Strategic Design and Optimization of Inorganic Sorbents for Cesium, Strontium and Actinides

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Outline

- Goals
- Benefits
- Research Strategy
- Findings
- Research Plans
- Acknowledgements
Goals

- Determine the structural factors of inorganic-based sorbents and ion exchange materials that control selectivity and kinetics for the removal of cesium, strontium and actinides from strongly alkaline waste solutions.

- Apply that understanding to the synthesis of materials with improved cesium, strontium and actinide removal characteristics.
Benefits

- Improved radiochemical separations
- Increased throughput
- Reduced solids handling
- Simplified radiochemical separation flowsheet
Research Strategy

- Synthesize and measure ion exchange characteristics of titanosilicate, titanate and polyoxometalate materials
- Determine solid state structures of IX materials
- Develop molecular models of IX materials
- Use molecular models to guide synthesis of new IX materials

monosodium titanate
NaTi$_2$O$_5$H (MST)

sodium nonatitanate
Na$_4$Ti$_9$O$_{20}$ xH$_2$O (SNT)

crystalline silicotitanate
Na$_2$Ti$_2$O$_3$(SiO$_4$)$_2$H$_2$O (CST)

Polyoxometalate (IPX)
M$_{12}$[Ti$_2$O$_2$][SiNb$_{12}$O$_{40}$]•16H$_2$O
where M = Na, K
Research Findings

Substitution of Nb for Ti in framework significantly enhances Cs selectivity.

Crystalline silicotitanate (CST)

Strontium uptake decreases with increasing ionic strength; influence greater for Nb-CST.

Uptake of Cs$^+$, meq/g vs. $c_{Na^+}$, mol/l

Uptake of Sr$^{2+}$, meq/g vs. $c_{Na^+}$, mol/l
Cs Exchanged CST

Less Na in tunnel with Nb-CST

Increased cesium coordination in Nb-CST

Molecular models of CST and Nb-CST agree well with XRD studies

Sr Exchanged CST

CST

CN = 10

Nb-CST

CN = 7

Reduced affinity for Sr with Nb-CST due to lower degree of coordination

A. Tripathi, D. Medvedev, A. Clearfield; Journal of Solid State Chemistry, in press
Na-IPX Model

- 40 possible sites per unit cell
- Charge neutrality requires 24 Na\(^+\) per unit cell
- XRD cannot distinguish Na\(^+\) and H\(_2\)O
- Molecular modeling indicates 4 sites

<table>
<thead>
<tr>
<th>Site #</th>
<th>Na Occupancy (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>98.1</td>
</tr>
<tr>
<td>3</td>
<td>53.7</td>
</tr>
<tr>
<td>4</td>
<td>7.8</td>
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</tbody>
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- Water diffusely located near Sites 2, 3 & 4
- Good agreement between predicted H\(_2\)O content and weight loss measured by TGA
- Substitution of Nb for Ti reduces Na\(^+\) population in Site 3

Performance of Keggin Chain Materials

- Keggin chain (IPX) materials remove Sr & actinides
- Not as effective as MST
- Na-IPX more effective than K-IPX
Titanosilicates with Pharmacosiderite Structure (TSP)

$M_3H(TiO)_4(SiO_4)_3\cdot xH_2O$

$M = Cs^+, Na^+, K^+, Sr^{2+}$

TSP materials do not exchange $Cs^+$ in HLW media, but do exhibit excellent Sr & actinide removal

Sr removal faster with Na-TSP

Pu removal faster with K-TSP
Sodium Titanate Materials

Excellent affinity for Sr & actinides, but not Cs in HLW solutions

Investigate methods to modify morphology
- chemically modified MST exhibits significantly improved Sr/actinide removal performance (EM-21)
- decreased SNT crystallinity improved Sr/actinide removal

Increased Capacity

<table>
<thead>
<tr>
<th>Sample</th>
<th>168-hour $K_d$ (mL/g)</th>
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<tbody>
<tr>
<td>Baseline MST</td>
<td>50,300</td>
</tr>
<tr>
<td>SNL-1</td>
<td>3,490,000</td>
</tr>
<tr>
<td>SRTC-1</td>
<td>679,000</td>
</tr>
</tbody>
</table>

Faster Kinetics

- Control
- Baseline MST
- SNL-1
- SRTC-1

<table>
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<tr>
<th>[Pu] (microg/L)</th>
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<tbody>
<tr>
<td>Time (h)</td>
</tr>
<tr>
<td>0.1 1 10 100 1000</td>
</tr>
</tbody>
</table>

Increased Capacity

Baseline MST exhibits significantly improved Sr/actinide removal performance (EM-21)
Research Plans

- Identify actinide binding sites for the TSP, Keggin and SNT materials
  - XRD
  - XAFS

- Complete development of and use molecular models for the design of new derivatives of CST, Keggin, TSP and SNT materials
  - Calculation of water isotherms
  - Calculation of selectivity and distribution coefficients for Cs\textsuperscript{+}, Sr\textsuperscript{2+} and UO\textsubscript{2}\textsuperscript{2+} versus Na\textsuperscript{+} in materials with various framework substitutions
  - Investigate Quench Simulation and Reverse Monte Carlo methods to model amorphous materials
Research Plans

- Synthesize, characterize and test performance of new derivatives of SNT/MST, CST, TSP, Keggin and trisilicate materials
  - Mixed phase SNT/CST
  - Metal-substituted TSP (e.g., Ge for Si)
  - Cationic layered materials intercalated with anionic polyoxometalates
  - Polyoxometalates materials with alternate counterions
  - Modified SNT/MST materials

- Test performance of promising new materials with actual tank waste solutions (SRS)
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