Radiochemistry Ph.D. Program
Fuel Cycle Separations Subgroup

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Radiochemistry Research Program Concepts

• Research areas
  ▪ Radiochemical materials synthesis and characterization
  ▪ Fuel cycle separations
  ▪ Radioanalytical separations

• Chemistry based analysis of actinides and technetium
  ▪ Interested in chemical species and coordination, focus on radioelements

• Research with radionuclides
  ▪ Kg quantity of Th and U
  ▪ Gram amount of Tc, Np, Pu
  ▪ Milligram quantity of Am and Cm

• Research coupled with education program
  ▪ Provide undergraduate and graduate students with actinide research opportunities

• Develop a center of excellence in radiochemistry
  ▪ Noted researchers, strong collaborations
Program Resources

- **Spectroscopy**
  - UV-Visible
  - Laser Fluorescence
  - NMR
  - IR
  - EELS
  - XAFS (APS @ ANL)

- **Radiochemical separation and detection**
  - Gross alpha/beta counting
  - α-spectroscopy
  - γ-spectroscopy
  - Liquid Scintillation Counting

- **Thermal methods**
  - TGA, DSC

- **Scattering**
  - Powder XRD
  - Single crystal XRD

- **Contactors for Separations**

- **Analytical**
  - ICP-AES
  - ICP-MS
  - Electrospray-MS
  - Laser Ablation MS
  - Automated Titrator

- **Microscopy**
  - Optical
  - SEM
  - TEM

- **General Equipment**
  - Box/Tube furnaces
  - Glove Boxes
  - Arc Welder
  - Ultracentrifuge
  - Ball Mill
  - 10 tonne die press
  - Electron microscopy sample preparation
Technetium Studies

- UREX process Tc/U separation
  - Resins are tested for Tc loading and strip efficiency
  - Steam reforming process developed for conversion to Tc metal for waste form

Analysis of waste forms
- Suitability for repository storage
- Leach characteristics
- Electrochemical behavior

\[ \text{UO}_2^{+2} + \text{TcO}_4^- \]
Electrochemical Corrosion Studies

Tc electrode: acceleration corrosion test

$m = 80 \text{ mg, } A = 3.3 \text{ mm}^2$

Tc electrode

Set-up for corrosion exp

$E_{corr}$: shift from $-54 \text{ mV (t= 2min)}$ to $+46 \text{ mV (t= 15 hours)}$

Transpassivation behavior around $+195 \text{ mV}$
Room Temperature Ionic Liquids

• RTILs are becoming more popular
  • “Green” solvents (some exceptions)
  • No measurable vapor pressure
• RTIL Advantages
  • Electrochemical windows up to 7 volts
  • Water free systems
    • Organic & inorganic synthesis
    • Separations
    • Polymerization
• U(III) systems
  • Utilizing lower oxidation state in inert atmosphere provides more
direct mechanism for metallic alpha uranium deposition
  • Metallic uranium has many potential uses
    • Vast interest in waste forms
    • Potential reactor fuel
    • Target material for generating medically useful $^{99}$Mo
Process Monitoring & Safeguards

• UV-Vis monitoring of process streams
  ▪ Confirm stated process chemistry
  ▪ Detect diversion attempts

• Fiber optic dip probe inserted into product of UREX demo in contactors at ANL for \([\text{UO}_2^{2+}]\) measurement
  ▪ Spectral acquisition time of 250 μs
  ▪ Focus on trends over time rather than single data points
  ▪ Coupled with flow meters
Contactor Bank

- Purchased and installed 3 CINC V02 (2”) contactors
  - 316 SS, suited for lab scale or pilot plant work
  - 1 or 2 phases (in the case of 1 mixed phase, can be used for separation)
  - 5 cm (2”) design reported to not exhibit pulsed flow problems
  - 1.9 LPM max throughput (combined phases)
  - 2000-6000 RPM, 100-900 Gs
  - 200 mL holdup volume
  - 220 V/3 phase, draws 0.2-0.4 amps

- Experimental parameters
  - Flow rate
  - Concentration
  - Process chemistry
  - Nuclide content

- Used as a test bed for MC&A, process monitoring techniques
TBP/dodecane/HNO₃ systems

- Basic physiochemical data incomplete in the available literature
  - Vapor pressure
  - Solubility
  - Density
- Investigation of properties as functions of T, [HNO₃], [HNO₂], [HDBP], [UO₂²⁺], and [Zr⁴⁺]
- TBP degradation in the presence of HNO₃ has been studied over several decades
  - Discrepancies remain in hydrolysis rates, products and reaction heats
  - Thermal analysis with mass spectrometric analysis of gaseous reaction products proposed
Actinide Speciation and Spectroscopy

- Actinide speciation data set is varied and incomplete
  - Determination of thermodynamic quantities
  - Modeling and experiment
- Titrations
  - Competitive titrations to determine the stability constants of the UO$_2^{2+}$-NO$_3^-$ system
  - Spectrophotometric titrations
- UV-Visible spectroscopy
  - Used for chemistry-based safeguards
    - Online monitoring of SNM
    - Real time Material Control and Accountability
    - Process/chemistry control
  - Development of a robust method for simultaneous, online determination of nitrate and uranium in a reprocessing plant
  - Adaptation of bench scale work (1 cm pathlength) to waveguide based (1 m pathlength) experiments for reduced higher actinide load
- Laser induced fluorescence of Curium for trace level determinations
Solvent Extraction Fundamental Chemistry

- **Extractant Aggregation**
  - Vapor Pressure Osmometry
- **Water Extraction**
  - Karl Fischer Titration
- **Stability Constant Titration**
  - Spectrophotometric
  - Potentiometric

\[ n_{agg} = \frac{6589}{3140} = 2.08 \pm 0.04 \]

\[ \frac{H_2O}{\text{Ligand}} = \frac{1.576}{1} \]
**Stability Constant Modeling**

8-Hydroxyquinoline Spectrophotometric Titration

**Stability Quotients from Absorbance Data**

![Absorbance Graph](image)

<table>
<thead>
<tr>
<th>Species</th>
<th>$\beta$ (log)</th>
<th>$K$ (log)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2(Q)$</td>
<td>15.38±0.01</td>
<td>5.30</td>
</tr>
<tr>
<td>$H(Q)$</td>
<td>10.08±0.01</td>
<td>10.08</td>
</tr>
</tbody>
</table>

**Fundamentals**

![Fundamentals Graph](image)
Radiochemistry Program – Fall 2009