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

EMSP Project #81949

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Presentation Outline

- Objective & Strategy
- Potential Applications
- Current Sorbent Materials
  - crystalline silicotitanate
  - monosodium titanate
- Research Findings
  - silicotitanates
  - titanates
  - heteropolymetalates
- Current/Future Activities

Objective & Strategy

Primary objective is the development of inorganic-based sorbents that exhibit increased selectivity for cesium, strontium and actinide species in the presence of high salt matrices

Research focused on

- **identifying structural characteristics responsible for the selectivity with a particular sorbate,**
- **develop computational models of sorbents that can be used as a design tool for the synthesis of new materials,**
- **synthesize novel sorbent materials, and**
- **evaluate new materials for cesium, strontium and actinide removal characteristics with simulated and actual waste solutions.**

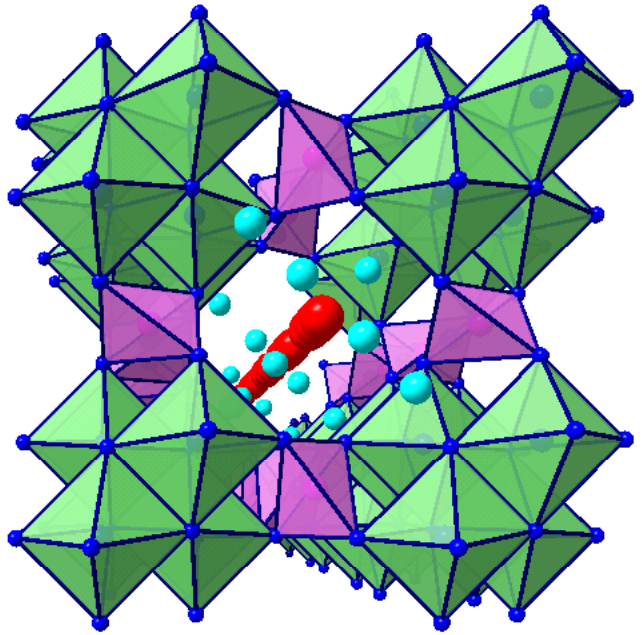
Potential Applications

- **High-Level Wastes**
  - **SRS**
    - **improved alternative to MST**
    - **one-stage process for Cs, Sr & actinide removal**
    - **in-tank/at-tank deployment**
    - **decontamination of DWPF recycle streams**
  - **Hanford**
    - **one-stage process for Cs, Sr & actinide removal**
    - **in-tank/at-tank deployment**
  - **INEEL**
    - **Sr/TRU removal from dissolved calcine**
    - **Cs/Sr/TRU removal from liquid wastes**
- **Subsurface & Contaminants**
  - **materials for reactive barriers**
  - **pretreat retrieved TRU and mixed wastes**
- **Deactivation & Decommissioning**
  - **limit transport of contamination from tanks**
  - **separate radioactive components from decon solutions**

Current Materials

Crystalline silicotitanate (CST)

- **highly selective for Cs^+ in high Na^+ solutions**
- **selective for Sr^{2+}**
- **low affinity for actinides**
- **Cs^+ and Sr^{2+} selectivity modified by substituting Nb for Ti in the framework**



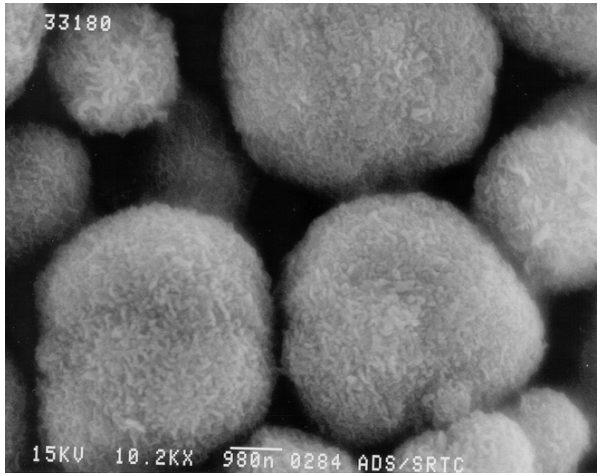
$HNa_3Ti_4Si_2O_{14}\bullet 4H_2O$

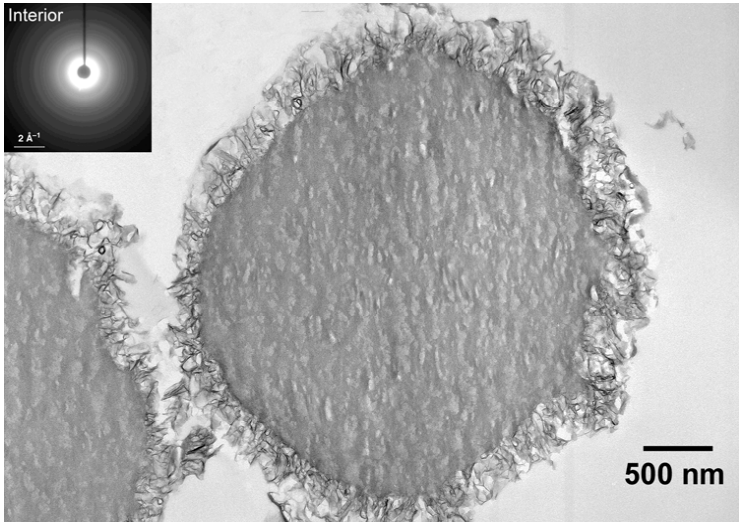
$HNa_2Ti_3NbSi_2O_{14}\bullet 4H_2O$

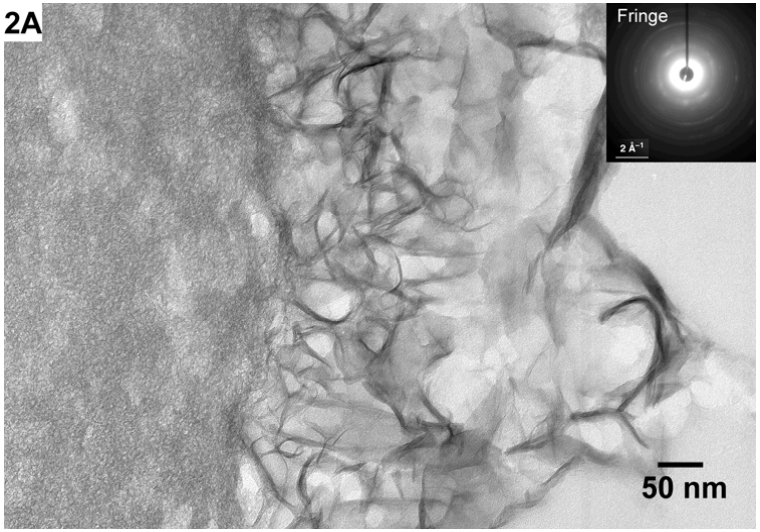
Current Materials

Baseline process at SRS uses a sodium titanate (MST) material for removal of ^{90}Sr and alpha-emitters (actinides) from HLW solutions

$$NaTi_2O_5H$$







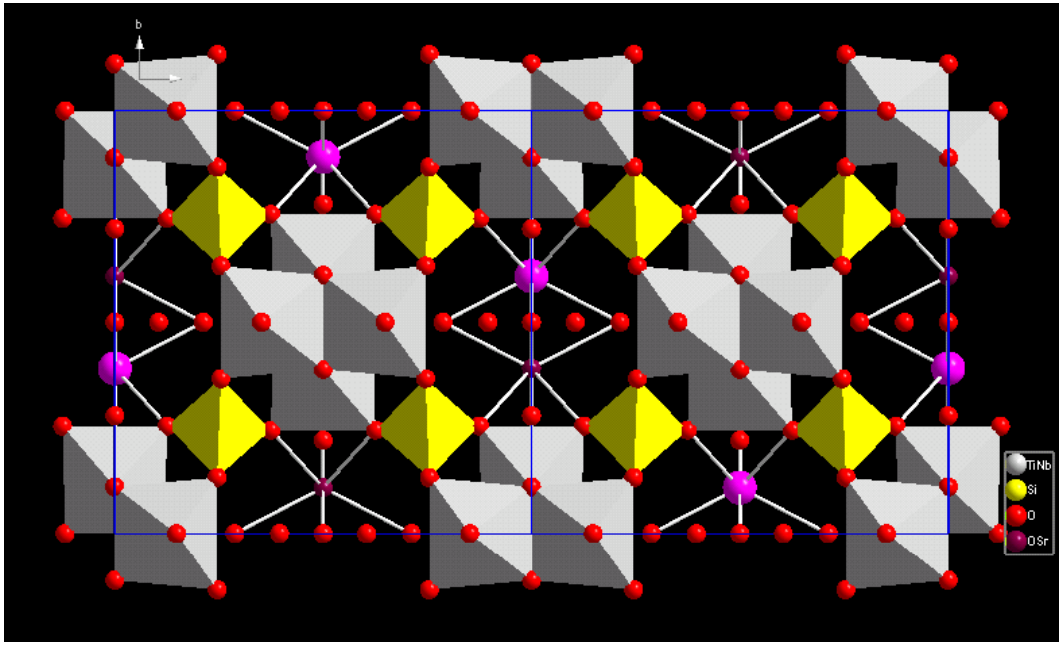
Research Findings - CST

Nb substitution increases Cs^+ selectivity & decreases Sr^{2+} selectivity

- **XRD studies indicate**
  - **Cesium located in center**
  - **Strontium located off-center**

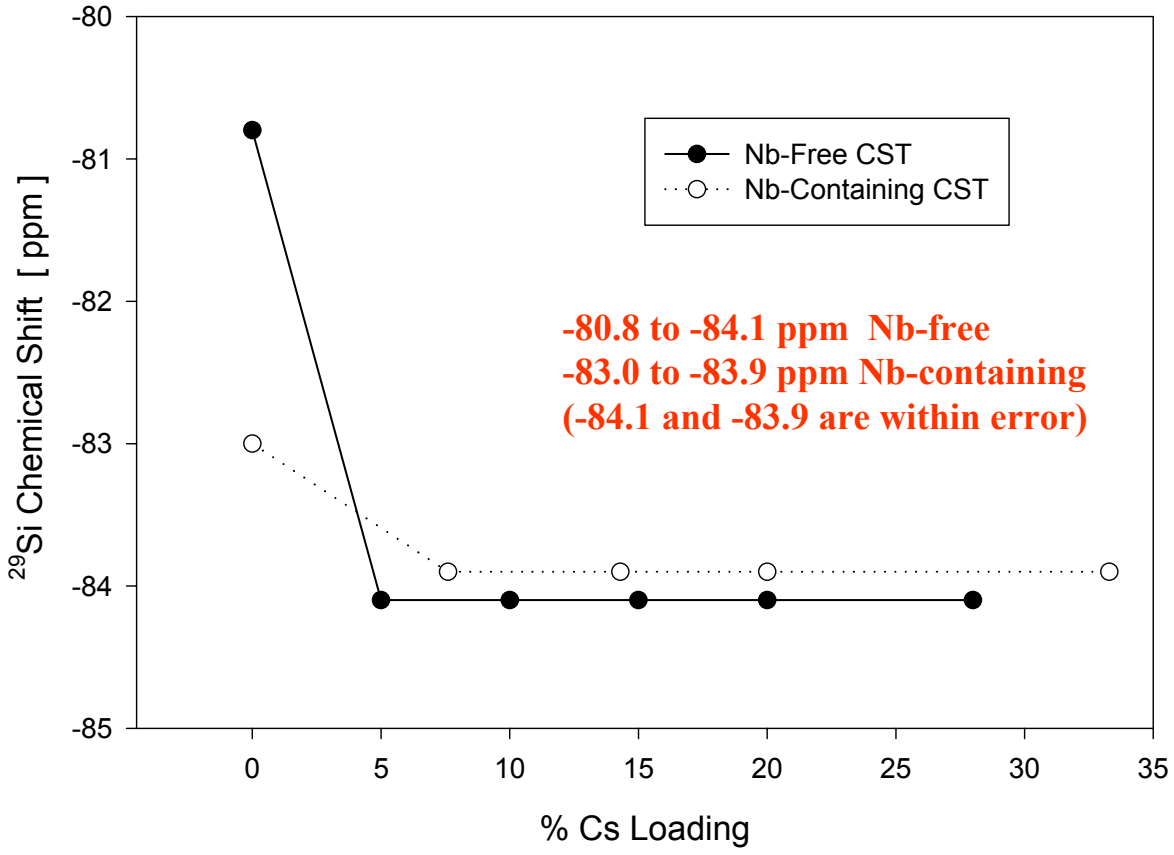
Increase in Cs^+ selectivity attributed to

- **higher coordination number**
- **increase in unit cell volume**
- **change in water/Na^+ population**



Research Findings - CST

NMR Studies

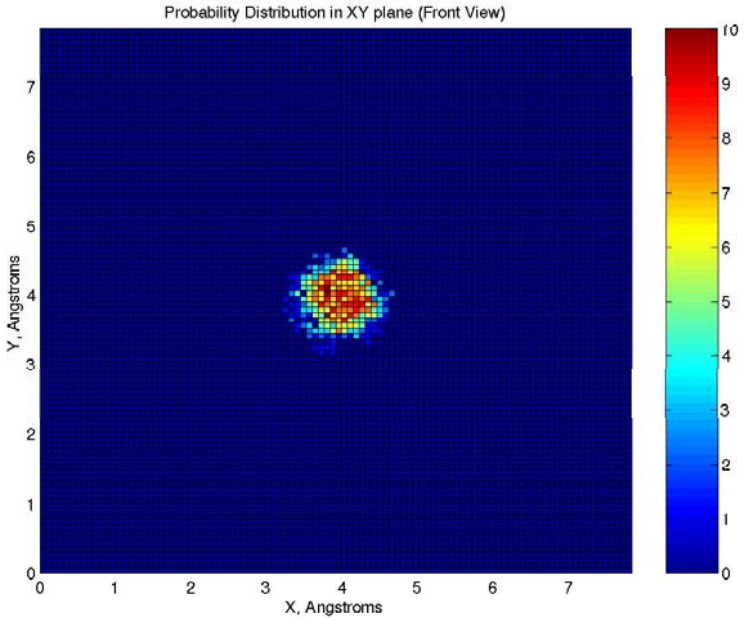


- Increasing negative ^{29}Si NMR shift indicates increased Si-O-Si bond angle
- CST framework "distortion" resulting from Cs^+ exchange is less for the Nb-CST than for the Nb-free CST

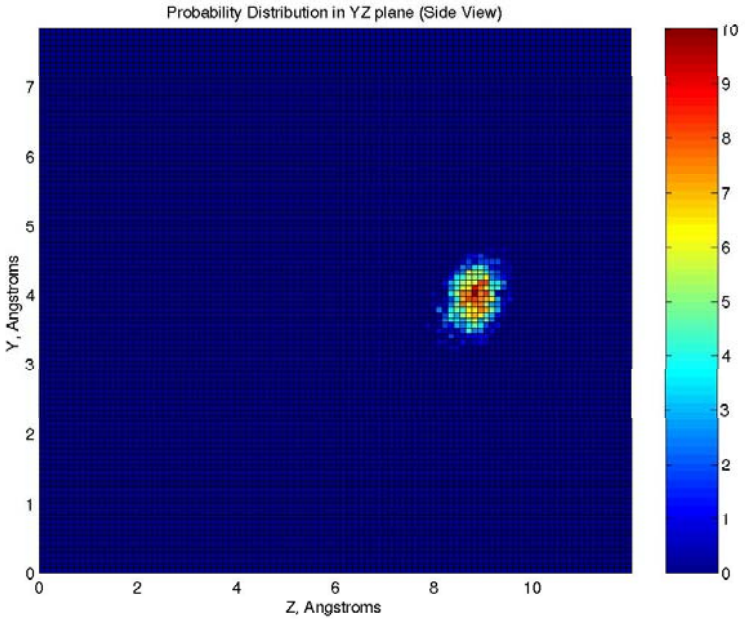
Modeling - CST

- **Use structural information to construct computational model**
- **Calculate locations of cations & water molecules**

Cs^+ positions in Cs-exchanged CST

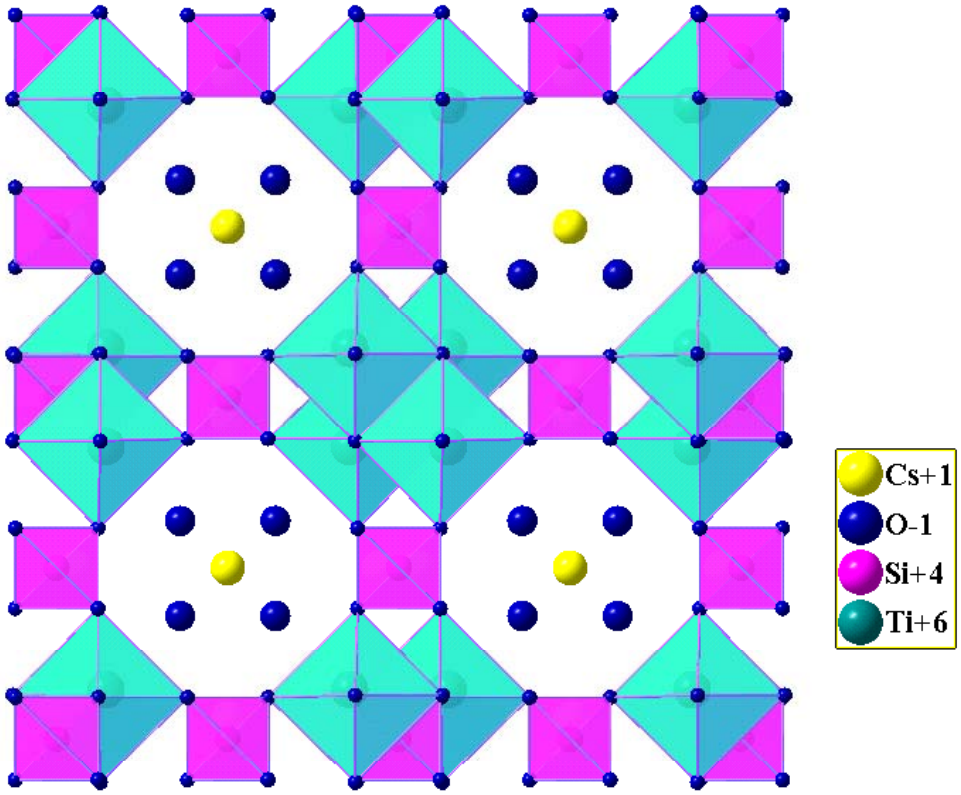


View of ab-face in CST



View of bc-face in CST

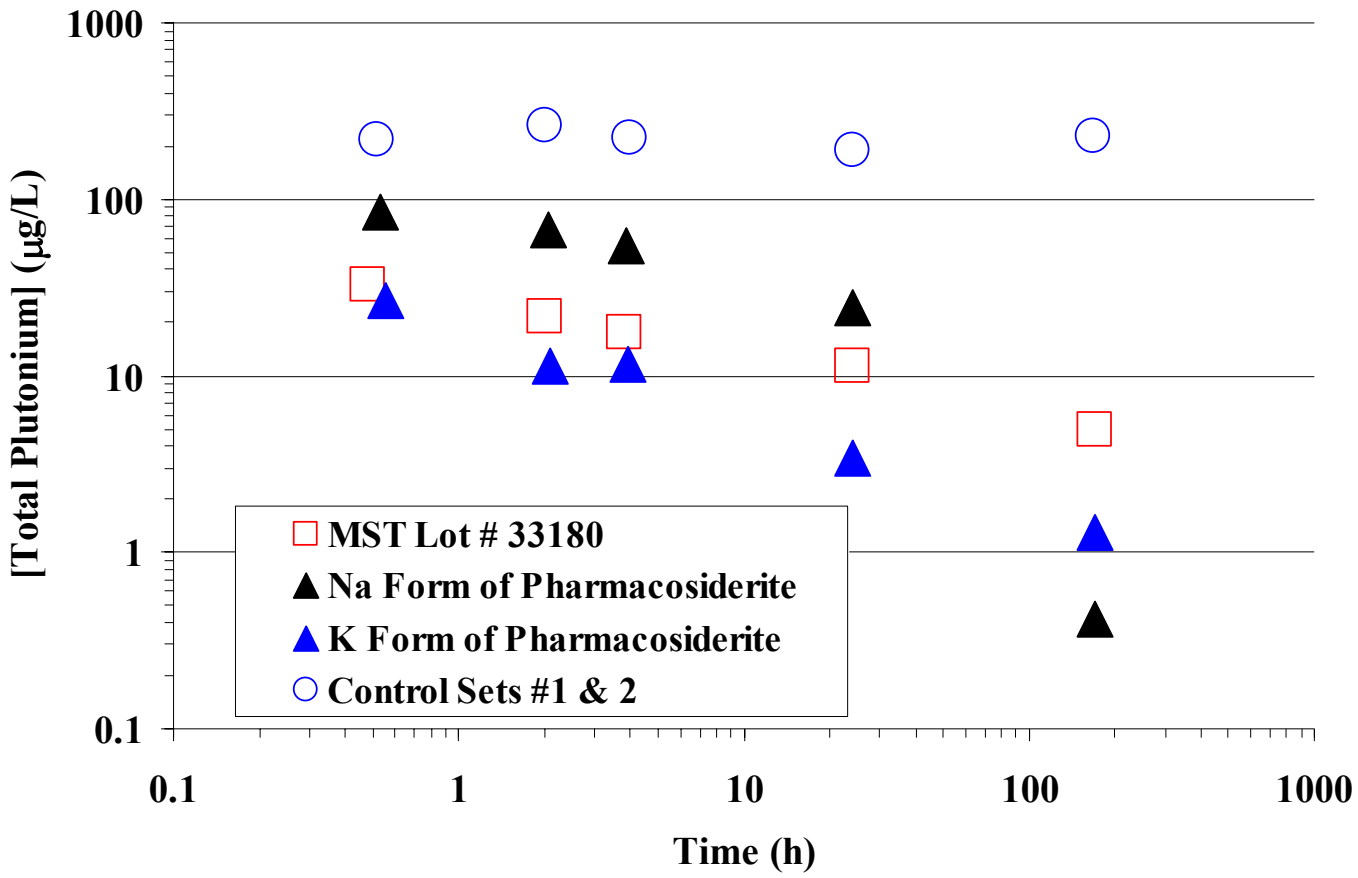
Research Findings – Titanosilicates with Pharmacosiderite structure (TSP)



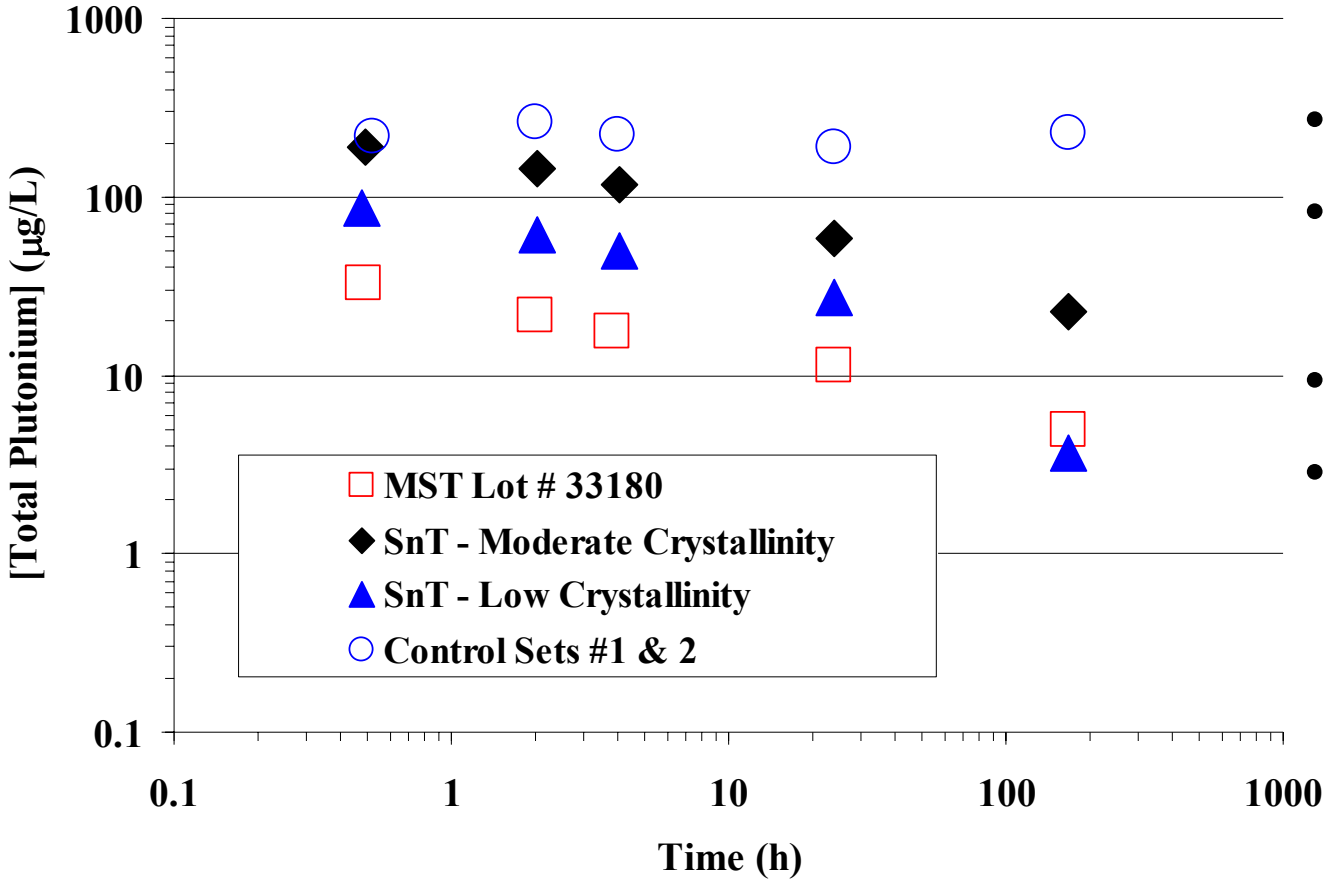
- $_3H(TiO_4)_4(SiO_3)_3.4H_2O$
  here M = K, Na
- milar structure to CST
- dimensional tunnels
  - more open network
- ıbstitute Ge for both Ti & in framework
  - Increase/decrease unit cell and selectivity for Sr

Research Findings - TSP

- Cs selectivity lower than CST
- Sr/actinide selectivity higher than CST
- Sr/actinide removal characteristics similar to MST



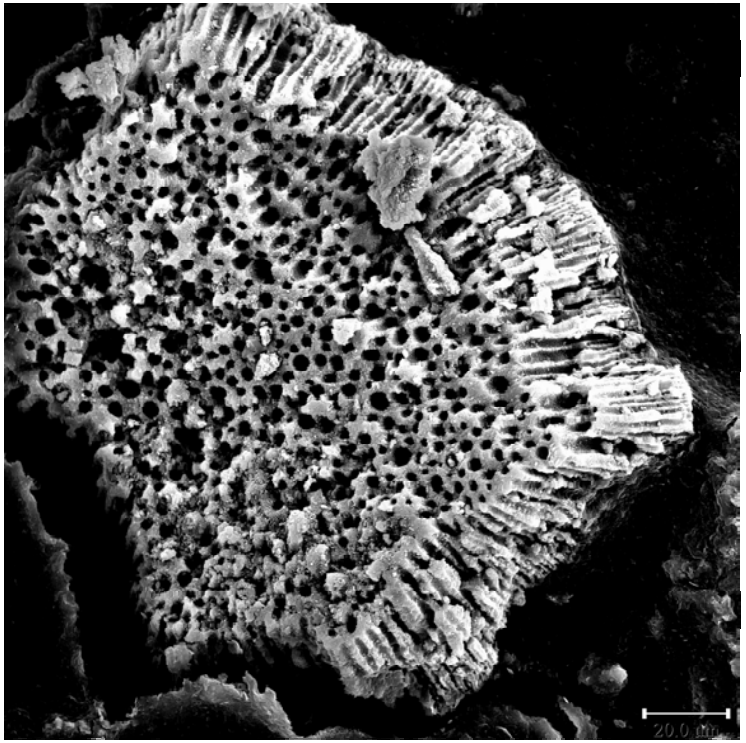
Research Findings – Sodium Nonatitanate (SnT)



- $Na_4Ti_9O_{20}{\cdot}xH_2O$
- Hydrothermal synthesis
- Layered structure
- Increased selectivity with decreased crystallinity

Research Findings – SnT

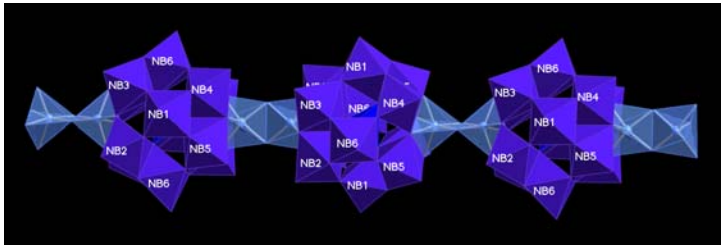
- **10 – 50 % substitution of Ti with Nb**
- **Coral-like particle morphology**
- **Evidence for 2nd phase at high Nb substitution**
- **Increased selectivity for Pu relative to other sorbates**

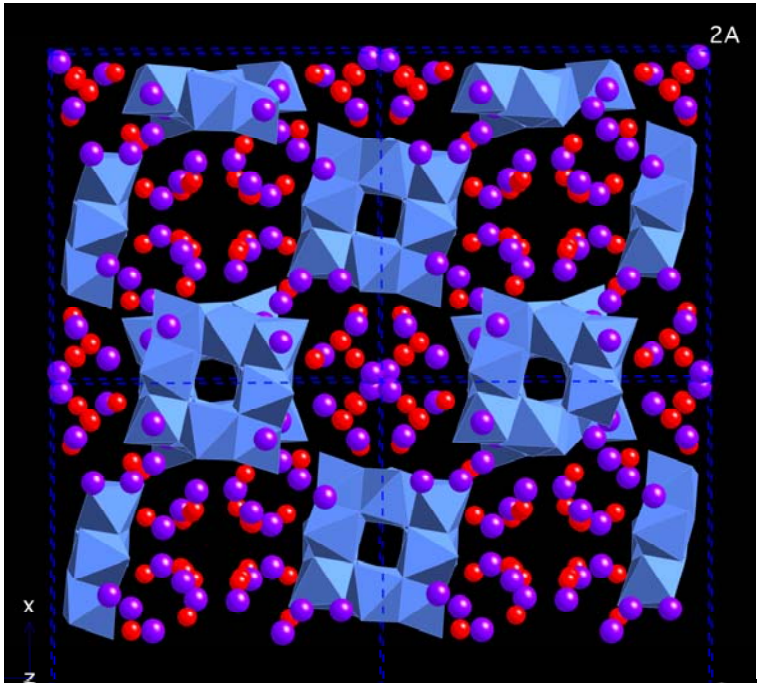


Material	K_d (mL/g) Sr	Pu	Np
MST (baseline)	90000-300000	7800-16000	3100-4300
10% Nb-SnT	28000	9400	200
50% Nb-SnT	44000	12000	440

Research Findings – Heteropolymetalates (IPX)

- $M_{12}[Ti_2O_2][SiNb_{12}O_{40}]\cdot 16H_2O$ where M = Na,K
- Increased selectivity for Pu relative to other sorbates





Material	K_d (mL/g) Sr	Pu	Np
MST (baseline)	90000-300000	7800-16000	3100-4300
KIPX	5100	12000	14
NaIPX	28000	9900	370

Current/Future Activities

- Complete studies on Cs/Sr exchange with CST, TSP and IPX materials
- Extend modeling to TSP and IPX materials
  - enhance binding of actinides: Pu(IV), Np(V), U(VI) & Am(III)
- Synthesis of new/modified materials
  - TSP
  - MST
  - IPX
  - SnT
- Evaluate performance of candidate materials