



A Method for Determining Deposition Rates in an Electrorefiner Using Electrode Potentials

D. S. Rappleye, M. S. Yim, R. M. Cumberland

2012 International Pyroprocessing Research Conference
August 26 – 29, 2012
Fontana, WI



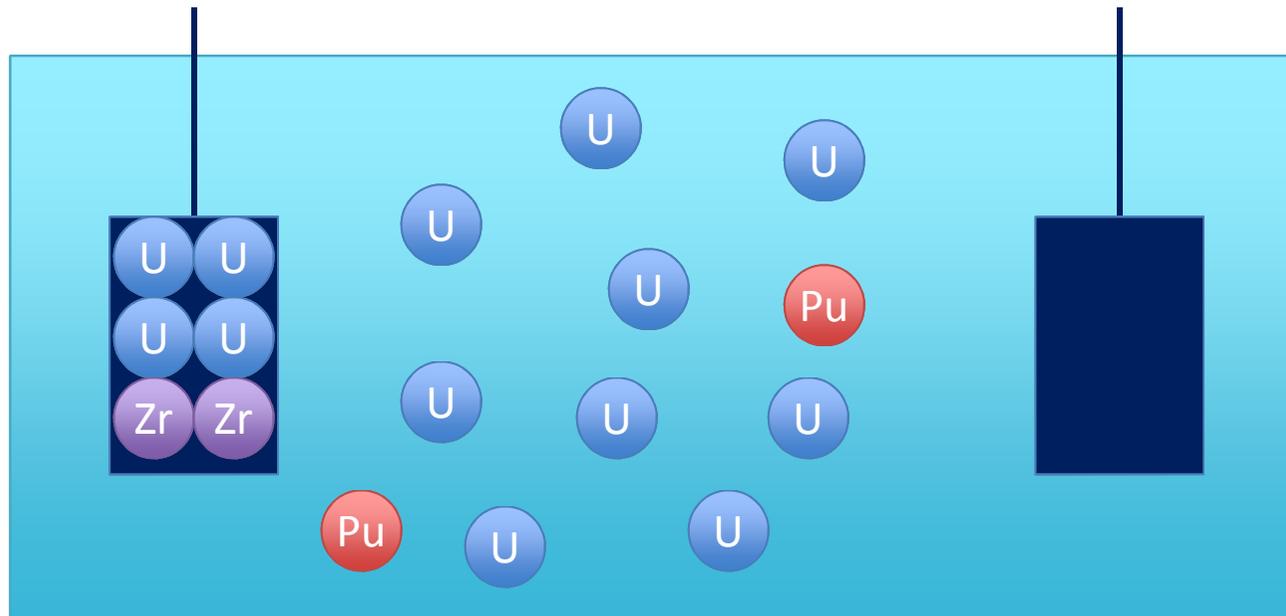
Objective

- Determine species deposition rates at the cathode
 - Product optimization
 - Safeguards
- Selected measures:
 - Electrode potentials
 - Cell current



Background

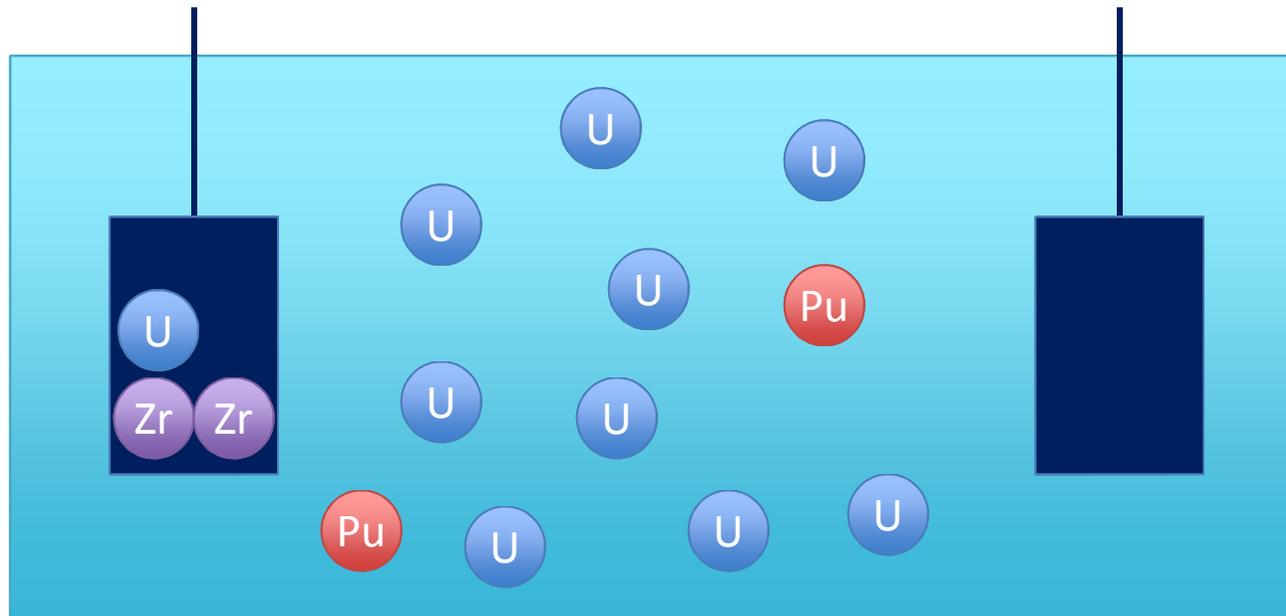
- “Normal” operating condition
 - Only uranium





Background

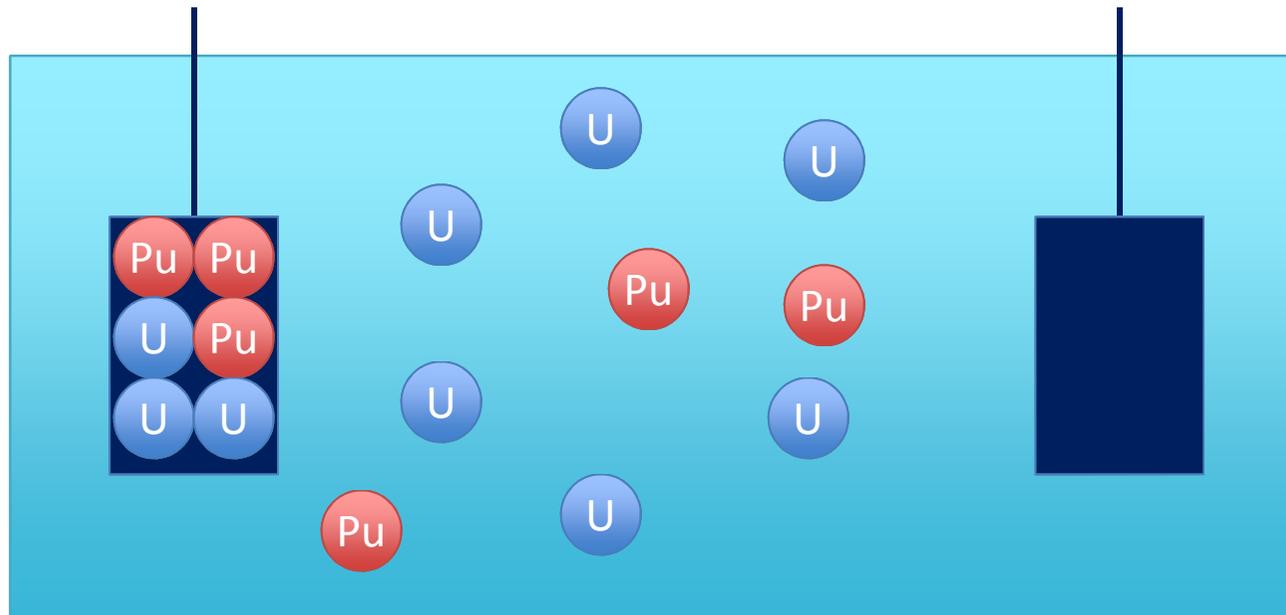
- Two “abnormal” scenarios
 - Zirconium co-deposition





Background

- Two “abnormal” scenarios
 - Plutonium co-deposition





Theory

- Notation and Symbols

A electrode area	E electrode potential	F Faraday's constant
I current	i current density	k_c mass transfer coefficient
n electrons transferred	R universal gas constant	r reaction rate
T temperature	X mole fraction	

Symbols

α transfer coefficient	γ activity coefficient	η overpotential
-------------------------------	-------------------------------	----------------------

Subscripts & Superscripts

c concentration	eq equilibrium	j species
k current step	o exchange/standard	s surface



Theory

- Cell Current

$$I_T = A \cdot \sum_j i_j(X_j, \eta_{s,j})$$

- Species current density

$$i_j = i_{o,j}(X_j) \cdot \left[\exp\left(\frac{n_j \cdot \alpha \cdot F}{R \cdot T} \cdot \eta_{s,j}\right) - \exp\left(-\frac{n_j \cdot (1 - \alpha) \cdot F}{R \cdot T} \cdot \eta_{s,j}\right) \right]$$



Theory

- Electrode Potential

$$E_T = E_{eq} + \eta_{c,j} + \eta_{s,j}$$

$$E_{eq} = E_j^o + \frac{RT}{n_j F} \ln(\gamma_j \cdot X_j)$$

$$\eta_{c,j} = \frac{RT}{n_j F} \ln\left(\frac{X_j^s}{X_j}\right)$$

$$\eta_{s,j} = E_T - E_j^o + \frac{RT}{n_j F} \ln(\gamma_j \cdot X_j^s)$$



Theory

- Cell Current

$$I_T = A \cdot \sum_j i_j(X_j, X_j^s, E_T)$$

– Additional relationship

$$i_j = n_j \cdot F \cdot k_c \cdot (X_j^s - X_j)$$

$$I_T = A \cdot \sum_j i_j(X_j, E_T)$$



Assumptions

- At low current
 - Bulk concentrations are constant
 - $3 \cdot 1F$ (289,455C) to reduce one mole of U and Pu
 - 4/3 as much for Zirconium

$$i_j = n \cdot F \cdot r_j$$

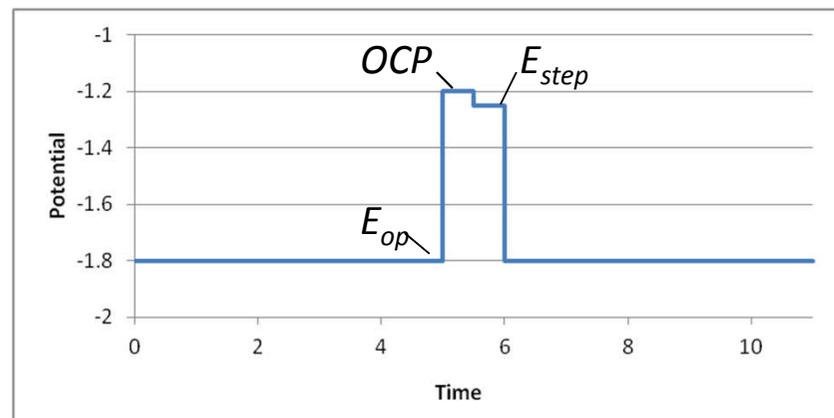
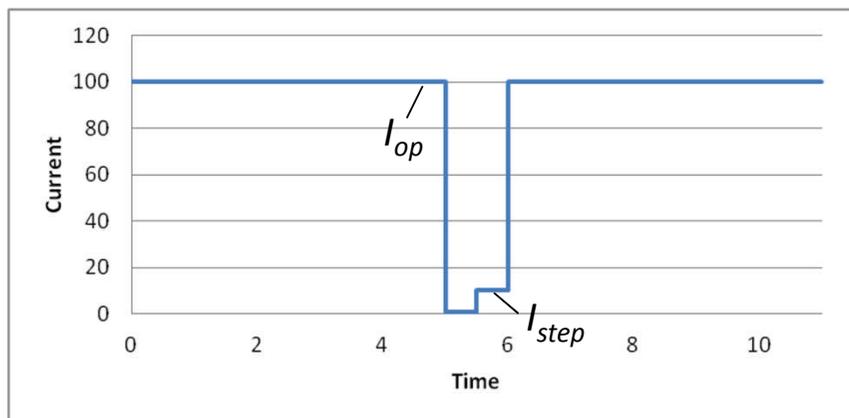
- Bulk concentration is equivalent to surface concentration

$$X_j^s = X_j$$



Method

1. Set current to zero
 2. Step current up incrementally
 3. Measure potential at each current setting
- Two-species example:





Method

- General Approach
 - Solve for bulk mole fractions at low current
 - $j = \#$ of species, $k = \#$ of low current steps

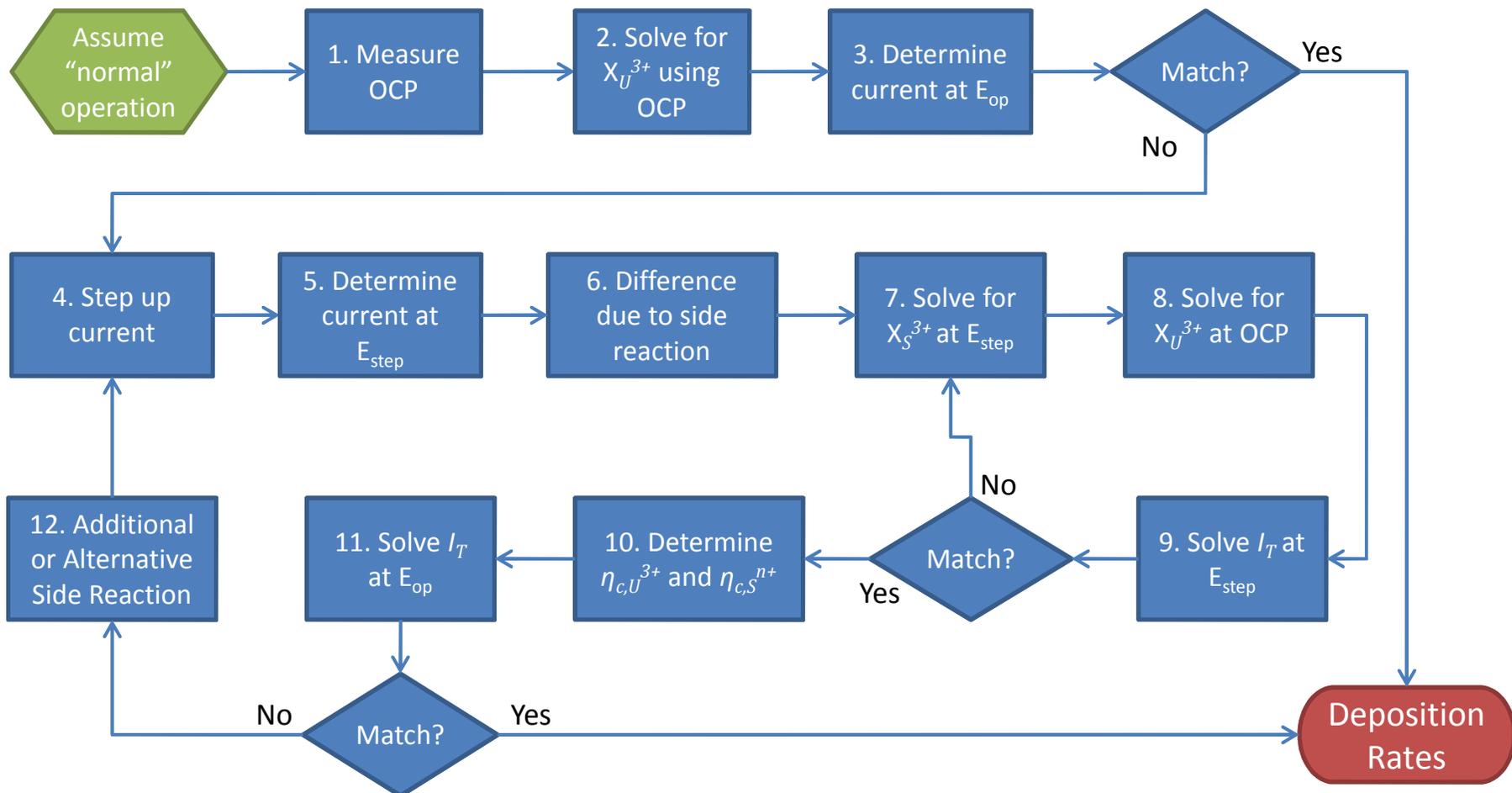
$$I_{T,k} = A \cdot \sum_j i_{j,k}(X_j, E_{T,k})$$

- Validate mole fractions at operating conditions

Mole Fractions are constant
between current steps



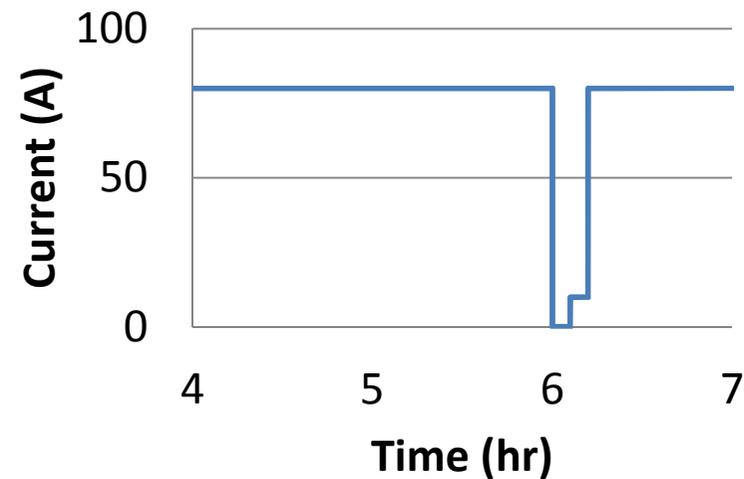
Method





Validation

- No experimental data
- Tested versus an existing model
 - Enhanced REFIN with Anodic Dissolution (ERAD)
 - Based on current and potentials from ERAD, mole fractions were predicted





Results

- Unknown variables
 - Species mole fractions
- Deposition rates based on mole fractions

Species	Predicted Mole Fraction	ERAD Mole Fraction
U	0.0194	0.0113
U, Zr	0.0210, 4.99E-4	0.0175, 4.48E-4
U, Pu	1.91E-3, 3.00E-3	2.08E-3, 4.22E-4



Limitations

- Number of species
- Low current steps
- High concentration of inactive species
- Solid cathode



Limitations

- **Number of species**
- **Low current steps**
 - Finite number of “low” current steps
- **High concentration of inactive species**
- **Solid cathode**



Limitations

- Number of species
- Low current steps
- **High concentration of inactive species**
- Solid cathode



Limitations

- Number of species
- Low current steps
- **High concentration of inactive species**
 - Actinide build-up
- Solid cathode



Limitations

- Number of species
- Low current steps
- High concentration of inactive species
- **Solid cathode**



Limitations

- Number of species
- Low current steps
- High concentration of inactive species
- **Solid cathode**
 - Liquid cathode
 - Additional concentration
 - Additional current step



Limitations

- Relax constant bulk mole fraction assumption

$$X_j^k = X_j^{k-1} + \frac{i_{j,an}^{k-1} - i_{j,cath}^{k-1}}{N_T^{k-1} \cdot n_j \cdot F} \cdot \Delta t^{k-1}$$

- Requires

- Analysis of anode potentials
- Account of all species in molten salt

- Resolves the first three limitations



Summary

- Molten salt compositions from
 - Cell current
 - Electrode potentials
- Initial modeling attempt
 - Constant salt composition
- Results are comparable to ERAD
- Potential resolutions to model limitations



Acknowledgements

- David McNelis
- Jun Li
- Michael Simpson
- Robert Hoover
- Supathorn Phongikaroon



References

- Hoover, R. O. (2010). *Development of a Computational Model for the Mark-IV Electrorefiner*. Idaho Falls, ID: University of Idaho.
- Park, B.-G. (1999). *A time-dependent simulation of molten salt electrolysis for nuclear wastes transmutation*. Seoul, South Korea: Seoul National University.
- Prentice, G. (1991). *Electrochemical Engineering Principles*. Englewood Cliffs, NJ: Prentice Hall.
- Zanello, P., Fabrizi de Biani, F., & Nervi, C. (2012). *Inorganic Electrochemistry: Theory, Practice and Application, 2nd Edition*. Cambridge: The Royal Society of Chemistry.