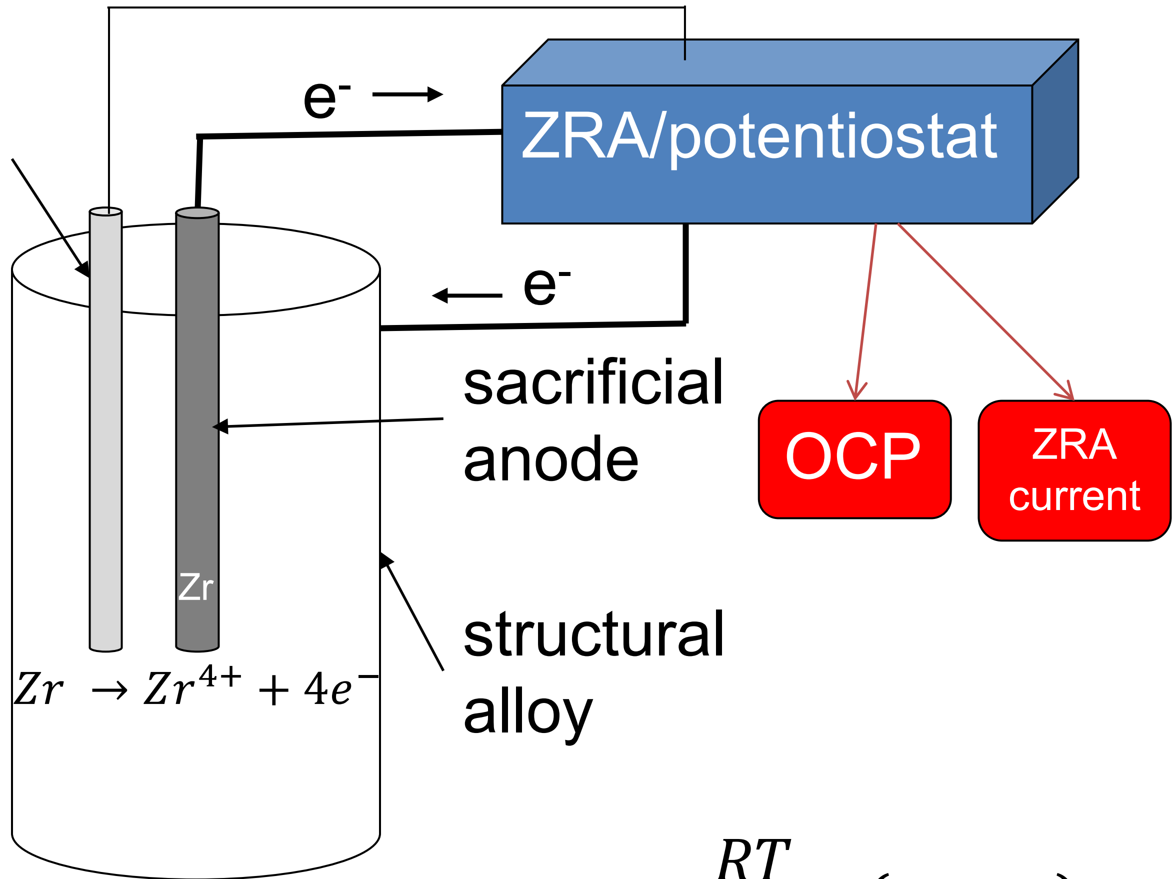
# Proposed Technology for MCFR

*Buffer and measure the redox potential, while measuring rate of corrosion of anode.*




$$Zr \rightarrow Zr^{4+} + 4e^-$$

$$4e^- + \left(\frac{4}{n}\right) M^{n+} \rightarrow M$$

$$E_{eq} = E^{o}_{ZrCl_4} + \frac{RT}{4F} ln\left(a_{ZrCl_4}\right)$$

# Redox Buffering Versus $NiCl_2$

$Zr + 2NiCl_2 = ZrCl_4 + 2Ni$ ← Spontaneous

Galvanic Coupling →

$Zr = Zr^{4+} + 4e^-$ (Zr rod) ↷ $e^-$

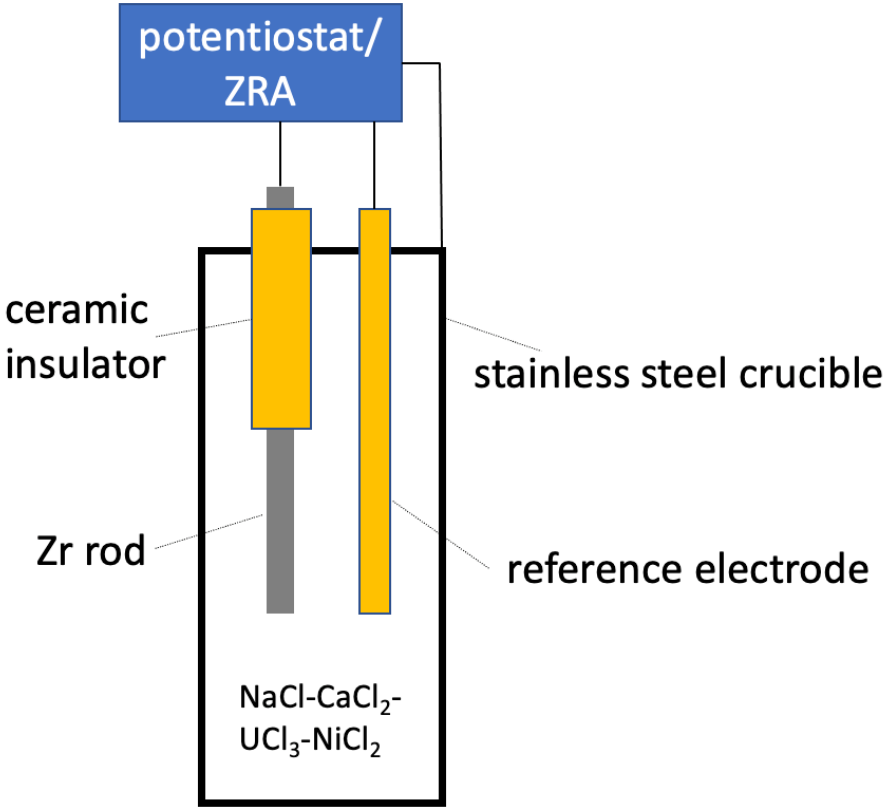
$2Ni^{2+} + 4e^- = 2Ni$ (SS crucible)

## Key Components:

- zero-resistance ammeter (ZRA) to measure rate of Zr oxidation
- Stable thermodynamic reference electrode

# ZRA Experimental Setup

- ZRA test setup
  - $NaCl-CaCl_2-UCl_3$ (5.5 wt% U)
  - Galvanic coupling between Zr rod and SS crucible
  - Ag/AgCl RE encased in mullite
  - T = 600°C
  - Gamry Reference 600+ potentiostat
- Inert Ar glovebox
  - (<10 ppm $O_2/H_2O$)
- $NiCl_2$ added to spike redox potential

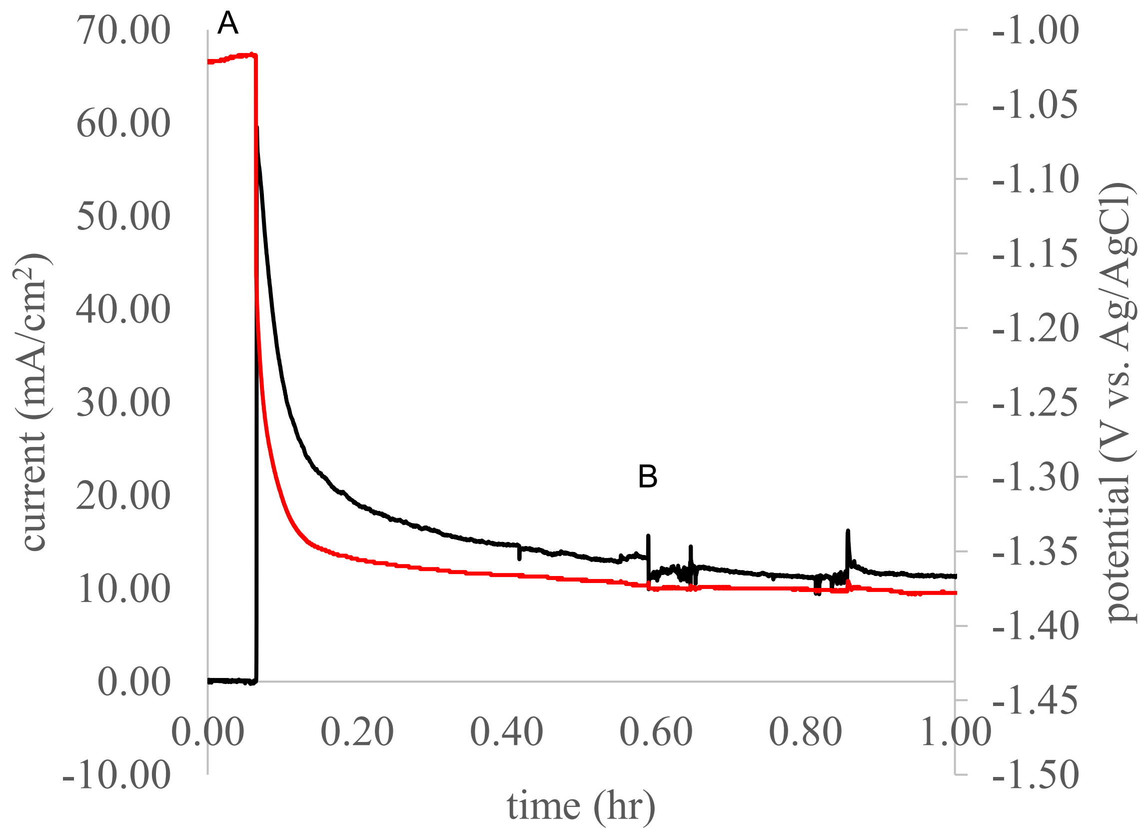





Hamilton et. al. JRNC 2022.

# ZRA Test with $NiCl_2$ added pre-melt

*Positive current corresponds to Zr oxidation, since it was connected as the WE.*




**A:** Insertion of Zr rod (WE), **B:** attempted addition of $NiCl_2$



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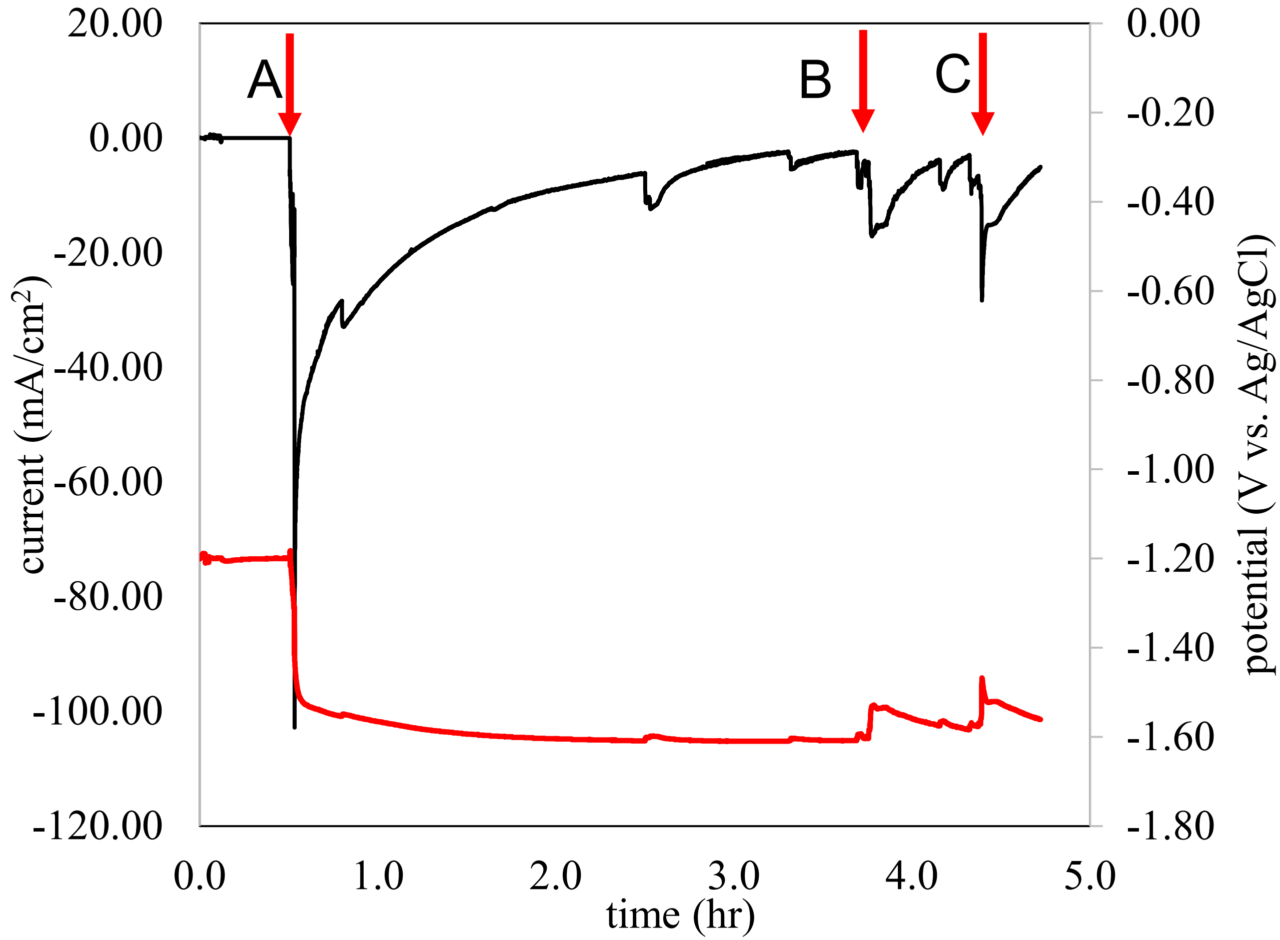
# ZRA Test with In-Situ $NiCl_2$ Addition

*Negative current corresponds to Zr (CE) oxidation*




**A:** Insertion of Zr rod (CE), **B:** 1st addition of $NiCl_2$, **C:** 2nd addition of $NiCl_2$

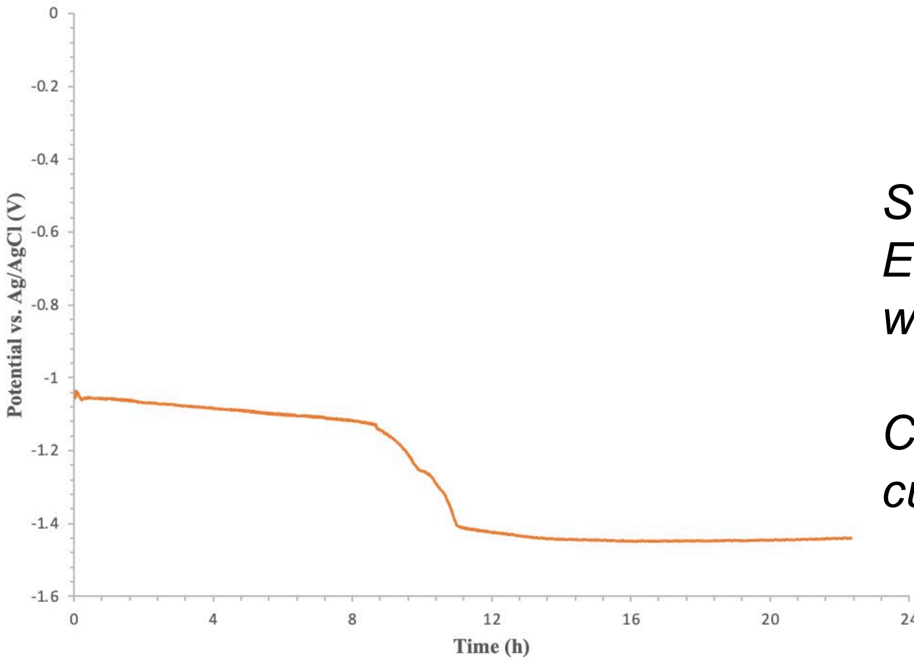


Hamilton et. al. JRNC 2022.

# What about using U metal as the anode?

$$U \rightarrow U^{3+} + 3e^-$$

$$Fe^{2+} + 2e^- \rightarrow Fe$$



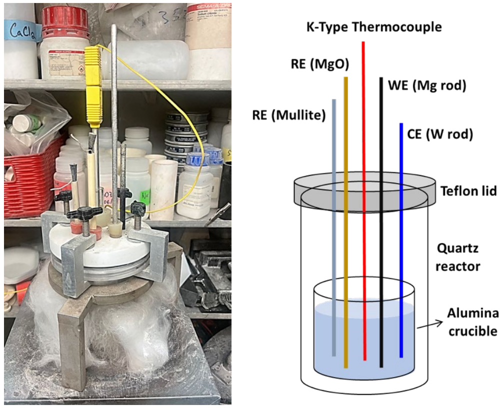

*Started with LiCl-KCl-$FeCl_2$ (4.8 wt%)*
*Ended with LiCl-KCl-$UCl_3$ (5.2 wt% U, 0.1 wt% Fe)*

*Could not measure galvanic corrosion current in this setup.*

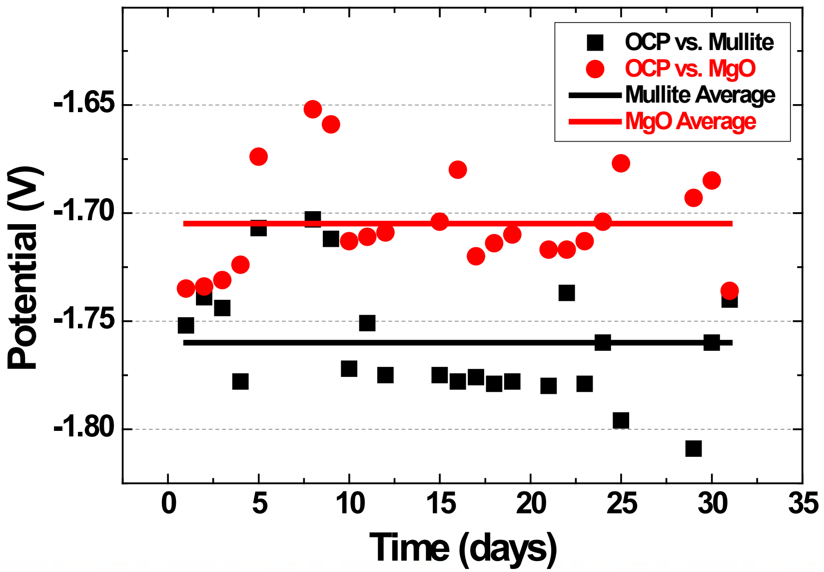
# Chloride Reference Electrodes

MgO

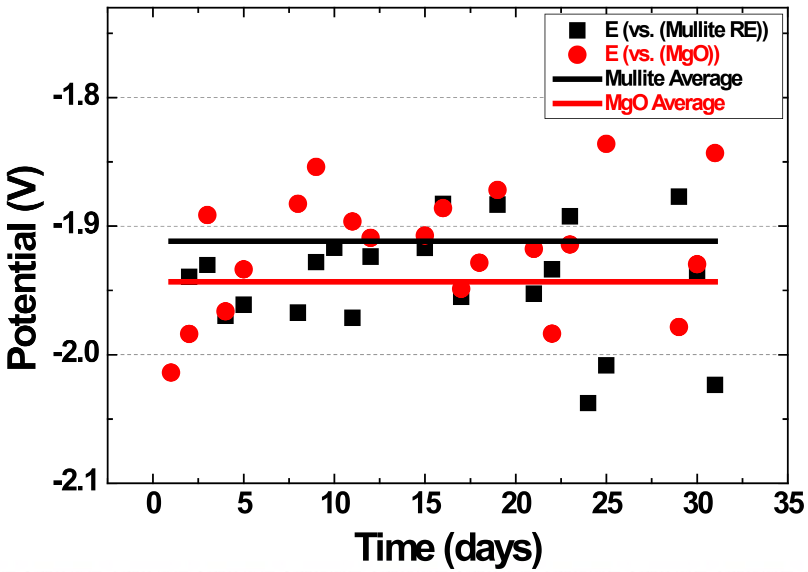
Mullite




## OCP




## The onset E of $Mg^{2+/0}$ reduction






Choi et. al. MARC-XII (2022)

# Ni/NiF$_2$ and Ag/AgF HTREs for Molten Fluoride Salts

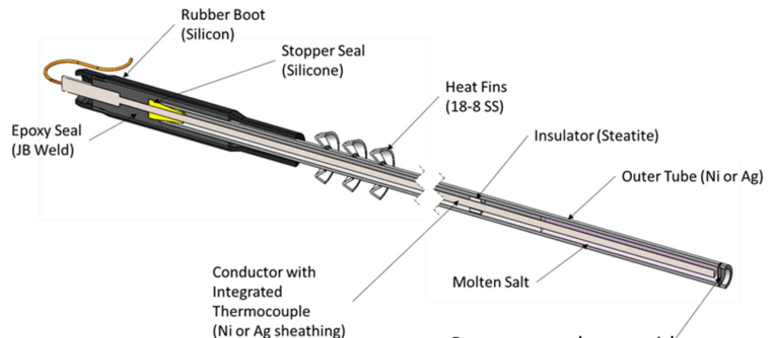
- Mullite, quartz, and alumina membranes are good for chloride melts, but are not compatible with FLiNaK
- HiFunda has teamed with INL and the UofU to develop, demonstrate, and commercialize standardized HTREs
  - Phase II SBIR, "Stable High-Temperature Molten Fluoride Salt Reference Electrodes"
  - Corrosion monitoring for nuclear, CSP, and other applications
- Three-fold HTRE functionality:
  1) Stable thermodynamic reference potential
  2) Integral temperature sensor
  3) Redox or open circuit potential (OCP) sensor
- HTRE features can be customized (reference wire and salt, length, membrane) for different applications

Mullite

Quartz

Alumina

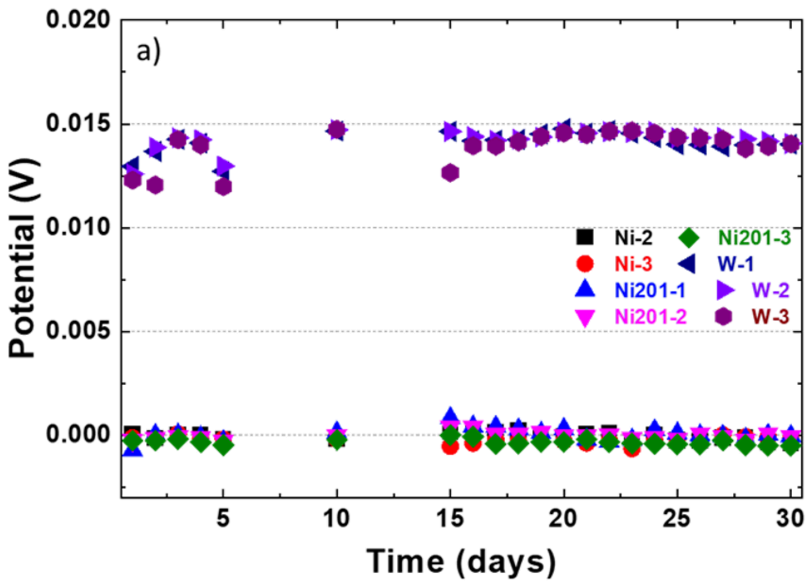
Sample images before/after 500-hours corrosion test at 750°C in FLiNaK
Top image is pretest and bottom image is posttest

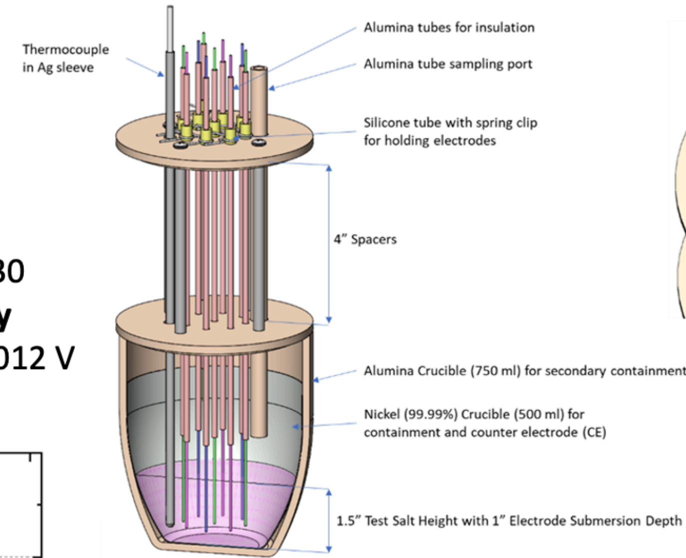


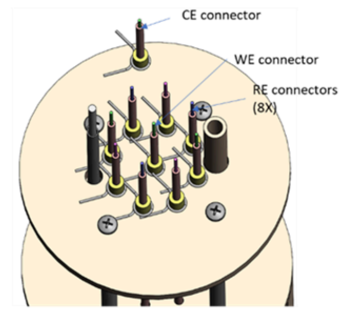

Custom membrane with similar resistance, and pressure drop to graphite membrane

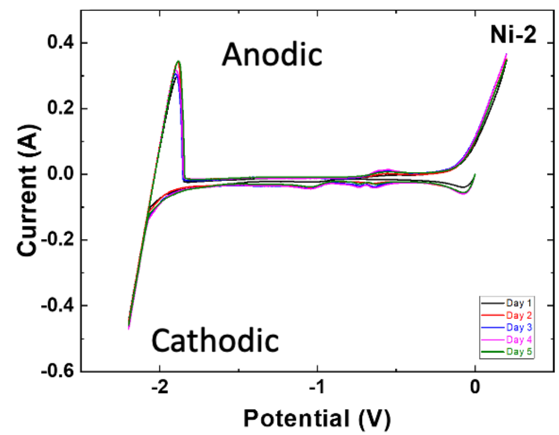
# Comparison of OCPs and CVs in FLiNaK/$NiF_2$ at 550 °C

- Testing performed to determine repeatability of $NiF_2$ reference compartment conditions
- Average OCP of Ni and Ni201 is -0.12 ± 0.20 mV
- OCP drift for the Ni and Ni201 electrodes during the 30 days of testing is very low ranging from **-7 to 5 µV/day**
- Average $E_{Li^+/Li}$ for all the nickel electrodes is -2.06 ± 0.012 V while average $E_{Li^+/Li}$ drift is 970 µV/day



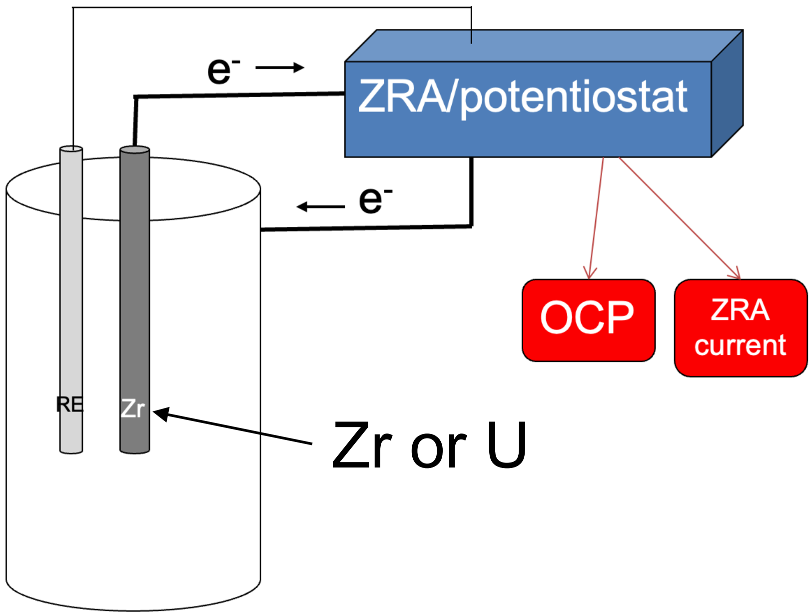




$Ni/NiF_2$ HTRE, WE= 1.5 mm W, CE= 1.5 mm W, 100 mV/s

# Summary

- Redox buffer using Zr or U metal
- Twin electrochemical measurements (OCP & ZRA)
- Tested successfully using oxidants $NiCl_2$ and $FeCl_2$
- RE's made of mullite and low density MgO exhibit excellent stability in Cl-salts
- HiFunda is working on a F-compatible RE




***Further Work Needed:***

- Test with better surrogate Cl-salts
- Test with more oxidants
- Test with F-salts with new RE's
- Compare Zr/U to inert WE materials

# Acknowledgments

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