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
- **\( T \)**: temperature
- **\( X \)**: mole fraction

#### Symbols
- **\( \alpha \)**: transfer coefficient
- **\( \gamma \)**: activity coefficient
- **\( \eta \)**: 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

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

\[ E_{eq} = E_j^o + \frac{RT}{n_jF} \ln(y_j \cdot X_j) \]

\[ \eta_{c,j} = \frac{RT}{n_jF} \ln \left( \frac{X_j^s}{X_j} \right) \]

\[ \eta_{s,j} = E_T - E_j^o + \frac{RT}{n_jF} \ln(y_j \cdot X_j^s) \]
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
    - $3\cdot1F (289,455C)$ 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

1. Measure OCP
2. Solve for $X_{U^{3+}}$ using OCP
3. Determine current at $E_{op}$
4. Step up current
5. Determine current at $E_{step}$
6. Difference due to side reaction
7. Solve for $X_{S^{3+}}$ at $E_{step}$
8. Solve for $X_{U^{3+}}$ at OCP
9. Solve $I_T$ at $E_{step}$
10. Determine $\eta_{U^{3+}}$ and $\eta_{S^{n+}}$
11. Solve $I_T$ at $E_{op}$
12. Additional or Alternative Side Reaction

Match?

Yes

No

Match?

Yes

No

Match?

Yes

No

Deposition Rates
 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

<table>
<thead>
<tr>
<th>Species</th>
<th>Predicted Mole Fraction</th>
<th>ERAD Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>0.0194</td>
<td>0.0113</td>
</tr>
<tr>
<td>U, Zr</td>
<td>0.0210, 4.99E-4</td>
<td>0.0175, 4.48E-4</td>
</tr>
<tr>
<td>U, Pu</td>
<td>1.91E-3, 3.00E-3</td>
<td>2.08E-3, 4.22E-4</td>
</tr>
</tbody>
</table>

8/28/2012
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

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

– 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