NEAMS Safe-Seps IPSC Development: Fuel Dissolution and E-chem Modeling

Candido Pereira, James Willit, and James Jerden

Argonne National Laboratory

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Model for Used Fuel Dissolution

2010 Tasks

- Literature review on the dissolution of oxide and mixed oxide fuels
- Use commercial code to develop preliminary model for the dissolution of oxide and mixed oxide fuels

Topics

- Thermodynamics
- Kinetics Model
- Preliminary Results
- Future Development

Modeling Methodology-Thermodynamics

Thermodynamic database

- Calculations implemented using the code "The Geochemist's Workbench®", Professional Release 8.0 (GWB)
  - The GWB uses a Gibb's free energy minimization technique to determine the equilibrium state of the system of interest.
  - Thermodynamic/kinetic database used for modeling with GWB was a version of the database, "thermo.com.V8.R6.full" (Wolery and Daveler, 1992)
    - Thermodynamic data for key species were added to the database from a number of sources

Activity Coefficients

- Activities of electrolyte species are calculated using two different methods
  - Extended form of the Debye-Huckel Equation ("B-dot" Equation)
  - Harvie-Møller-Weare implementation of the "Pitzer Equations".
    - The Debye-Huckel activity model was generally used to generate activity diagrams and for kinetic calculations due to the lack of data needed to use the "Pitzer Equations"

Modeling Methodology-Redox Chemistry

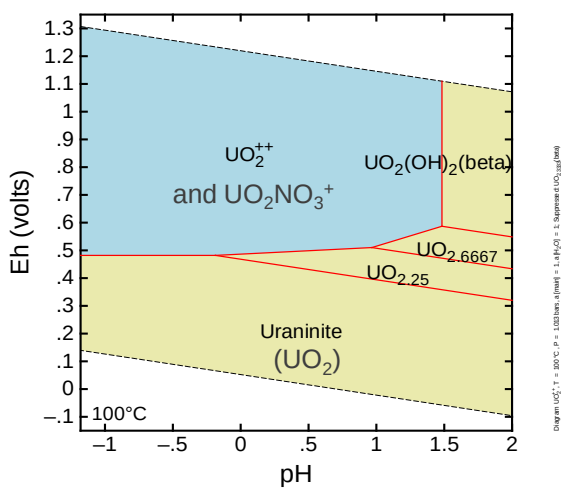
Redox speciation

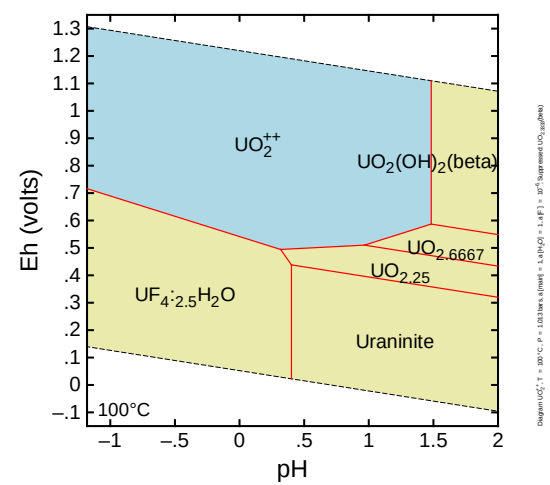
- Redox speciation (E_h - pH or *Pourbaix)* diagrams identify the key chemical characteristics of the systems of interest,.
  - E_h is the oxidation/reduction potential (in volts) of an aqueous solution relative to the standard hydrogen electrode:
    - For the half reaction: aA + bB + ne$^-$ = cC + dD

$$E_h = E^o + \frac{RT}{nF} \ln \frac{(A)^a (B)^b}{(C)^c (D)^d}$$

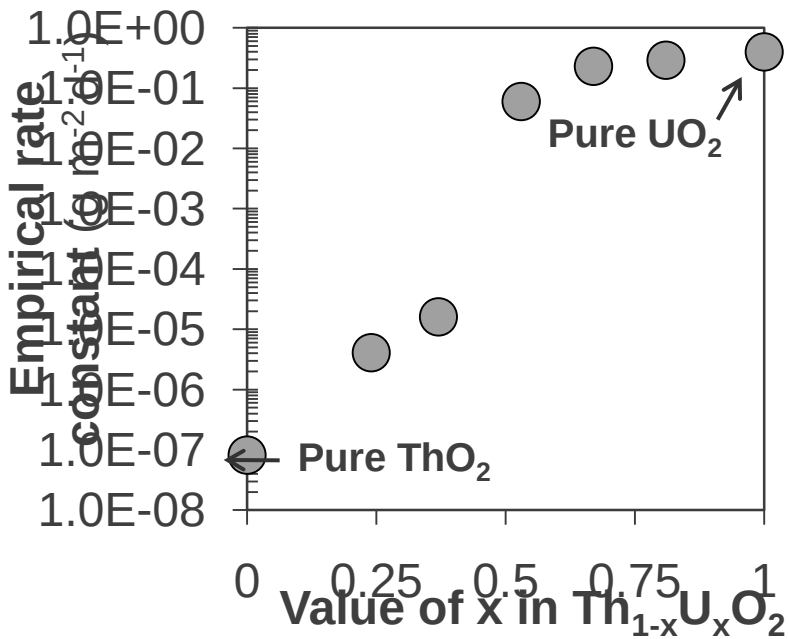
E_h – pH diagrams for the H-O-U and H-O-U-F systems at 100°C

[UO_2]= 1.0 m and [F^-]= 10^{-6} m





Basis of Model for Spent Fuel Dissolution



- Empirical rate constants for $Th_{1-x}U_xO_2$ in dilute nitric acid (from G. Heisbourg et al., *J. of Nuclear Materials*, 335, 5–13)

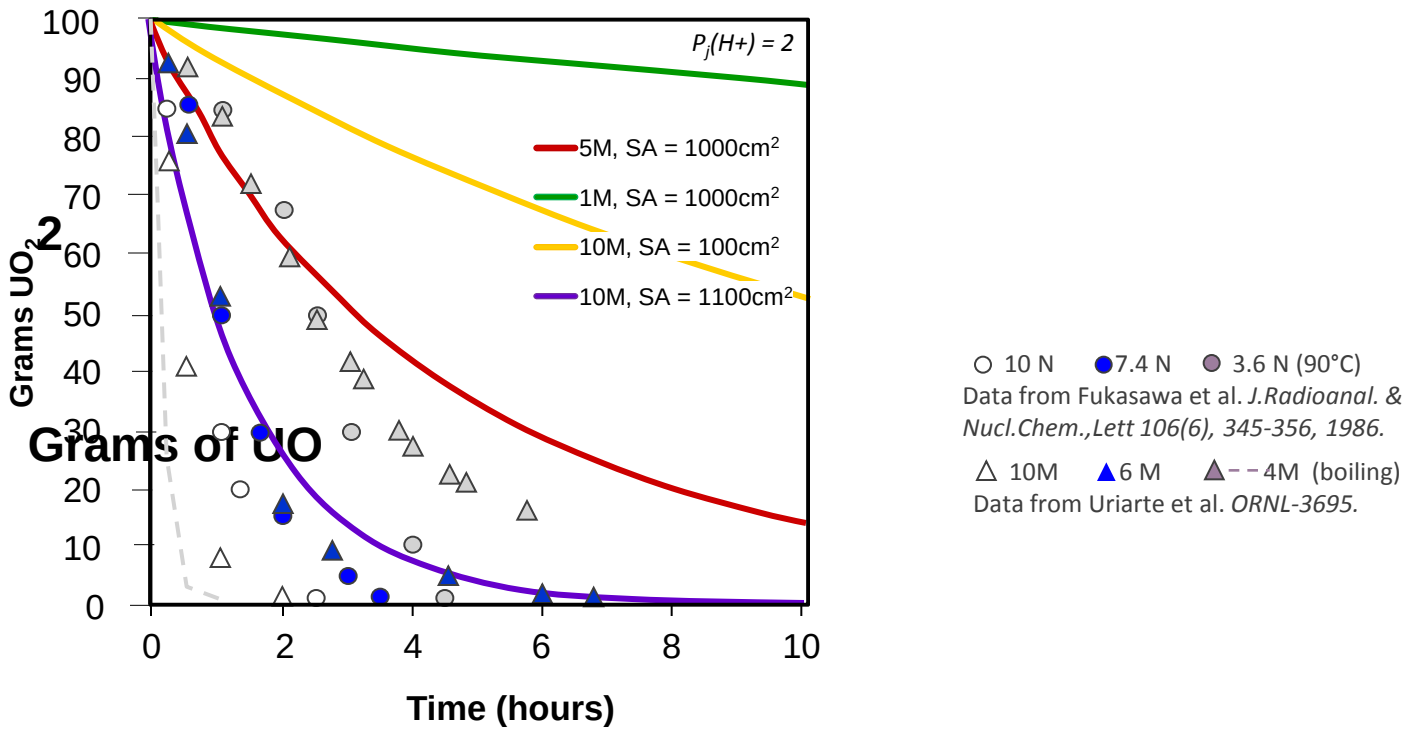
Model Basis

$$\frac{dC_i}{dt} = \frac{SA}{V} v_i k_+ \prod^{j} (a_j)^{P_j} \left(1 - \frac{Q}{K}\right)$$

$\frac{dC_i}{dt}$	Change in concentration of ion (i) with time
$\frac{SA}{V}$	Surface area per volume of solution in contact with solid
v_i	Stoichiometric factor (moles (i) in solid)
k_+	Rate constant
(a_j)	Activity of species that promote or inhibit dissolution
P_j	Power of species (j) in the rate law
$\left(\frac{Q}{K}\right)$	Reaction quotient / equilibrium constant (saturation state)

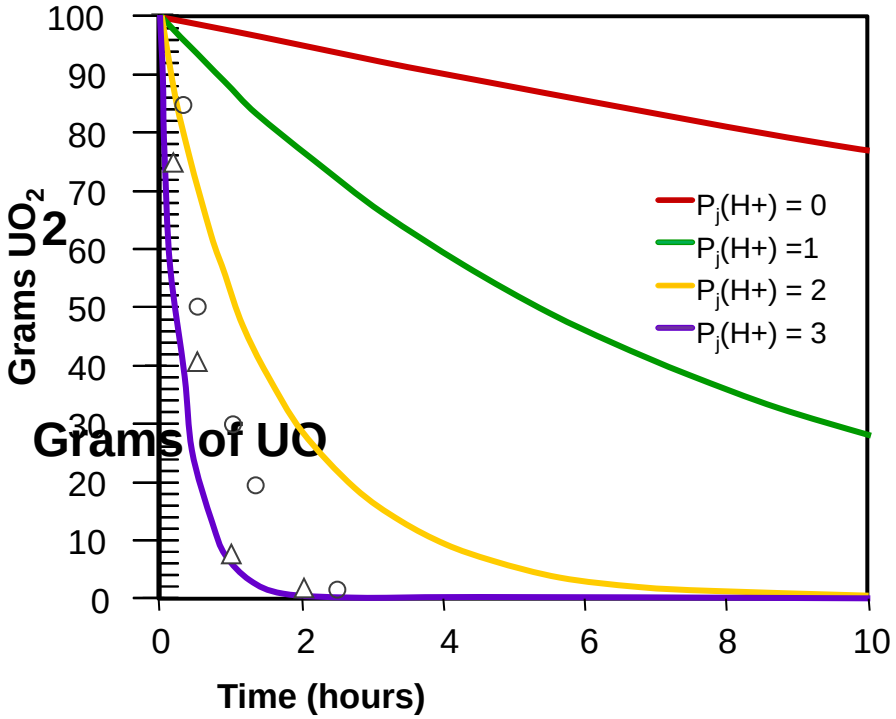
Initial Results for UO_2 at Different Nitric Acidities

- Initial results for the dissolution of pure urania show impact of acid concentration and initial surface area



Effect of H^+ Activity Order on Dissolution Time

- Initial results examining the kinetics of the dissolution of pure urania demonstrate a strong effect with selection of H^+ activity order

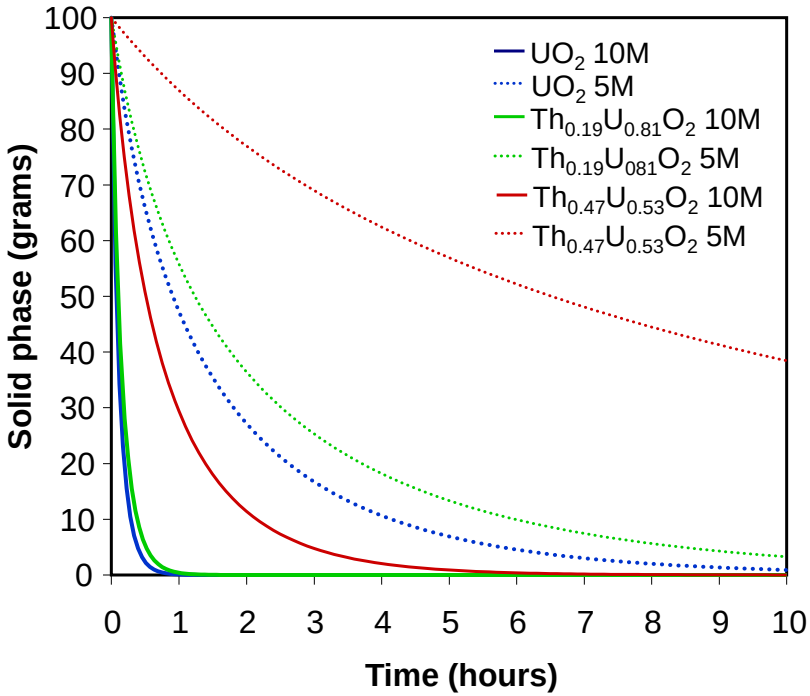


○ 10 N (90°C)
Data from Fukasawa et al. *J.Radioanal. & Nucl.Chem.,Lett 106(6), 345-356, 1986.*

△ 10M (boiling)
Data from Uriarte et al. *ORNL-3695.*

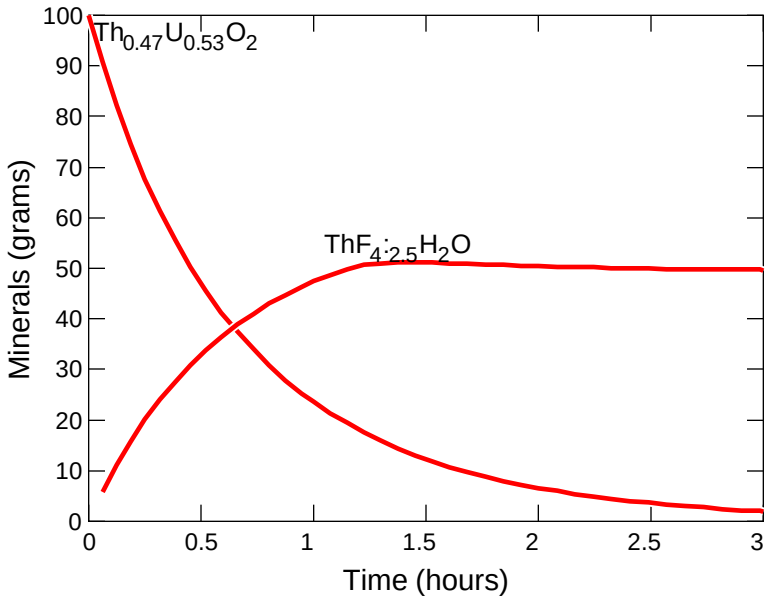
Effect of U/Th Composition on Dissolution Time

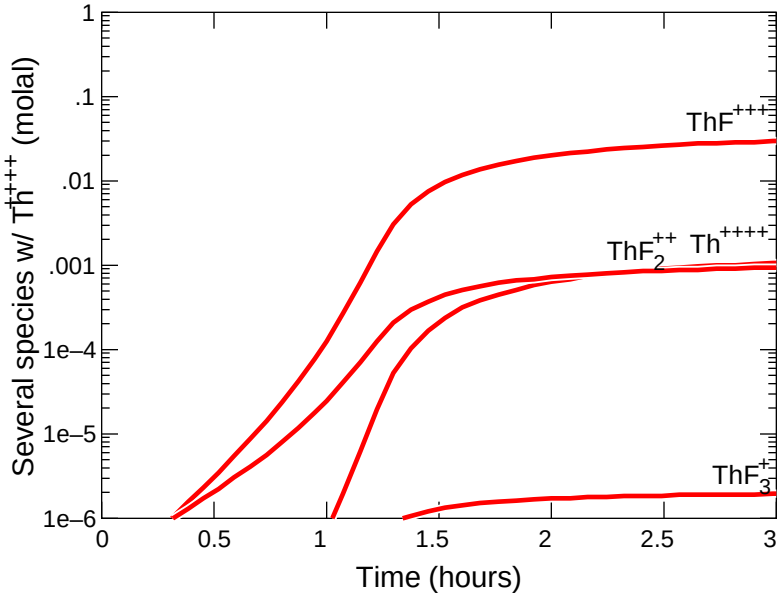
- Initial application of the rate equation the dissolution rate of uranium oxide and thoria-urania mixed oxides in nitric acid were calculated
  - Results are preliminary as not all of the parameter values have been established: notably the values for the activities, (a_j), of species that promote or inhibit dissolution.



Model for spent fuel dissolution-HF Complexation

- The model accounts for complexation and the precipitation of secondary phases.
  - Examples for a run in which a urania-thoria phase was dissolved in nitric acid in the presence of 0.5M HF.
- The model can be used to predict HF concentrations that will enhance thoria dissolution kinetics without precipitating thorium fluoride.





Future Work on Spent Fuel Dissolution Modeling

- Refine model by incorporating additional chemical phenomena (e.g., precipitation, redox kinetics, solid/solution interface)
- Extend the model to account for other fuels of interest.
  - Refine model to simulate the dissolution of urania-plutonia and lanthanide bearing uranium oxide spent fuel
  - Refine model to account the influence of fission and activation products
- Develop a mechanistic understanding for reduction in dissolution rates for uranium oxide solid solutions and annealed uranium oxide fuels
  - Incorporate mechanisms into dissolution model
    - Removal of non-U cations
    - Semi-conducting properties of solid solutions may affect the rate of electron transfer and oxidation
    - Preferential dissolution preferentially along crystal defects
- Develop interface between spent fuel dissolution model and process/plant-scale IPSC models

Non-equilibrium model of U-TRU Co-deposition

FY10 Tasks

- Develop non-equilibrium model for U-TRU co-deposition at solid cathode incorporating mass transfer effects, and validate experimentally

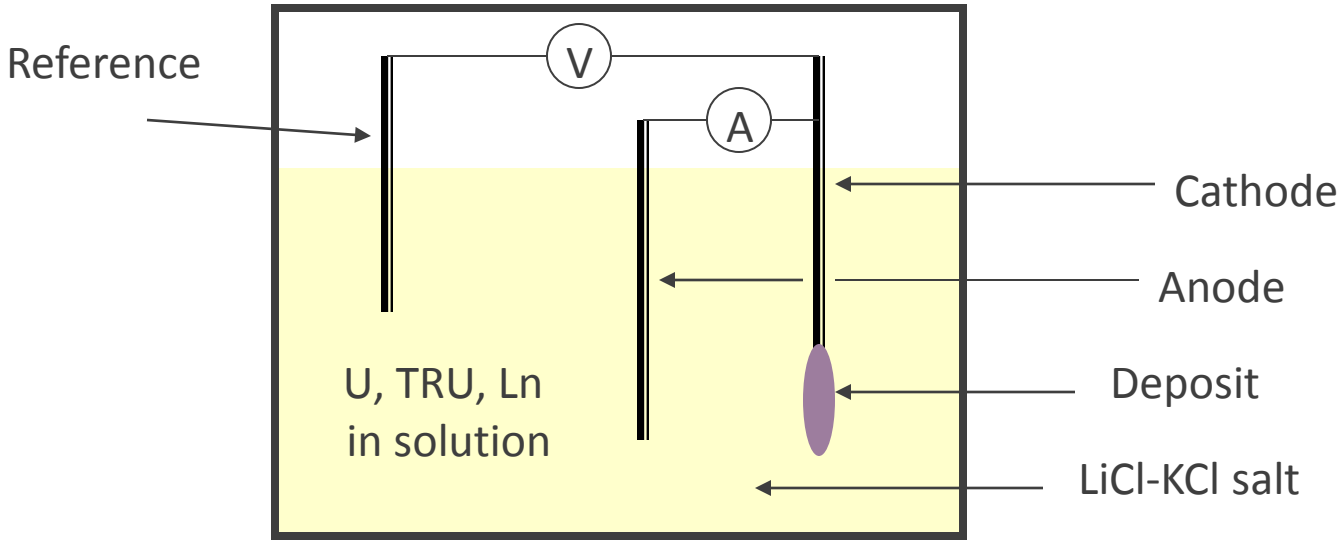
Topics

- Co-deposition model overview
- Experimental validation
- Further development

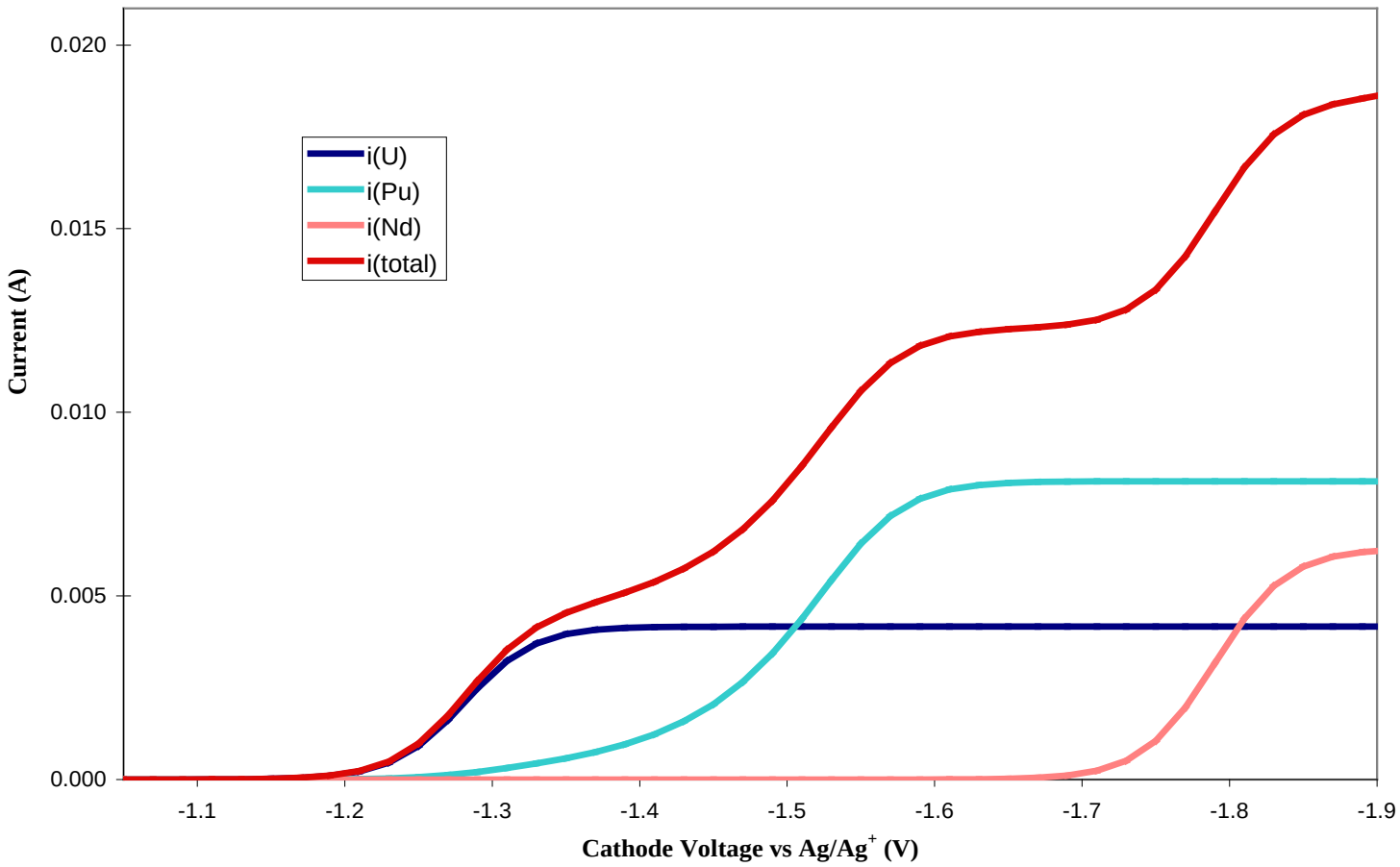
U-TRU Co-deposition Model

- Model deposition of metals at cathodes as a function of applied voltage
  - Spreadsheet-based model with links to thermodynamic data package
  - Deposition is tracked by changes in current with applied voltage
    - Metal is deposited at solid cathode as a solid solution
    - Co-deposition occurs when current density exceeds the limiting current density for uranium electrodeposition

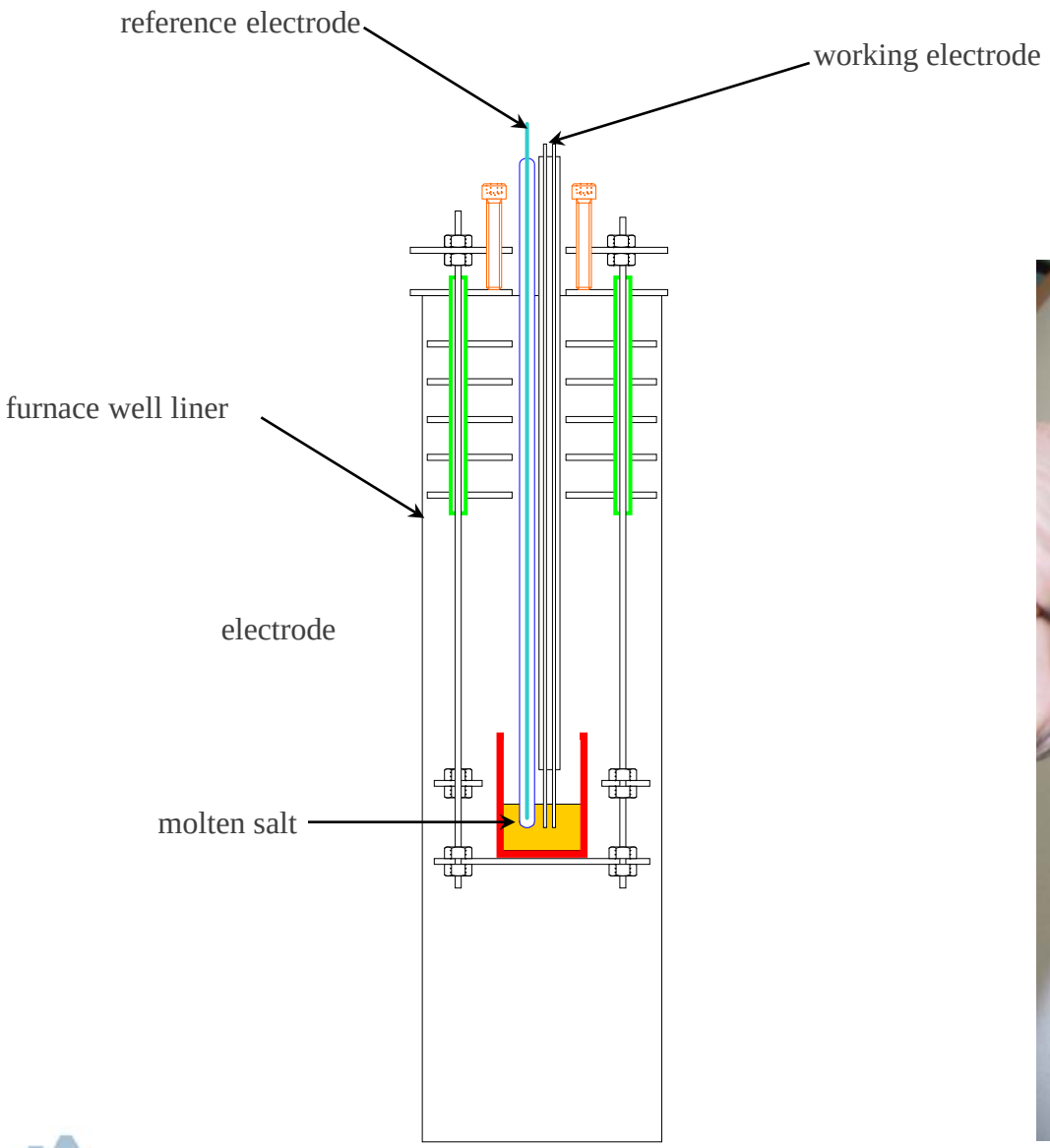
$$i_M = \frac{i_{M,\lim}}{1+\exp\left\{\ln\left(\frac{i_{M,\lim}}{i^o_{cath}}\right)+\frac{\alpha nF}{RT}\cdot\left[\left(E_{cath}-E^{\circ'}_M\right)+\frac{RT}{F}\ln\left(\frac{x_M}{x_{tot}}\right)\right]\right\}}$$



Calculated Current vs. Potential Plot

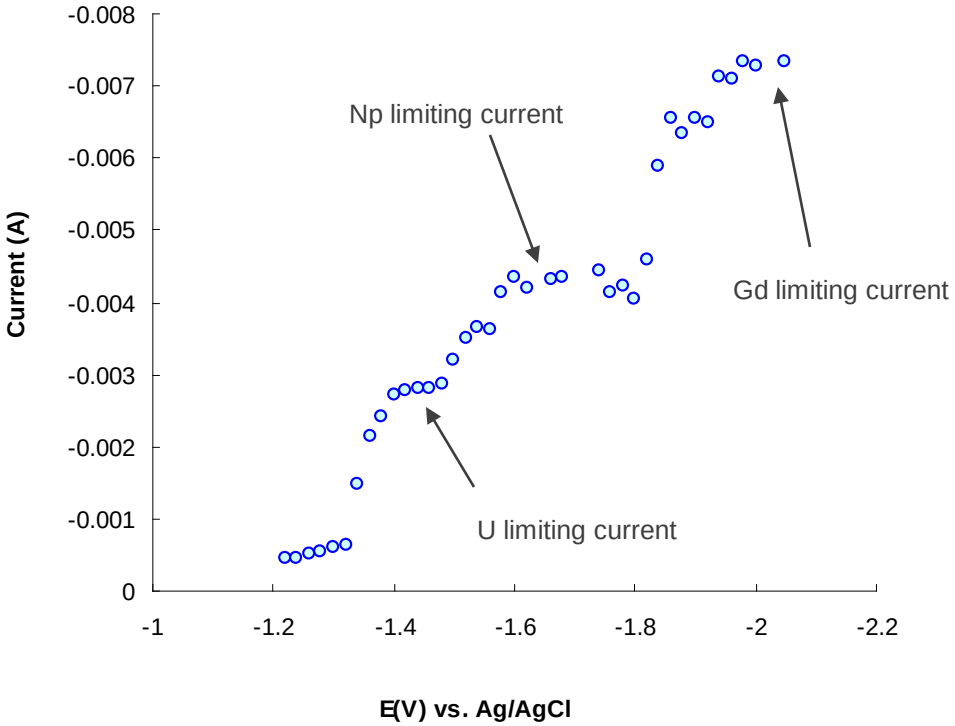


Electrochemical Cell



Experimental Validation of Non-Equilibrium Model of U-TRU Co-Deposition

- U-TRU co-deposition at a solid cathode occurs only when current density exceeds the limiting current density for uranium electrodeposition
- Non-equilibrium condition with multiple concentration gradients at the cathode/molten salt interface
  - Modeled using a "partial current" approach developed for electroplating
- Steady state current vs. cathode potential measurements exhibit the multiple plateaus predicted by the non-equilibrium model



Understanding the Morphology of the Deposit by Understanding Nucleation Phenomena

- Growth of the co-deposit occurs as a competitive process between growth at nucleation sites and creation of new nucleation sites.
- These competitive processes are affected by concentration of depositing species, cathode potential, and current density.
  - Large crystals form when electrodeposition is dominated by growth on a limited number of nucleation sites
  - Small crystals form when electrodeposition is dominated by continuous formation of new nucleation sites.
- Develop a model that predicts both composition and morphology (crystal size) of the electrode co-deposit as a function of composition and deposition conditions.

FY-11 Tasks

- Develop a refined electrodeposition nucleation model
  - Predicts composition of deposit
  - Includes nucleation behavior as a function of composition of the electrodeposit and electrodeposition conditions.
- Develop an initial model of electrorefiner operations that can be integrated into the NEAMS IPSC framework
  - Includes anodic dissolution, as well as cathodic behavior

Intermediate-term Pyrochemical Separations Modeling

- Electrochemical Cells
  - Initial framework for integrated electrochemical cell simulation capturing salient cell phenomena for electrorefining and electroreduction processes
    - Map current distribution in cell
    - Identify concentration of ionic species in electrolyte, at anode and at cathode
    - Elucidate process reaction kinetics
- Thermodynamic Properties
  - Initial model development describing thermodynamic activity of relevant species based on measured or predicted data
  - Build corresponding thermochemistry database to support model development
- Transport Properties
  - Review and evaluate existing correlation models for relevant transport properties
  - Develop initial model from review to predict transport parameters
- Reaction Mechanisms
  - Evaluate and adapt existing electron transfer reaction mechanisms for electrorefining process
  - Develop initial framework for electron transfer reaction mechanisms occurring in electroreduction