Functionalized Silicates for Tc Retention

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Technical Need

- Thermal treatment systems planned for the Hanford Waste Treatment Plant (WTP) immobilization of High-Level Waste (HLW), Low Activity Waste (LAW), and supplemental treatment or tank-side treatments generate secondary waste streams.
- The primary sources are off-gas scrubber systems on the vitrification systems. The scrubber system effluents can capture volatile and semi-volatile radionuclides (e.g. ^{137}Cs, ^{99}Tc, ^{129}I) and other Resource Conservation and Recovery Act (RCRA) contaminants of concern.
- the key contaminant for groundwater impacts and ^{129}I to a lesser degree for disposal of wastes at Hanford and other sites. The leachability and mobility of these two long half-life isotopes are currently projected to control the IDF performance assessment at Hanford.

Current Technology

- Secondary waste forms at DOE sites are typically cementitious and release soluble radionuclides by diffusion processes through pores.
- If the Tc is encapsulated in its most oxidized state (Tc^{VII}), it is readily dissolved in the cement pore water and released.
- Even when Tc is reduced to Tc^{IV} or Tc^{0} on particle surfaces, it will readily oxidize to Tc^{VII} and be released.
- Therefore, methods to incorporate Tc^{IV} (or other reduced state) into minerals that resist pore water corrosion and oxidation will allow for the low-temperature immobilization of Tc.

Objective

- Develop a means to manage the ^{99}Tc in LAW, secondary wastes, and off-gas recycle streams as described in task 2.2.3 of the Alternative Waste Pretreatment Task Change Request.

Approach

FY10

- Evaluate a series of substrates that can be incorporated into Cast Stone or geopolymers functionalized with various ligands capable of selectively complexing ^{99}Tc in caustic salt solutions.

- Prepare and characterize Hanford secondary waste simulant using sodium perrhenate as surrogate for technetium.
- Let subcontract to University of Idaho (Bitterwolf)
  - Select appropriate ligands for testing
  - Prepare ligands
  - Prepare MCM-41 mesoporous silica substrate
  - Functionalize MCM-41 and Class F fly ash provided by SRNL
- Perform screening of functionalized substrates
- Contact functionalized substrates with simulant
- Separate functionalized substrates from waste simulant and measure remaining rhenium

FY11

- Prepare larger quantities of the ligand/substrate combinations with promising rhenium sequestration.
- Prepare waste forms with/without functionalized substrates (Pozzolans)
  - Measure compressive strength
  - Measure leach index
  - Measure TCLP
- Prepare simulant with sodium pertechnetate.
  - Repeat waste form testing

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Accomplishments

- Issued Task Technical and Quality assurance Plan, SRNL-RP-2010-01170, "Task Technical and Quality Assurance Plan for Improving Technetium Retention in Secondary Waste."
- Let subcontract to the University of Idaho (Bitterwolf) to:
  - select and prepare ligands for complexation of technetium (rhenium),
  - prepare MCM-41 substrates, and
  - functionalize MCM-41 and Class F fly ash provided by SRNL
- Prepared and characterized secondary waste simulant using sodium perrhenate as surrogate for technetium.

Results

- University of Idaho synthesized and attached six different ligands that were expected to chelate Tc to both fly ash and mesoporous silica.
  - Trimethyl ammonium thiosulfate
  - 2-methyl imidazol
  - Amino dipyridyl triazine
  - Imidazolium
  - Imidazolium poly ethylene glycol
  - 1,10-phenanthroline-5-amine

  Both imidazolium poly ethylene glycol and amino dipyridyl triazine ligands proved to be the most effective at binding and holding Re.
  - >30% of Re removed from salt solution
  - Expect >30% reduction in release from Cast Stone and geopolymer

  These results were consistent with those provided by the University of Idaho from their Re binding tests.

Substrate	Ligand	Re (ppm)
None	None (salt solution)	309
Fly Ash	None	326
	Imidazolium	281
	Amino dipyridyl triazine	286
	1,10-phenanthroline-5-amine	304
	Trimethyl ammonium thiosulfate	312
	Imidazolium poly ethylene glycol	317
	2-methyl imidazol	318
MCM-41	Imidazolium poly ethylene glycol	193
	Amino dipyridyl triazine	202
	2-methyl imidazol	288
	Imidazolium	315

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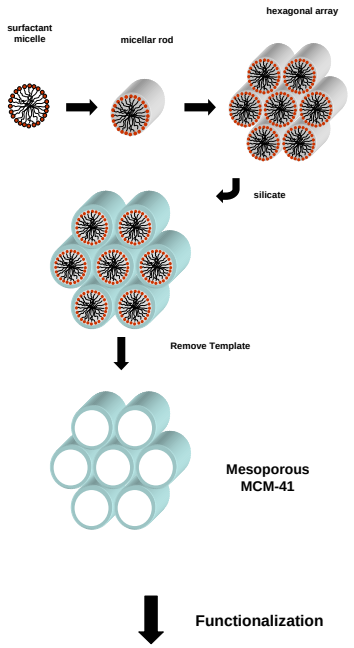
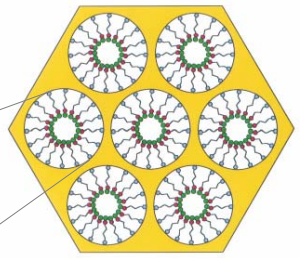
Materials Synthesis

- Two silica-based substrates were identified to serve as solid supports: MCM-41 and fly ash.
- MCM-41 is a mesoporous silica material consisting of a silica honeycomb with pores that may range in a controlled manner from 30 – 100 Å.
- MCM-41 surface areas of these materials have been measured at 990 m^2/g (BET Measurements)
- MCM-41 involves a one-pot synthesis
  - tetramethyl ammonium hydroxide
  - cetyltrimethyl ammonium bromide
  - fumed silica
  - calcination
- Class F fly ash was used.

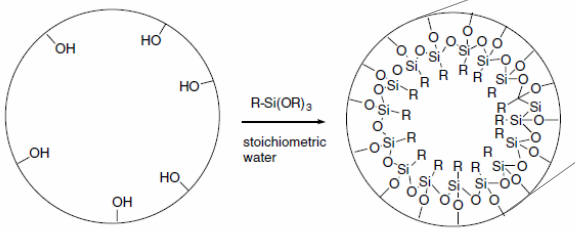


Functionalization

- Functionalization of mesoporous silica was developed by Dr. Glen Fryxell and others at PNNL.
- Mesoporous silica materials are prepared by a calcining step which removes the template materials from the pores.
- A monolayer of water is added to convert surface oxide groups to silanol groups.
- Reaction of silyl ethers of the form $X(CH_2)_3Si(OEt)_3$ with the hydrated surfaces results in loss of alcohol, HOEt, and formation of Si-O-Si bonds which covalently affix the organic groups to the mesoporous surface.
- Functionalization of fly ash follows a similar process, except that the ligands are attached to the outer surface instead of internal pores.



Functionalized Mesoporous Silica



Calcined mesoporous silica pore surface

Self-assembled monolayer

Ligand Candidates

- Imidazolium PEG
  - The pertechnetate ion is weakly solvated by water and forms only poor interactions with most common ligands.
  - The imidazole PEG ligand was specifically designed to utilize a combination of Coulombic attraction and water displacement to draw the TcO_4^{1-} ion into a cavity where it interacts with several imidazolium ion.
- Dipyridyl Triazine
  - The dipyridyl triazine ligand was modeled after polydentate ligands used to bind Tc(IV) in medicinal applications.
  - Since technetium speciation is a complex function of redox and pH conditions a ligand was incorporated that would specifically bind reduced forms.