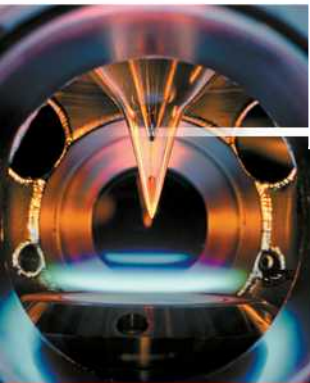


SAND2014-17629PE

# SANDIA NATIONAL LABORATORIES

## Overview of Sandia Radioactive Waste Management and Remediation Capabilities and Technologies

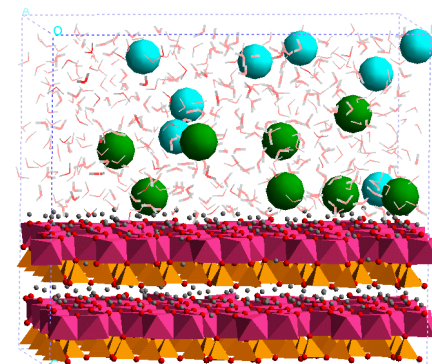
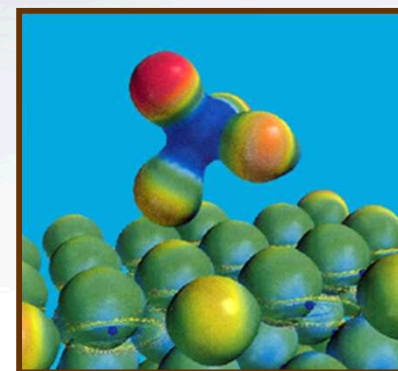


**Mark Rigali**  
**Manager, Geochemistry Department**  
**Sandia National Laboratories**  
**PO Box 5800 , Mail Stop 0754**  
**Albuquerque, NM 87185**  
**505-284-2727**  
**[mjrigal@sandia.gov](mailto:mjrigal@sandia.gov)**

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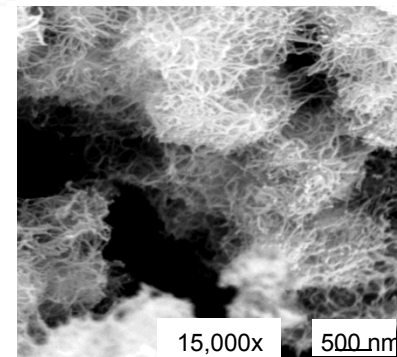
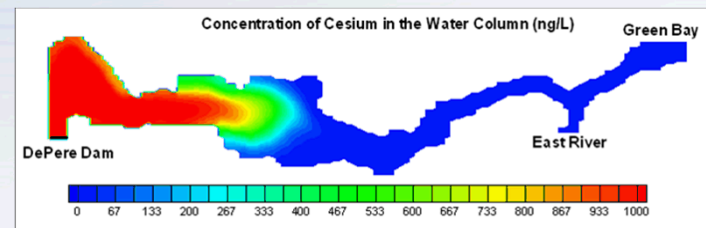
# SNL Capabilities Applicable Radionuclide Contaminant Remediation

- **Characterization of groundwater flow and radionuclide transport**
  - Well tests and well test analysis
  - Tracer tests
  - Subsurface flow and transport modeling
  - Monitoring network design
- **Water treatment**
  - In-situ and Ex-situ Removal of Contaminants
  - Novel Membrane Technologies
- **Integrated Geochemical Studies: Modeling, Laboratory and Field**
  - Natural and engineered attenuation/sequestration of metals and contaminants
  - MD Simulations: sorption of radionuclides and interactions at water-mineral interfaces



# SNL Capabilities Applicable Radionuclide Contaminant Remediation

- **Disposal cell/landfill cover design and analysis**
  - Geomechanical testing and analysis
  - Cell landfill cover design and analysis
  - Probabilistic, risk-based performance assessment
  - Sampling, site characterization, long-term monitoring
- **Soil and Sediment Transport**
  - Erosion and transport measurements
  - Contaminated sediment transport modeling
  - Habitat impacts
- **Materials Development**
  - Radionuclide getters
  - High capacity, rapid exchange materials that are element selective
- **Performance Assessment**
  - Probabilistic modeling
  - Sensitivity and uncertainty analysis



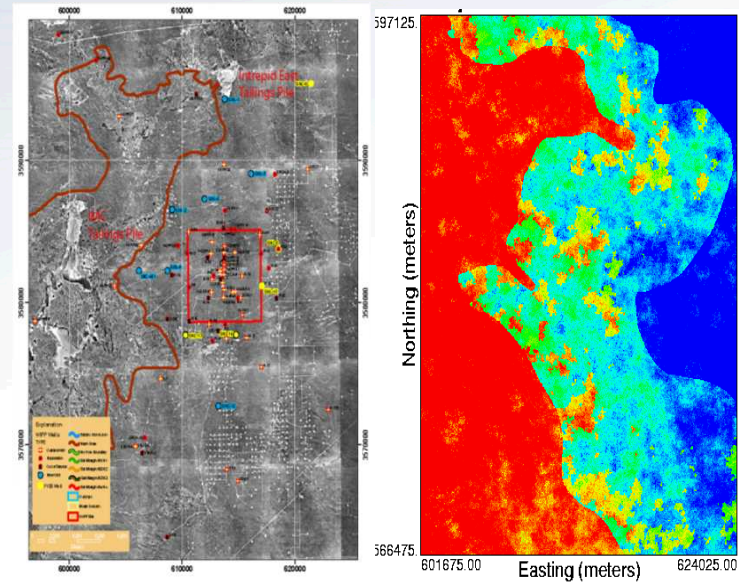
*Modified titanate:  
selective for U, Pu, Ac*

# Hydrology Science with Application at the Front and Back ends of the Nuclear Fuel Cycle

- Unique SNL mobile hydraulic testing and data acquisition capabilities for aquifer testing
- Unique SNL aquifer test analysis software
- Incorporate hydrogeologic facies and heterogeneity into 3D groundwater model
- Tracer test characterization of in-situ solute transport processes
- Stochastic modeling of subsurface flow and transport
- Optimized design of production and monitoring well networks
- Reduce and quantify uncertainty in production and remediation phase life cycle costs



mobile  
aquifer  
testing  
trailer



geologic map

transmissivity map

# Optimized Tailings Disposal Cell Design

- Probabilistic modeling of subsurface and atmospheric releases, flow and transport, human exposure
- Alternative covers for waste isolation
- Sampling network design and long-term monitoring
- Erosion and sediment transport measurement and modeling
- Reduce uncertainty in long-term risks associated with tailings to better address regulator and stakeholder concerns



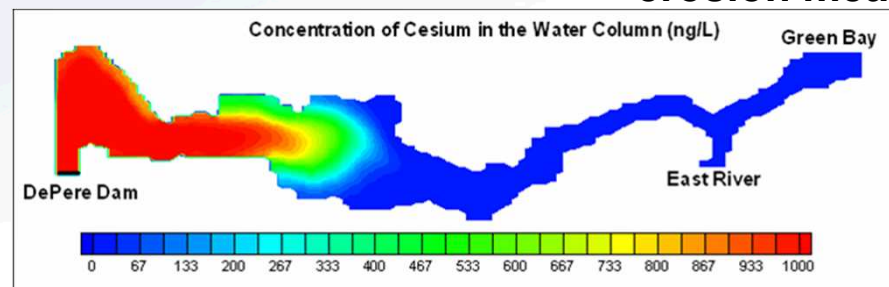
landfill cover study



erosion measurement flume



sediment core collection



sediment transport modeling



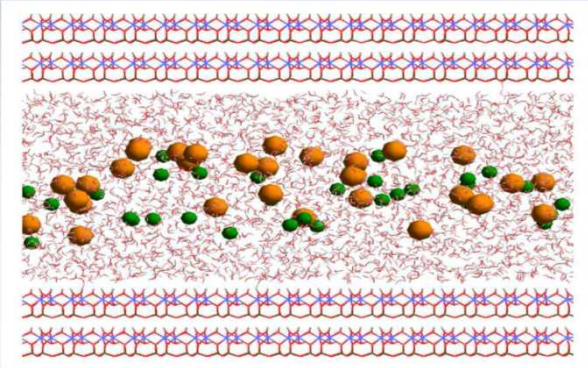
monitoring

# Adsorption Mechanisms through Simulation

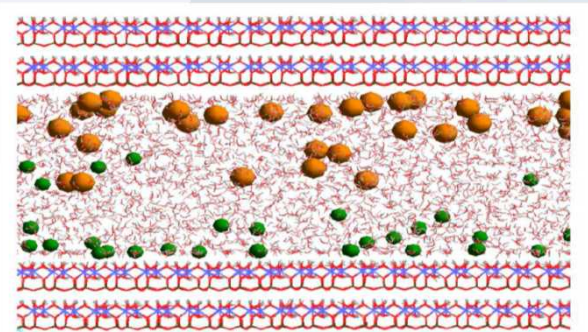
## Interfacial Structure of Radionuclides on Minerals

0.5 M CsCl solution in  
Kaolin Nanopore

57.1 Å



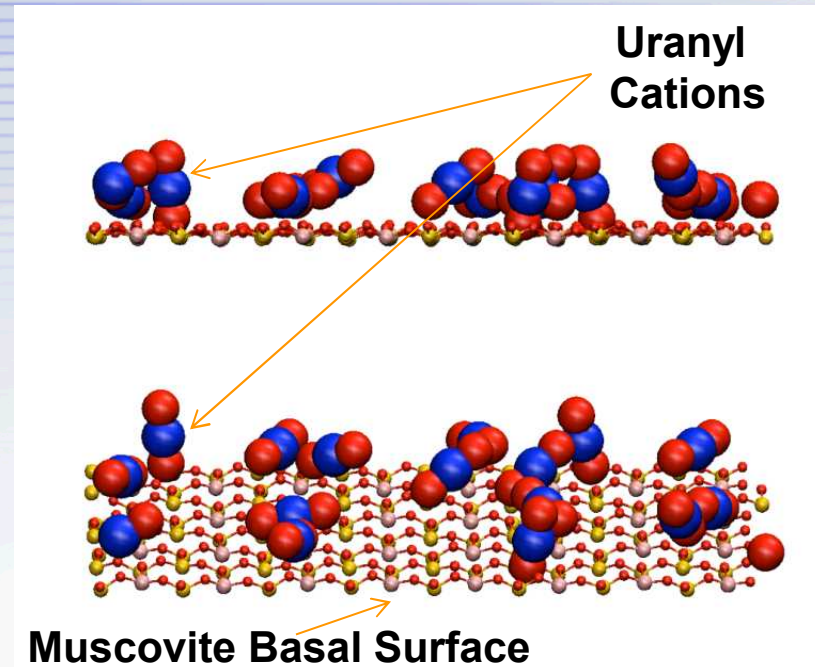
Initial  
configuration



Equilibrated  
after 600 ps

Cygan R.L. and K.Tazaki\*, Interactions  
of Kaolin Minerals in the Environment,  
Elements, v.10, no.3 (June 2104)

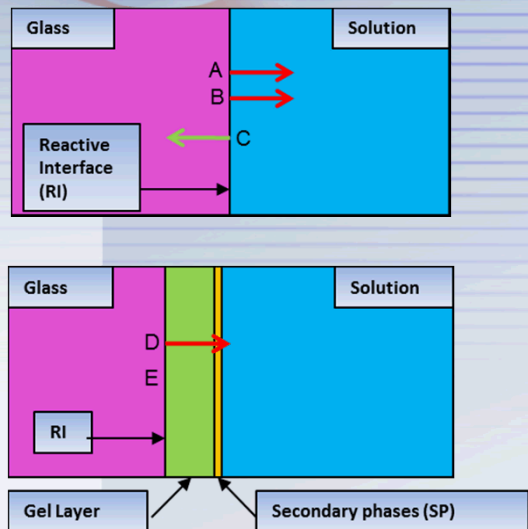
\*Kanazawa University, Japan



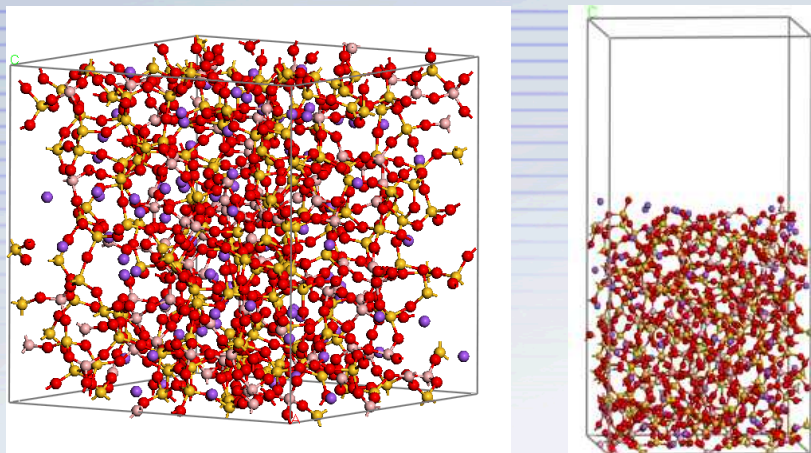
Teich-McGoldrick, S.L., Greathouse, J.A., and  
Cygan, R.T. (2013) Molecular dynamics  
simulations of uranyl adsorption and structure  
on the basal surface of muscovite. *Molecular  
Simulation*, in press.

# Atomistic Modeling to Better Predict Nuclear Waste Glass Dissolution

## Glass Dissolution Process



## MD Simulations of Na Borosilicate Glass and Surface



## Calculation of Bond Breaking by ab initio MD

How does the glass composition influence long-term glass dissolution rates?

- How are changes in glass composition reflected in the glass surface?
- How do changes in surface site types and densities influence glass dissolution rates?

	Initial State	Transition State	Final State
Protonated	 1.70, 1.58	 3.03, 1.45	 2.95, 1.43
Neutral	 1.63	 1.63, 1.51	 2.92, 1.36
Deprotonated	 1.62		

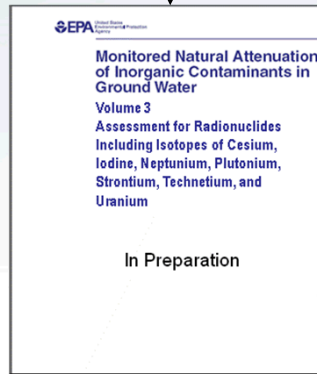
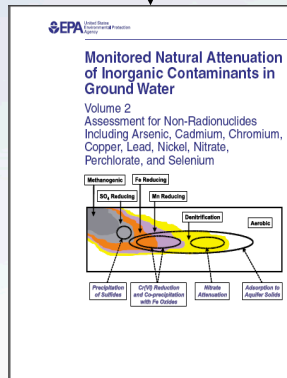
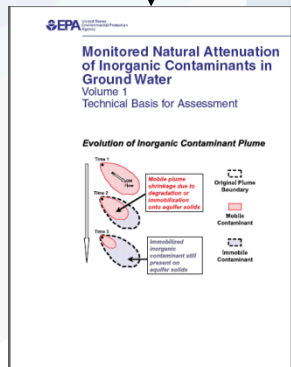
Figure 3. Water Attack at the  ${}^3\text{B}(\text{Q}^2)\text{-O-}{}^3\text{B}(\text{Q}^3)$  bridge under protonated, neutral and deprotonated conditions. Atoms participating in the reaction are represented by magenta (Si), green (B), red (O) and blue (H) spheres, other atoms are shaded. Bond lengths are in Å.

# Monitored Natural Attenuation (MNA) of Radionuclide Plumes

Sandia has led the development and application of MNA for metals and radionuclides by:

Establishing the technical basis for MNA of Metals/Radionuclides

Helping EPA write MNA Guidelines for Metals/Radionuclides



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Vol. 52, No. 5 March 10, 2000

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Tonopah, Nevada | Nevada Test Site | Amarillo, Texas



## Sandia scientists study 'natural' alternative to cleaning up uranium-contaminated sites

Natural attenuation may replace costly traditional remediation techniques

By Chris Burroughs

[Back to Lab News Table of Contents](#)

An innovative "natural" alternative to cleaning up uranium-contaminated sites is being studied by Sandia scientists as a way to replace costly and sometimes ineffective traditional techniques.

Called natural attenuation, the method relies on a naturally occurring process that adsorbs soluble uranium and metals onto a mineral surface. As the coatings age and recrystallize, the uranium eventually becomes encased in the mineral and cannot escape into groundwater or soil.

"This is an innovative approach to uranium cleanup," says Malcolm Siegel (6233), who has been working with fellow Sandian Charles Bryan (6821), former postdoc Ming-Hsu Li, and several students to characterize the process for three years. "Natural attenuation has become an accepted method for cleaning up soils and groundwaters contaminated with toxins that can be eliminated through biological processes - where microorganisms break down organic contaminants. Here, instead, the uranium becomes strongly bound to the mineral naturally."

Such processes are of interest to those who want to clean up sites contaminated by uranium or heavy metals in as natural and inexpensive a way as possible. Malcolm says traditional methods of cleanup, called active remediation, frequently involve "suck, muck, and truck" - digging up waste and physically removing it - and "pump and treat" - pumping contaminated water from the ground, treating it, and returning it. These techniques are generally costly and time-consuming.

### Promises cleanup savings

Costs of cleaning up hazardous waste sites, including uranium-contaminated sites, over the next three decades have been estimated at between \$373 billion and \$1.694 trillion. If natural attenuation is used instead in appropriate situations, the cleanup expense could



THE NATURAL WAY - Malcolm Siegel (6233), left, and Pat Brady (6188) review notes in their laboratory. They are researching natural attenuation, a "natural" alternative to cleaning up uranium-contaminated sites. (Photo by Randy Montoya)

NUREG-CR-6820

## Application of Surface Complexation Modeling to Describe Uranium (VI) Adsorption and Retardation at the Uranium Mill Tailings Site at Naturita, Colorado



U.S. Geological Survey

U.S. Nuclear Regulatory Commission  
Office of Nuclear Regulatory Research  
Washington, DC 20555-0001



# Sandia's Water Treatment Programs – From “Nanoscale” to Field Test

- **Molecular dynamics simulations to understand surface adsorption phenomena at a fundamental level.**
- **Experience in developing element-specific scavengers that remove trace levels of “heavy metal pollutants” from waters: Cs, Sr, Tc, U, Th, Ra, Actinides on an industrial scale.**
- **Design and fielding of pilot-scale water treatment systems for applications in remote areas**
- **Field tests that compared performance of various sorptive media in differing groundwater chemistries**
- **Reduce uncertainty in remediation phase costs**



# Permeable Reactive Barriers: *In Situ* Formation of Apatite

**An effective reactive barrier for Sr, U, Ra, Pu, Np, Am and others.**

**Very economical; all reagents are commercially available (sodium phosphate and calcium citrate)**

**Patent Status: U.S. Patent 6,592,294.**

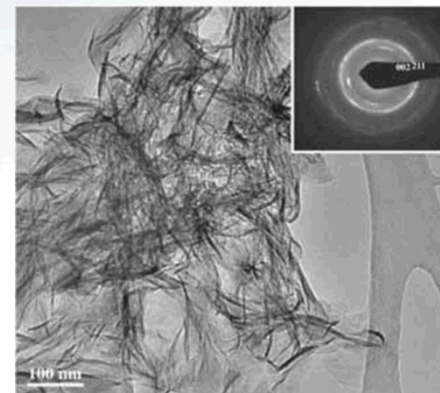
**Commercialization Considerations:**

**Mature technology deployed at Hanford site, USA and under consideration for use at old uranium mills and mines.**

**Site specific characteristics including porosity and permeability of sediments, phosphate concentration, need to be considered to insure successful application of technology.**



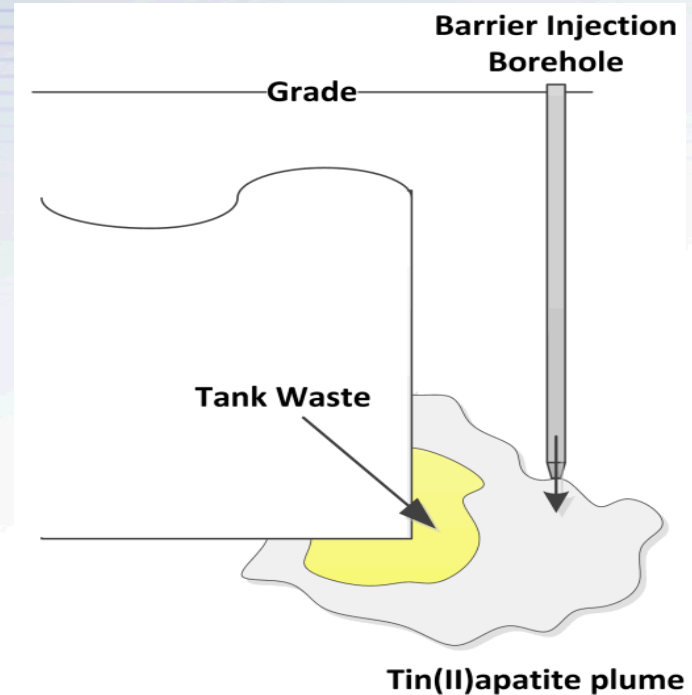
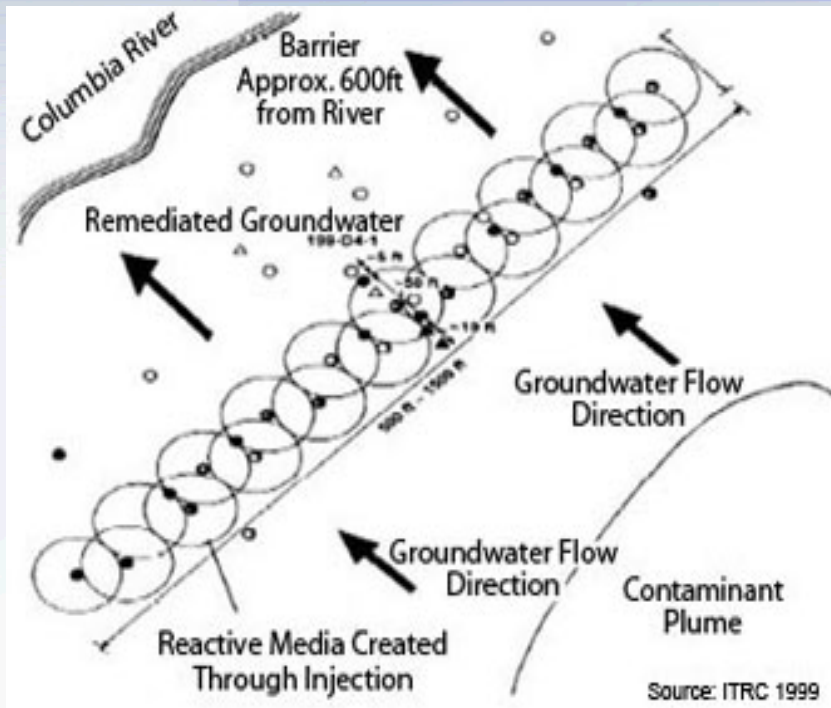
**Injection of apatite forming solution at Hanford 100N site for immobilization of Sr-90. June, 2006.**



**Calcium apatite crystals formed in sediment.**

# Apatite-based Permeable Reactive Barriers for Radionuclide Remediation

## Reactive Barrier Applications



# Reactive Barriers: *In Situ* Formation of Magnetite

Magnetite, strong sorbent for Technetium (Cui & Eriksen, *Environ. Science & Technology*, 1996)

Reactive solutions are injected into the sediment to form in situ magnetite ( $\text{Fe}_3\text{O}_4$ ).

Avoids all of the problems associated with conventional methods including jet grouting and extensive excavation of contaminated soil.

Very economical; reagents are commercially available.

Patent Status: U.S. Patent 6,527,691

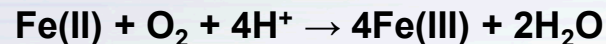
Commercialization Considerations:

Requires larger scale pilot and field testing

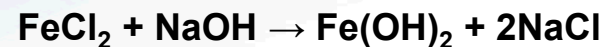
Long term retention of Tc a question.

The formation of magnetite is a two step process

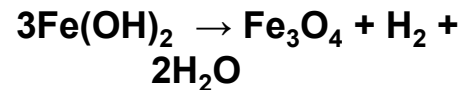
1)  $\text{FeCl}_2$  or another reagent is injected into the soil to remove all  $\text{O}_2$ .



2) Then,  $\text{FeCl}_2$  and  $\text{NaOH}$  are injected into the soil to form magnetite

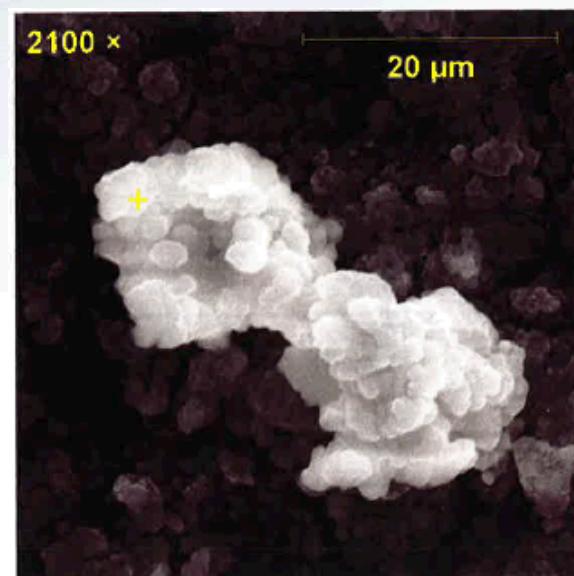
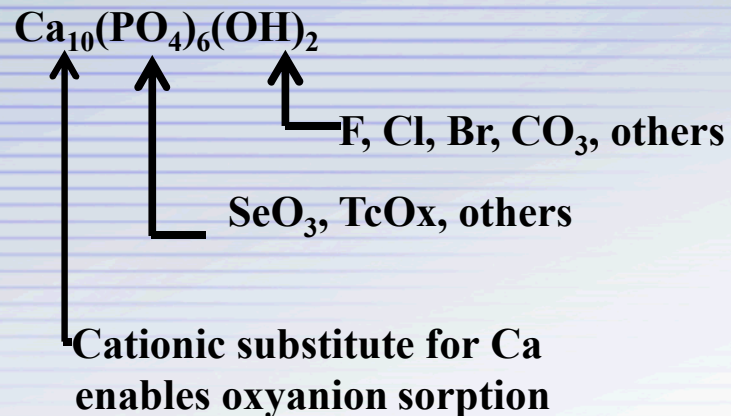


under anaerobic conditions:



# Permeable Reactive Barriers: *In Situ* Formation of Chemically Modified Apatites for Oxyanions

- Rapid uptake of Tc over a wide range of pH ( $K_d > 170,000$   $2.5 < \text{pH} < 10.2$ )
- Tc does not re-oxidize when placed in a water column and sparged with air (tested for > 6 weeks)
- Leachability index in cast stone of 12.8
- Will also sequester a wide variety of radionuclides and metals **Sr**, **U**, **Ra**, **Th**, **Am**, **Np**, Pb, Co, Zn, Cd, Rb and others.
- Sandia U.S. Patents pending for Tc reactive barrier and sorbent technologies.
- Versatile groundwater/soil remediation technology. Can be deployed as a permeable reactive barrier or as a granular solid for traditional pump and treat.



Substituted Apatite

# Clay - Bismuth Oxide Seals for Rad-Waste Applications

Sorbent is a swelling clay ( bentonite) – bismuth-oxide getter combination that acts both to seal holes and as a radionuclide scavenger over a range of temperatures and salinities.

Effective at trapping both cationic (Cs, Am) and anionic (I<sup>-</sup> etc.) radionuclides in saline brines up to the boiling point of water.

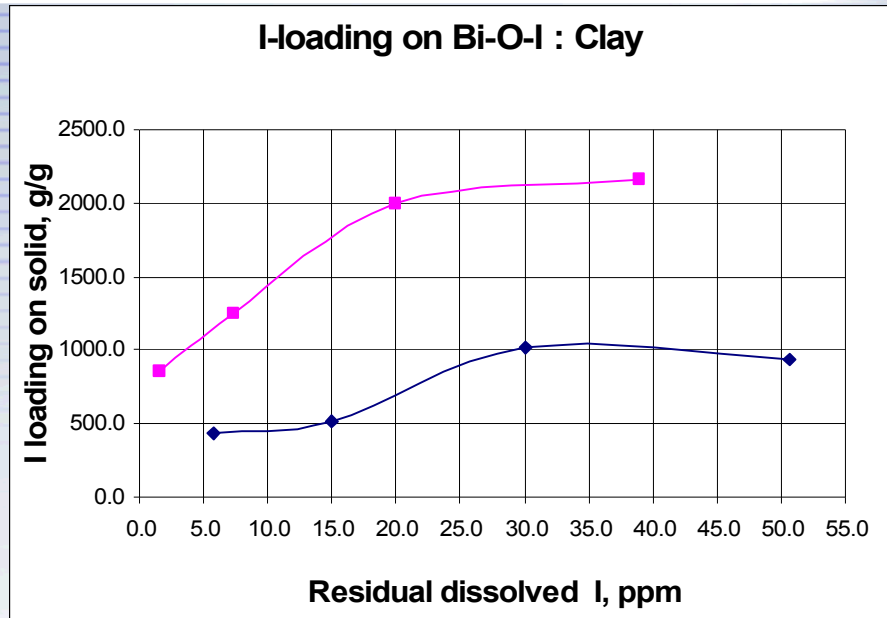
Patent Status: Technical Advance Filed - SD10928 (11/17,2010).

TRL: 2 (Multiple varieties and preparations)

Barriers to Commercialization:

Customer base outside of DOE yet to be identified;

Some interference from groundwater anions - notably carbonate, and high chloride.



Significant Iodine Uptake at 60° C  
in 0.5 M NaCl

$$K_d \text{ for } I^- = 10^{2.0 - 2.6}$$

$$K_d \text{ for } Cs^+ = 10^{1.6 - 1.8}$$

$$K_d \text{ for } Eu \text{ (Am}^{+3}) = 10^{3.9 - 4.6}$$

$$K_d \text{ for } ReO_4^- \text{ (TcO}_4^-) = 100^{0.6 - 1.1}$$

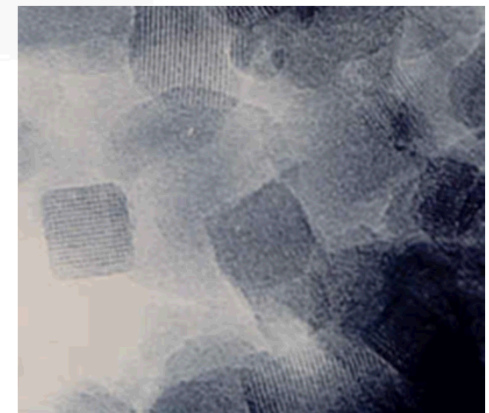
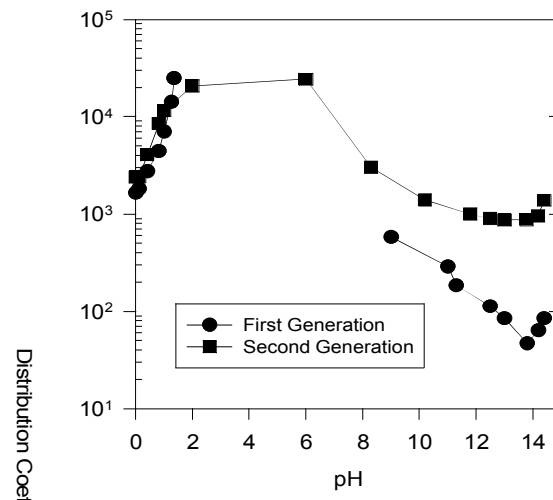
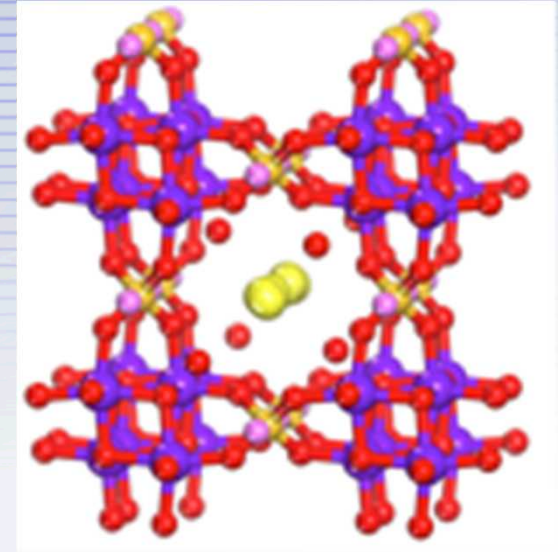
# Crystalline Silicotitanates (CSTs)

## Removal of Rad-Cs<sup>+</sup> from Pooled Seawater

### CST Properties

- Exceptional Cs<sup>+</sup> selectivity, and mechanical, thermal and radiological stability
- Stable over entire pH range
- Stable in extreme environments
- 
- *Commercially available as Honeywell UOP IONSIV™ IE-910 & IE-911*
- *Currently in use at Fukushima for Cs removal*

**Patent: Novel Silico-titanates and their Method of Making and Using, International Patent No. WO 94/19277.**

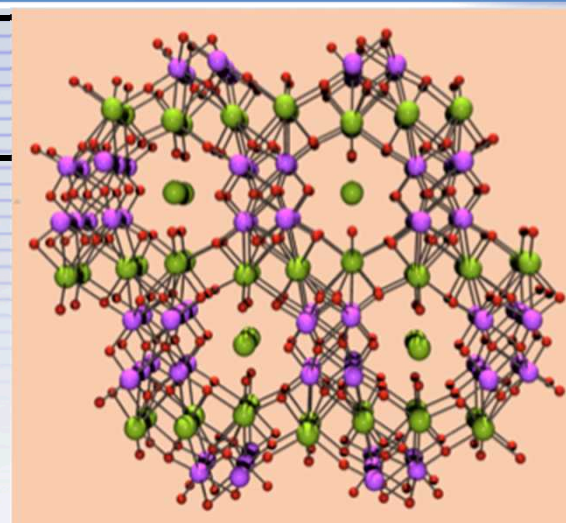


20 nm  
Sandia National Laboratories

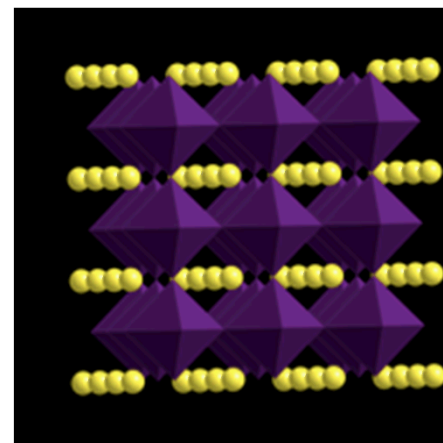
# Sandia Octahedral Molecular Sieves (*SOMS*)

## Selectivity (heat treat to perovskite WF)

metal ion	Ti-niobate phase Nb:Ti = 1:4	Zr-niobate phase Nb:Zr = 1:6
-----------	---------------------------------	---------------------------------



450°C heat treat  
1 step to waste form  
to perovskite



<b>Ba<sup>2+</sup></b>	> 99,800 *	> 99,800 *
<b>Sr<sup>2+</sup></b>	> 99,800 *	> 99,800 *
<b>Ca<sup>2+</sup></b>	2,300	2,657
<b>Mg<sup>2+</sup></b>	226	458
<b>Pb<sup>2+</sup></b>	66,467	22,022
<b>Cr<sup>3+</sup></b>	> 99,800*	> 99,800 *
<b>Co<sup>2+</sup></b>	> 99,800 *	> 99,800 *
<b>Ni<sup>2+</sup></b>	> 99,800 *	> 99,800 *
<b>Zn<sup>2+</sup></b>	> 99,800 *	> 99,800 *
<b>Cd<sup>2+</sup></b>	> 99,800 *	> 99,800 *
<b>Cs<sup>+</sup></b>	150	169
<b>K<sup>+</sup></b>	95	153
<b>Li<sup>+</sup></b>	8	35

**Radionuclides** ←

High concentration  
in natural systems ←

**Industrial  
Waste  
Metals**

Publication: Nyman et al., A New Family of Octahedral Molecular Sieves: Sodium Ti/ZrIV Niobates, JACS, 2001, 123, 1529-1530

Patent: Nyman and Nenoff, Niobate Octahedral Molecular Sieves US Patent # 6,596,524

# Contaminant Getters: Mono-Sodium Titanates (MSTs)

## MST Properties

- Amorphous solid, poorly crystalline solid.
- Exceptional  $\text{Sr}^{2+}$  selectivity, and mechanical, thermal and radiological stability.
- Selective for Pu and other actinides.
- Stable over pH range of 3 to 14.

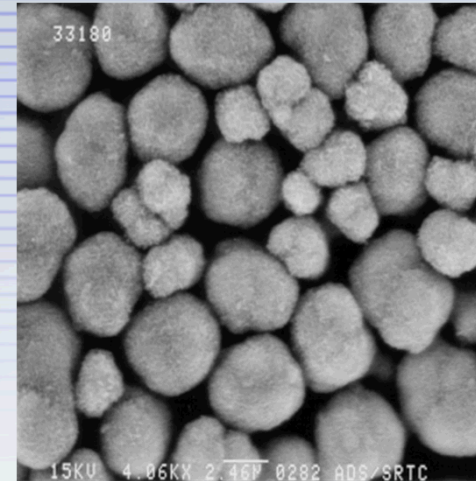
**Publication:** Lynch, R. et al., IAEA Symposium on the Management of Radioactive Waste, Vienna Austria 1976, 360-372.

**Patent Status:** publically disclosed in 1976.

**Commercially available:** *Optima Chemical Company Inc. and Harrell Industries*

**Other considerations:**

Detailed performance on testing in sea water and dilute sea water has not been performed.



# Contaminant Getters:

## Peroxide Modified Mono-Sodium Titanates (mMSTs)

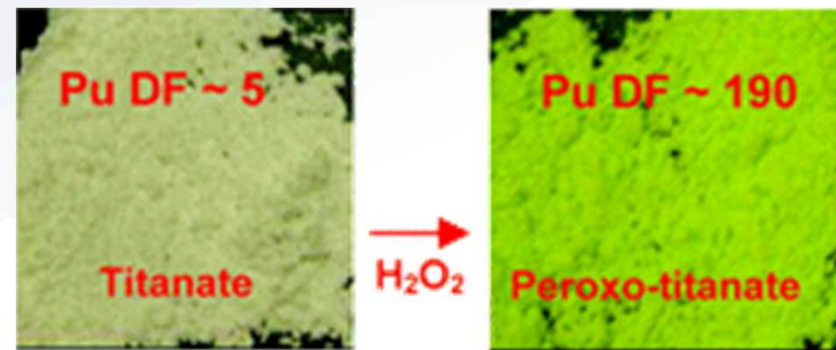
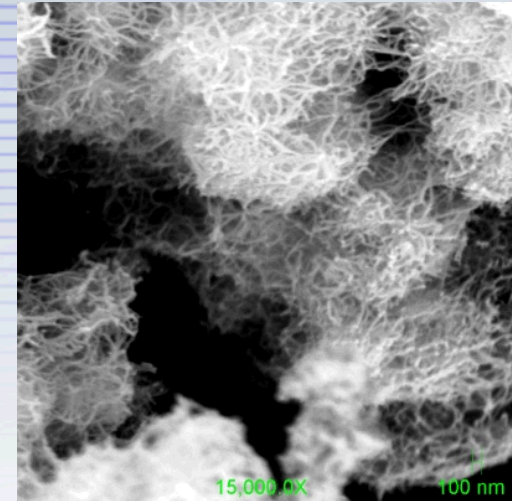
Modified MSTs are tailored materials for optimal Sr and Actinide (Pu, Am, Np) sorption

Patent Status: Hydrogen Peroxide Modified Sodium Titanates with Improved Sorption Capabilities (U.S. Patent 7,494,640 Issued 2/24/2009).

Publication: May Nyman and David T. Hobbs Chem. Mater.; 2006; 18(26) p. 6425-6435

Commercialization Considerations:

Of considerable interest for SRNL waste treatment in combination with CSTs.



# Contaminant Getters: Alumina Nano-particles

Nanoporous alumina synthesized as a getter for volatile radionuclides such as  $^{129}\text{I}$ . Also capable of sorbing Tc from aqueous solutions.

High iodine sorption capacity: 3 - 8 wt% over a temperature range of 50 – 90 °C.

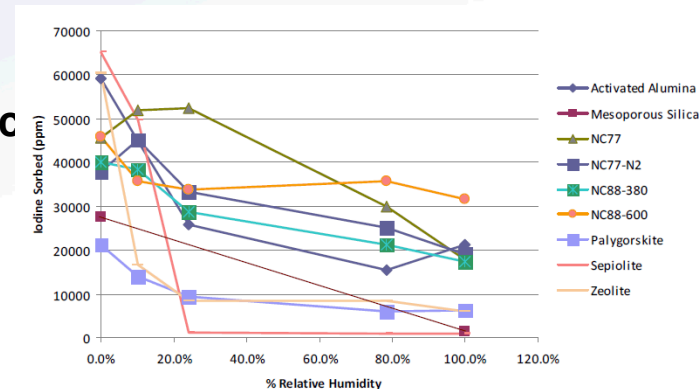
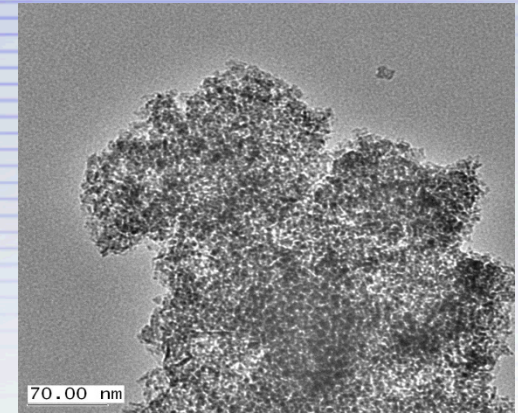
Iodine is fixed by simple chemical conversion process to non-volatile species in the alumina nano-pores. It can then be encapsulated in glass for long term immobilization.

Very economical, using off the shelf materials.

Patents: Method of making nanostructured glass-ceramic waste forms, U.S. Patent Nos. 8334421 and 8772566

Commercialization Considerations:

Requires larger scale pilot and field testing.



# Contaminant Getters: Metal Oxide-Carbon Nanocomposite

**Metal Oxide-Carbon Nanocomposite adsorbent for removal of both cationic and anionic metal contaminants from aqueous solutions. Should be selective to Sr, Tc, and other radionuclides.**

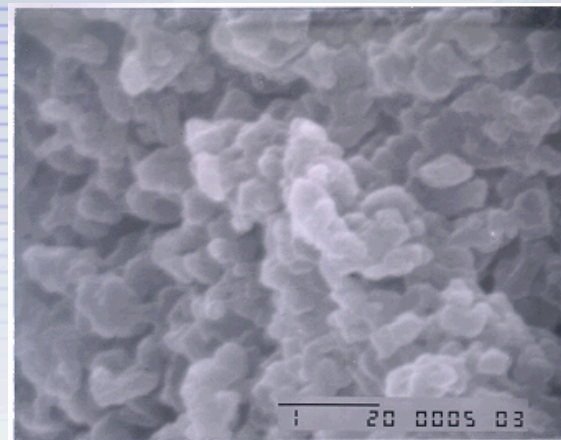
**Simple synthesis pathway intercalating a layered double hydroxide with a long-chain surfactant and then calcining under an N<sub>2</sub> atmosphere.**

**Landfill and pond liners, waste water and process water treatment**

**Patent: Method for absorbing an ion from a fluid, US 7238288B1.**

## **Commercialization Considerations:**

**Performance characteristics need to be verified over a range of geochemically relevant waters. Sorption performance with Tc has not yet been done.**



**Metal Oxide-Carbon Nanocomposite**

Sample	As		Se	
	pH	K <sub>d</sub> (ml/g)	pH	K <sub>d</sub> (ml/g)
ZA S400N1	6.9	270,000	6.8	46,000
ZA S400N3	7.0	208,000	6.9	16,000

# Layered Bismuth Oxide Getters for Anion Removal

Sorbent is a layered bismuth oxide.

Highly selective for As, Se, I<sup>-</sup>, IO<sub>3</sub><sup>-</sup> (Kd>10<sup>2</sup>) and moderately selective for TcO<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> (Kd = 10-100) in drinking water matrix.

Inexpensive and easily prepared using commercially available materials.

Technical POC: Jim Krumhansl

Patent Status: Public Disclosure in 2006.

Barriers to Commercialization:

As synthesized, the material is a fine powder requiring binder for column use;

Some interference from groundwater anions - notably carbonate.

Log[Kd - As ]  
4.2 - 6.3

Log[Kd - I<sup>-</sup>]  
2.9 - 5.2

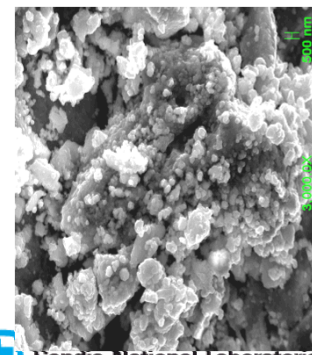
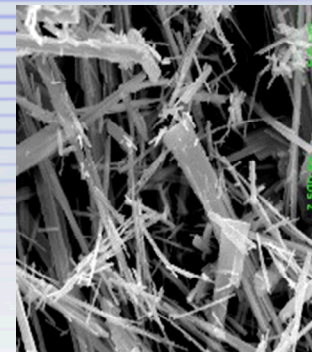
Log[Kd - IO<sub>3</sub><sup>-</sup> ]  
1.7 - 4.9

Log[Kd - I<sup>-</sup> ]  
2.9 - 5.2

Log[Kd - Se ]  
1.4 - 3.9

Log[Kd - TcO<sub>4</sub><sup>-</sup> ]  
1.2 - 2.5

Kd - ClO<sub>4</sub><sup>-</sup>  
0-20



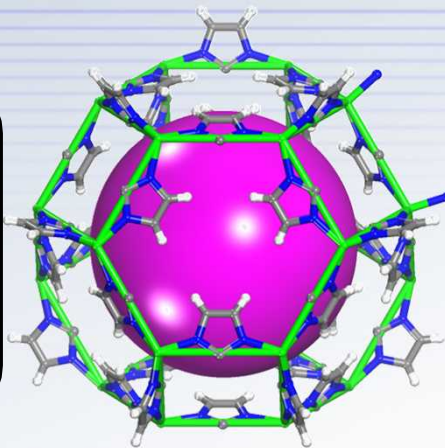
# Use of Metal Organic Frameworks (MOFs) for Radiological Gas Sorption

Depending on Selectivity Needs:  
Tunability of MOFs

Size (Pore) vs. Open Metal Center Hydrophobic vs Hydrophilic MOFs For  
 $I_2$  Sorption in complex stream (eg.,  $H_2O$ )

*JACS*, 2011, 133 (32), 12398

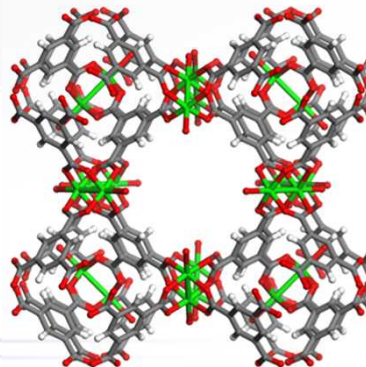
Basolite Z1200, ZIF-8  
Constricted Pore Opening ( $\approx 3.4\text{\AA}$ )  
1100 – 1600  $m^2/g$   
Pore Volume = 0.636 cc/g  
stable in Air &  $H_2O$   
High Selectivity for  $I_2$ , slow kinetics



$I_2@ZIF-8 \sim 125 \text{ wt.}\% I_2$

*Chem. Mater.*, 2013, 25 (13), 2591

Basolite C300, Cu-BTC, HKUST-1  
Open Channels,  $\approx 1\text{nm}$  in 3D  
1500-2100  $m^2/g$   
Exposed Metal Sites of Framework  
 $I_2$  selectivity in Humid Stream



$I_2@HKUST-1 \sim 175 \text{ wt.}\% I_2$

