Phase Chemistry of Tank Sludge Residual Components

Principal Investigators:

J.L. Krumhansl, SNL (505) 844-9093 (jlkrumh@sandia.gov)

P.V. Brady, SNL (505) 844-7146

J. Liu,PNNL, (509) 375-3430

K.L. Nagy, C.U., (303) 492-2606

Principal investigators:

J.L. Krumhansl, SNL
P.V. Brady, SNL
J. Liu, PNNL
K.L. Nagy, C.U.

Contributors:

M.A. Molecke, SNL
H.L. Anderson, SNL
C. Bryan, SNL
S.M. Von Drasek, SNL

Problem: The chemistry of tank sludges is poorly known and incredibly expensive to measure (~$10^6$$ per sample).

Result: It is impossible to predict the composition of the after-cleaning residuum, or the long-term health threat it will pose.

Our Approach: Develop tank sludge simulants that can be used to estimate long-term residuum stability.

1. Must demonstrate that the major element behavior of the tank sludge simulants matches that of real tank sludges.

2. Must then measure the chemical stability/leachability of trace elements (Radionuclides) in tank sludge residuum simulants.

We greatly appreciate funding by the Environmental Science Management Program (EM-52)

Methodology

1. Use process knowledge to identify waste streams and then synthesize appropriate sludges.

2. Compare the phase chemistry of synthetic and HLW tank sludges.

4. Evaluate the behavior of radionuclides in association with the principal sludge components.

5. Assess how the sludge phases will age and how the radionuclides will respond to changing environments.

I How did sludges originate?

Early Waste Reprocessing Activities

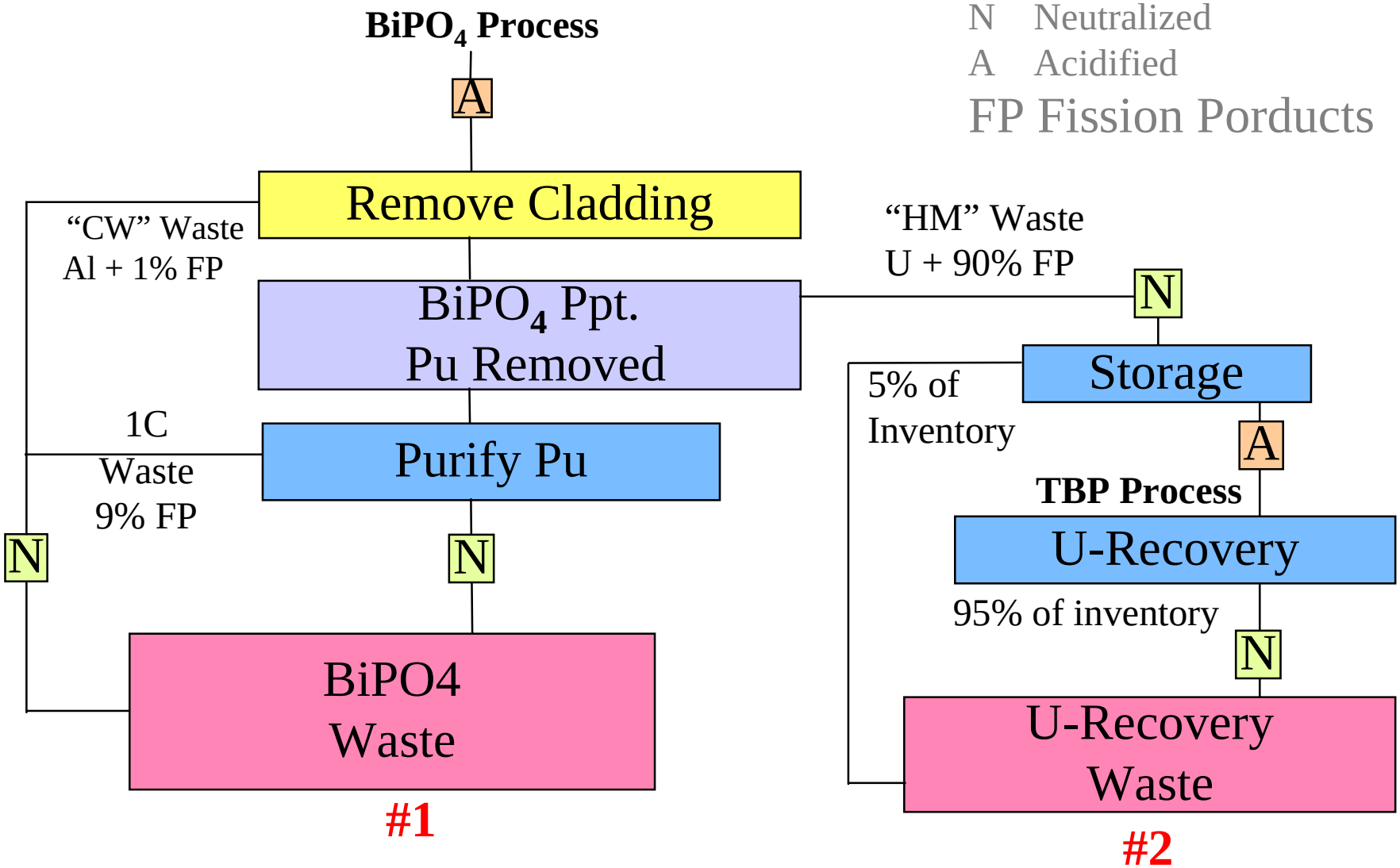
$BiPO_4$ Process: Fuel was dissolved in HNO_3 and Pu separated by co-precipitating on $BiPO_4$ and LaF_3. U was discarded as a heavy metal waste along with 90% of the fission products. Other wastes contained 10% of the fission products as well as some of the Al cladding and process chemicals (#1).

TBP Process: $BiPO_4$ metal wastes were re-acidified and the U recovered by solvent extraction. Wastes include the remaining 90% of the fission products (#2).

Early Reprocessing Technologies

7,800 MTU Al clad fuel
0 MTU Zr clad fuel
7,800 MTU Total

MTU Metric Tons Uranium
N Neutralized
A Acidified
FP Fission Porducts

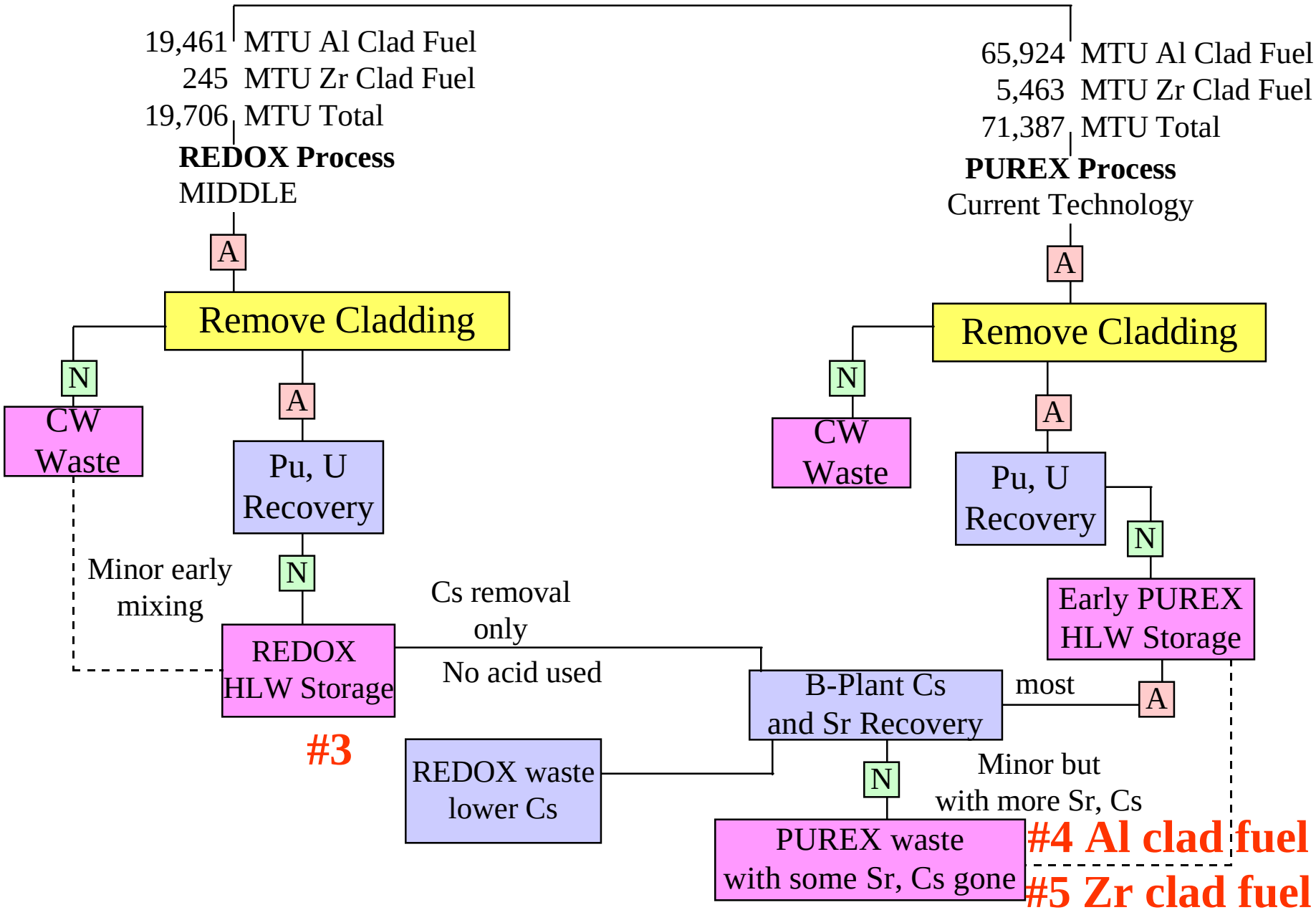


Later Waste Reprocessing Activities

REDOX Process: After cladding removal fuel was dissolved in nitric acid. Wastes contained $Na_2Cr_2O_7$, $Al(NO_3)_3$, and Fe^{+2}-sulfamate that was added to facilitate U and Pu removal by solvent extraction with MIBK (#3).

PUREX Process: Fuel was dissolved in nitric acid and both U and Pu were extracted with TBP. The first PUREX waste streams came from Al clad fuel (#4). Later PUREX wastes involved reprocessing Zr clad fuels (#5).

Later Reprocessing Technologies



Simplified Waste Stream Chemistry (molar)

	$BiPO_4$ #1 (Al Clad)	TBP#2 (Al Clad)	REDOX#3 (Al>Zr)	PUREX#4 (Al>Zr)	PUREX#5 (Zr Clad)
Al	8E-2	0	1.1	8E-1	0
Fe	3E-2	5E-2	5E-2	1E-1	4E-2
Cr	3E-3	3E-3	7E-2	8E-3	3E-3
Ni	2E-3	2E-3	4E-3	1E-2	1E-3
Zr	3E-4	0	0	0	1E-1
Bi	1E-2	0	0	0	0
Ca	2E-2	2E-2	0	6E-2	2E-2
Si	6E-2	4E-3	4E-2	5E-2	0
F	2E-1	0	0	0	8E-1
P	3E-2	1E-1	0	2E-2	0
Pb	4E-4	1E-4	1E-2	1E-3	0
Mn	7E-3	0	0	3E-2	0
Cd	1E-5	8e-6	0	1E-3	1E-3

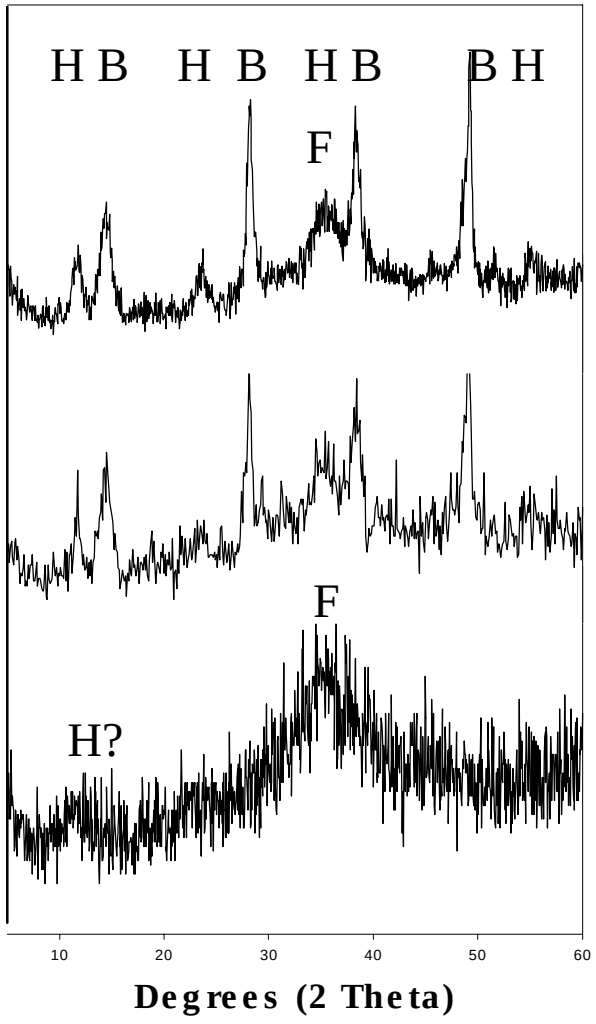
Agnew, S.F., 1997, Hanford Tank Chemical and Radionuclide Inventories, Rev. 4, LA-UR-96-3860
Colton, N.G., 1994, Sludge Pretreatment Chemistry Evaluation:Enhanced Sludge Washing Separation Factors,TWRSPP-94-053, Appendix E
Kupfer, M.J., et al., 1997, Standard Inventories of Chemicals And Radionuclides in Hanford Site Tank Wastes, HNF-SD-WM-TI-740

Reprocessing eventually produced five major waste streams that were made strongly basic prior to storage in tanks. Most sludge components precipitated during or shortly after this process.

II What phases precipitate during artificial sludge preparation?

PUREX Waste, No Excess Silica

X-ray diffraction results



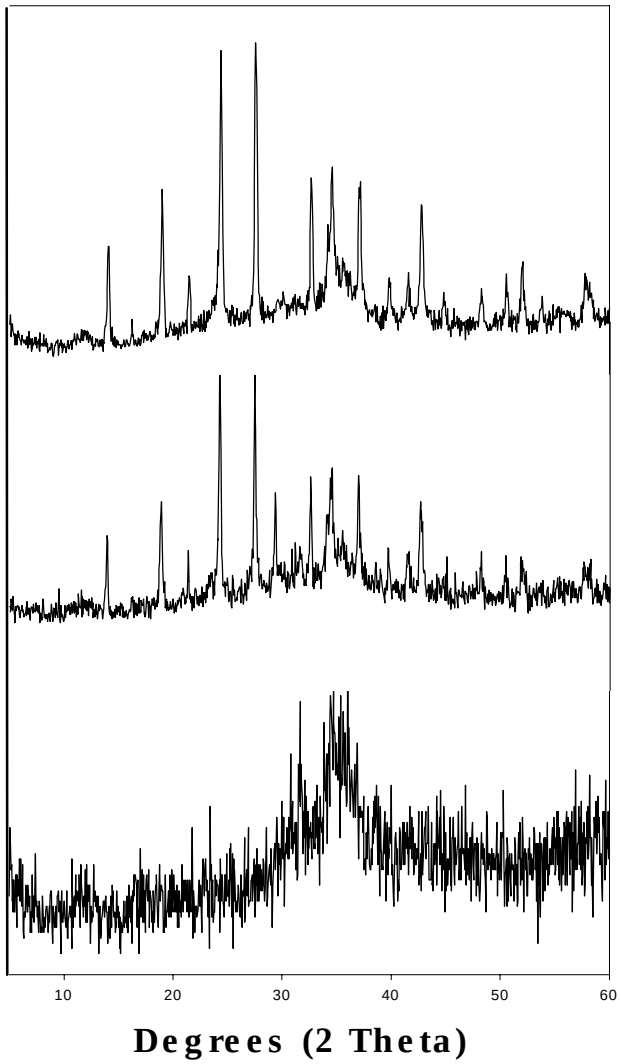
Dialysis and 90°C treatment in deionized water failed to produce either hematite or goethite.

Boehmite (B) and hydrotalcite (H) appear after 90 days at 90°C, but was hardly detectable after 90 days at 60°C.

Ferrihydrite (F) precipitated initially.

PUREX Waste With Excess Silica

X-ray diffraction results

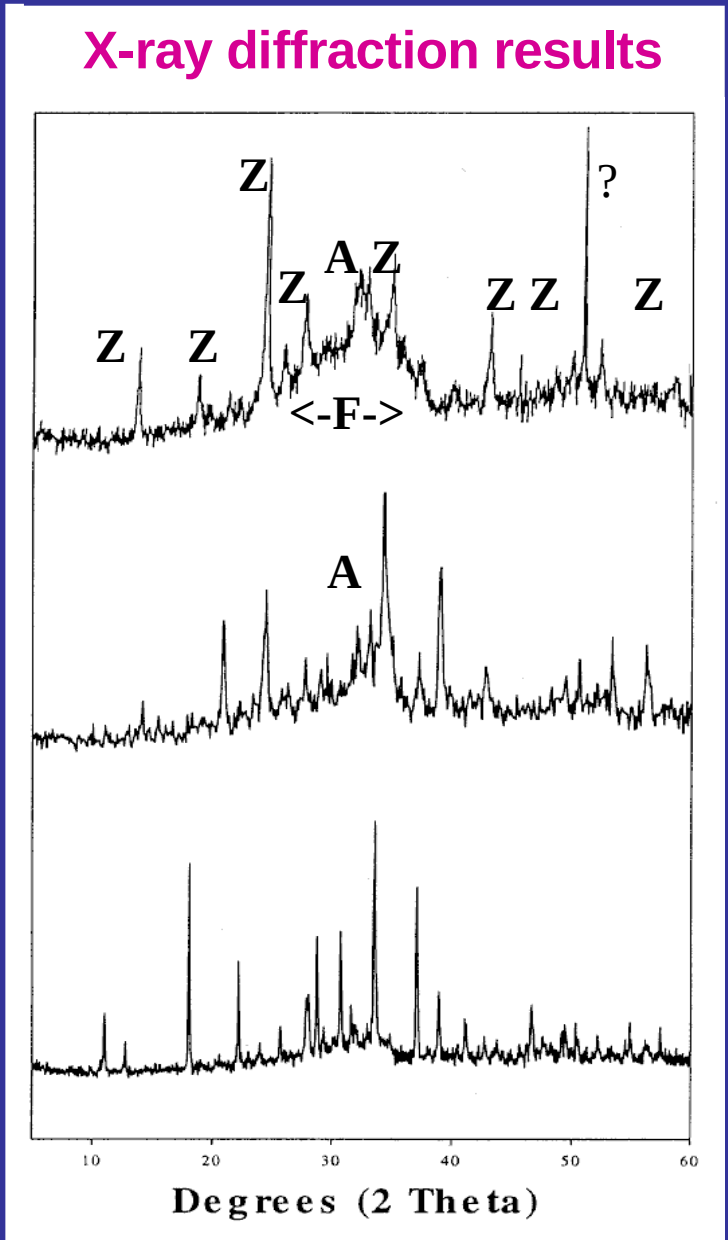


Dialysis removed the strongly basic synthesis fluid but 90°C heating in deionized water still producs niether hematite or goethite.

Excess silica from Pyrex causes rapid zeolite precipitation (sharp peaks). Removing Al inhibits hydrotalcite formation. Zeolites formed In 6 days at 90°C but not in 182 Days at 23°C.

Initially just ferrihydrite precipitates.

$BiPO_4$ Process Waste



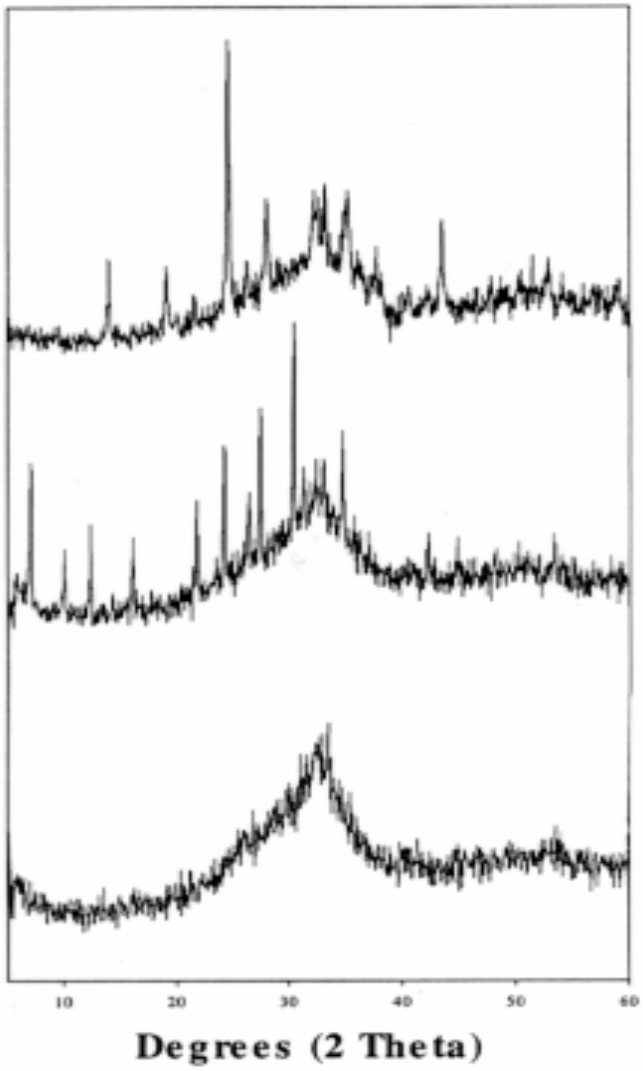
Dialysis removed soluble salts revealing apatite (A), zeolite (Z), and ferrihydrite (F). Heating at 90°C in deionized water caused no changes.

After a month at 90°C apatite (A), ferrihydrite, and another sparingly soluble phase formed.

Numerous sparingly soluble salts initially precipitated with ferrihydrite. In 98 days a SAPO zeolite forms at 23°C.

$BiPO_4$ Process Waste

X-ray diffraction results



Cancrinite zeolites, apatite, and ferrihydrite formed after 98 days at 90°C. Dialysis of the sample and heating at 90°C in deionized water produced no additional changes.

SAPO zeolite and ferrihydrite formed after 98 days at 23°C.

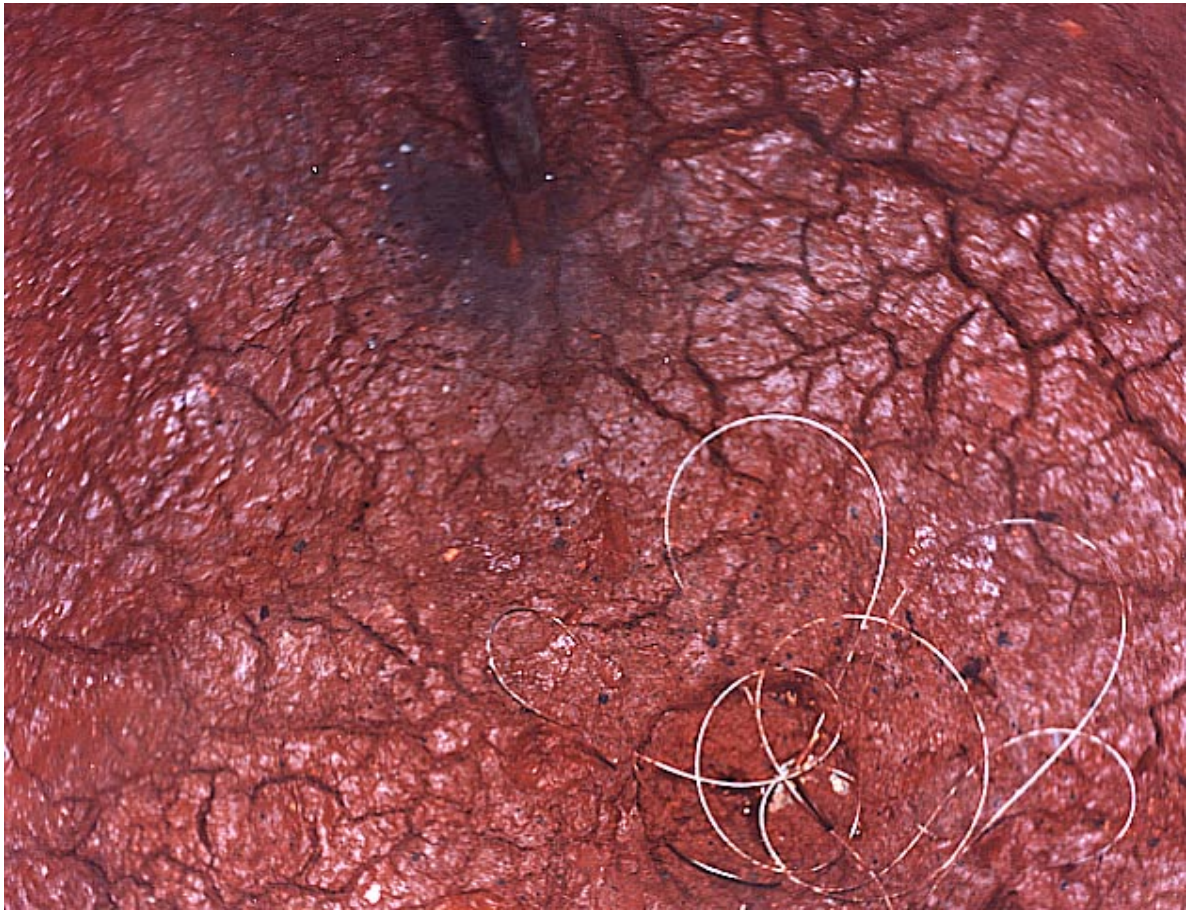
Initially only ferrihydrite precipitated.

After ageing mixtures of ferrihydrite, apatite, hydrotalcite, boehmite, SAPO-type zeolites, and cancrinite-group zeolites are found. Different wastes produce different phase assemblages.

III Do artificial sludges match real sludges?

Fe-Rich Tank Sludge

Many tank waste sludges are rich in iron, as indicated by the red color in the photograph. The insert is a typical TEM image of the iron hydroxide mineral phase in the tank waste.



Jun Liu, PNNL, Richland

Typical Fe-Rich Granules In Real Sludge

Many tank wastes contain iron hydroxide as the insoluble phase. The iron hydroxide usually form dense spherical agglomerates about 0.5 μ m is size. The crystallinity varies from tank waste to tank waste.

Fe

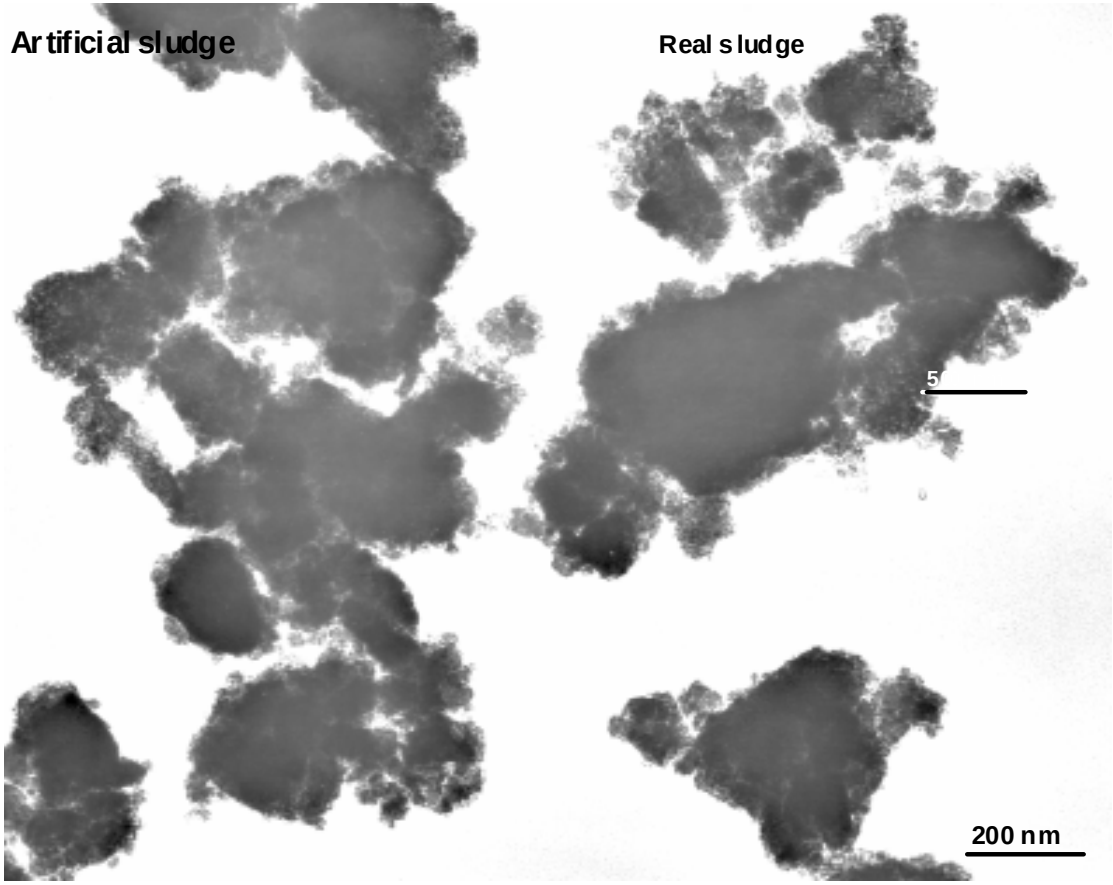
Fe

500 nm

Jun Liu, PNNL, Richland

Artificial and Real Sludges Compared

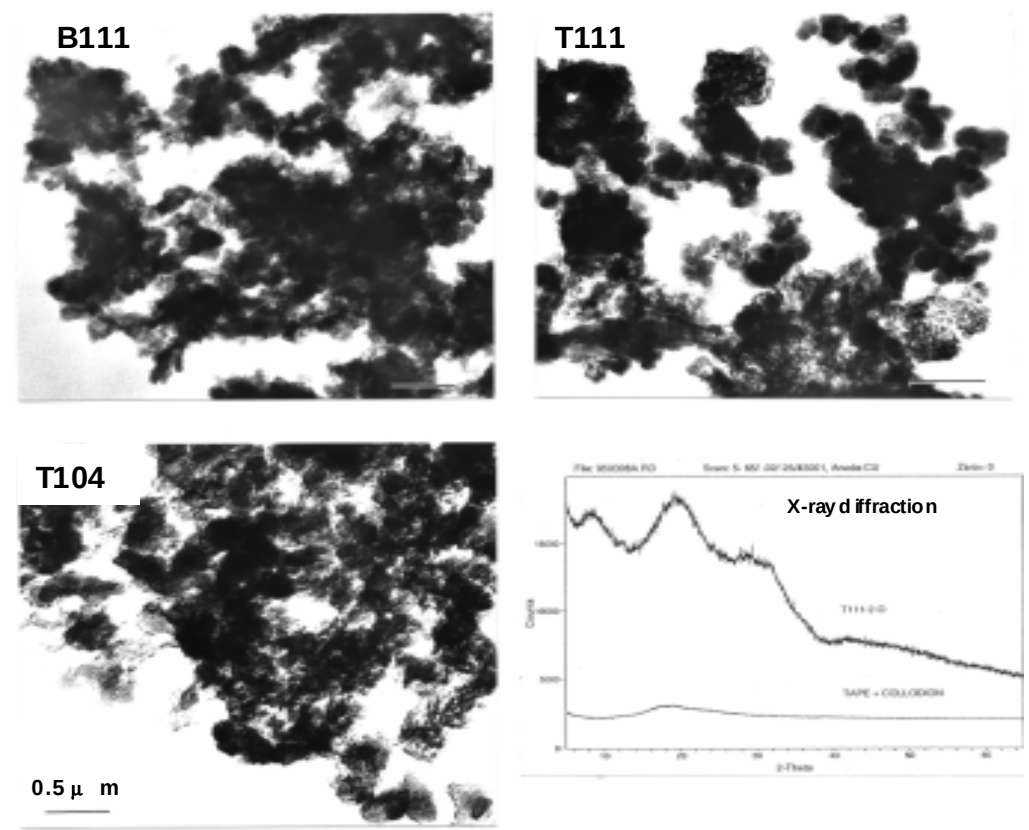
Artificial sludge containing dense agglomerates of Fe, Si, Bi has similar morphology to real tank waste (insert).



Jun Liu, PNNL, Richland

Typical Fe-Bi-Si Particles In Tank Sludges

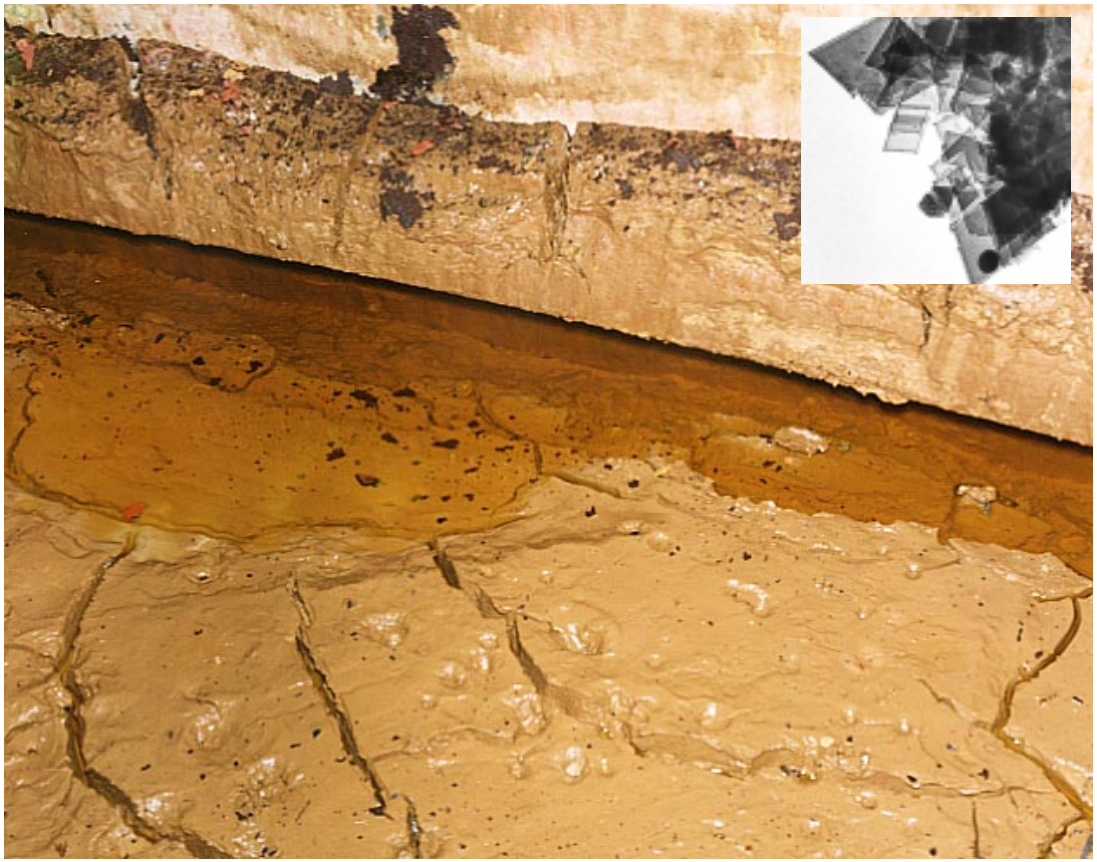
Poor crystalline Bi, Fe, Si containing phases (iron bismuth silicates) are observed in many tank waste samples, including B111, T111, T104. The primary agglomerates are spherical in shape and have a diameter about 0.5 μ m.



Jun Liu, PNNL, Richland

Al-Rich Tank Sludge

Al containing phases are abundant in tank wastes. This figure shows a photograph of the Al rich tank waste and the TEM image (insert) of the boehmite (AlOOH) in the tank waste.



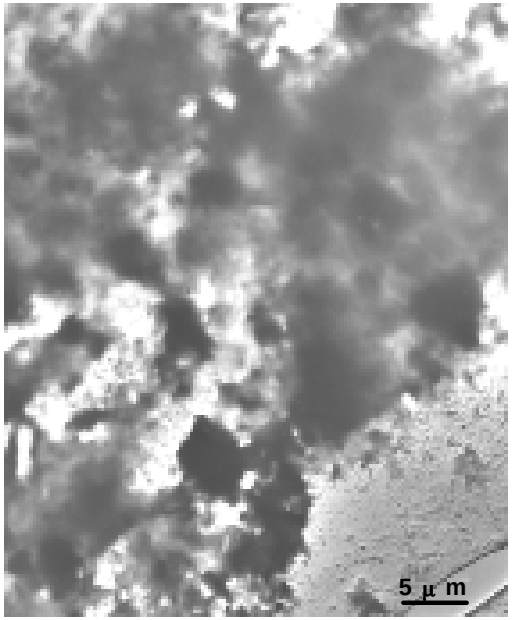
Jun Liu, PNNL, Richland

Major Al-Bearing Phases In Tank Wastes

Al is a major component in many tank waste samples. The dissolution and precipitation of Al containing phases play a critical role in tank waste processing (transportation, washing, sedimentation, ion exchanger and filtration, etc.), and in the leaching of radionuclides.

Gibbsite, $Al(OH)_3$, in C112.

Boehmite, AlOOH, in S104

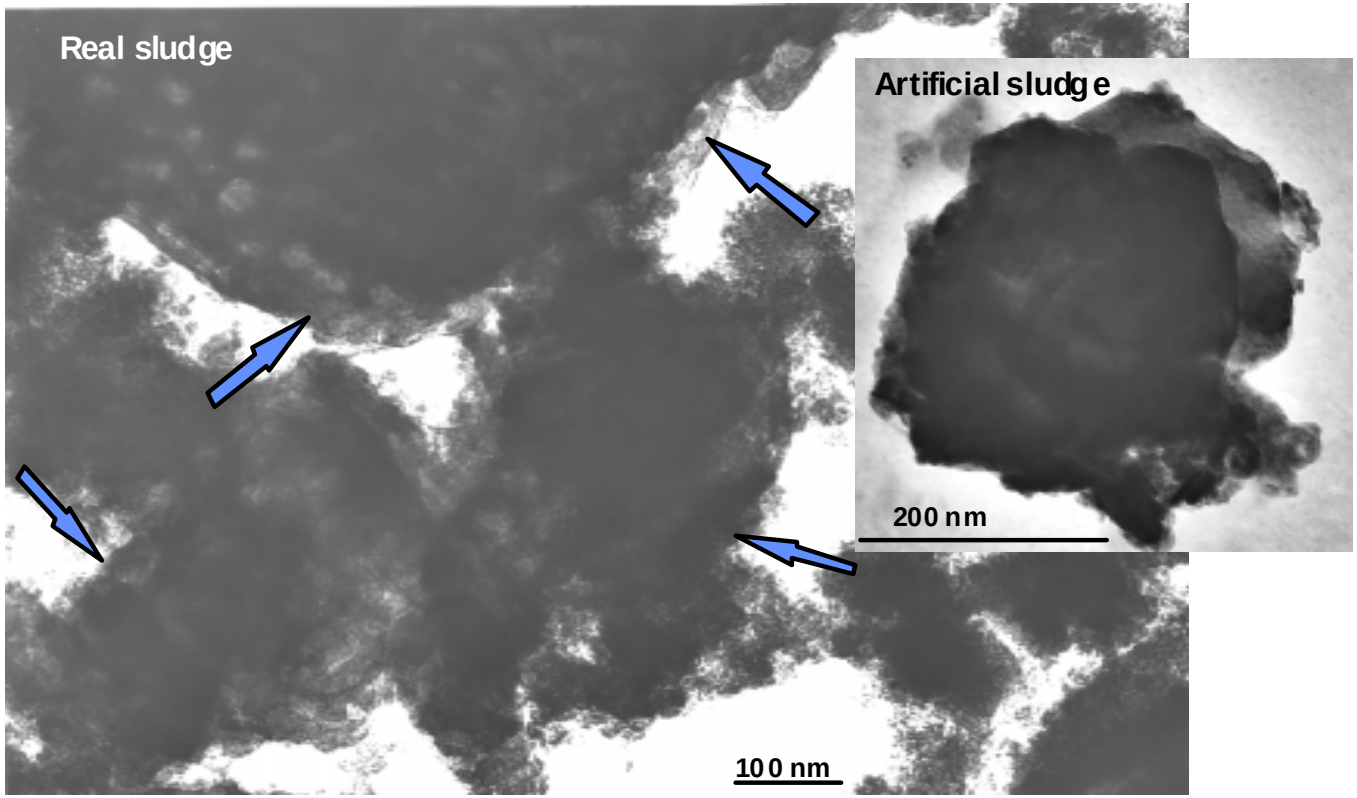


Dissolved $Al(OH)_3$ in SY102

Jun Liu, PNNL, Richland

Zeolites - In Both Tank and Artificial Sludges

Aluminosilicates in real tank waste and in artificial sludge have similar morphologies.

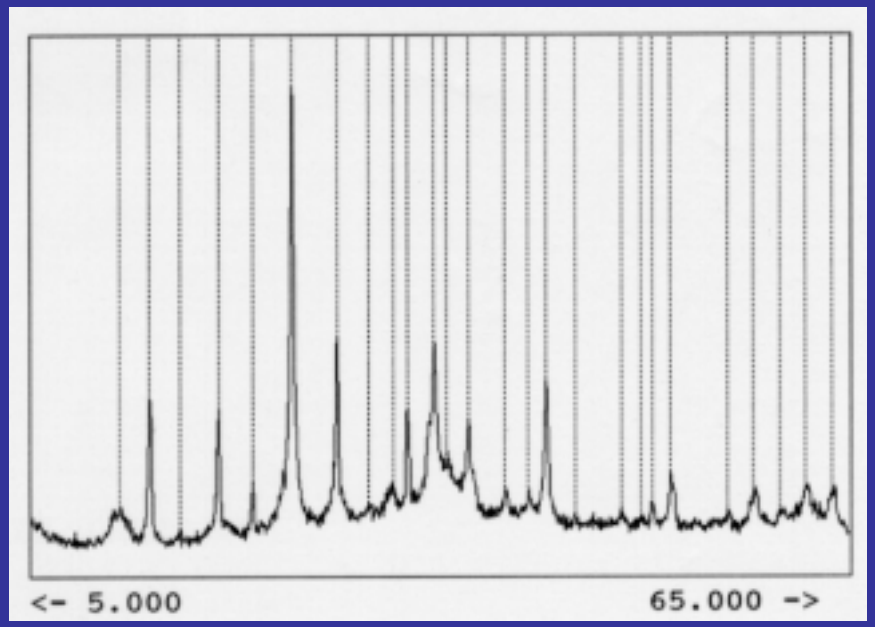


Jun Liu, PNNL, Richland

Zeolite Synthesis

Zeolites readily formed when sludges were synthesized in Pyrex flasks. $Na_6Al_6Si_6O_{24}(NO_3)_2.4H_2O$ was the most common zeolite. Naturally occurring cancrinite-type zeolites contain carbonate, chloride, sulfate, hydroxide and fluoride. A second SAPO - type zeolite also formed ($Na_2Al_2Si_{1.7}O_{7.9}$ $(PO_4)_{0.48}.3H_2O$) but was less common.

The number of different anions in these structures suggested that zeolites might be a Tc sink. However, when zeolites were grown in 10 ppm Tc fluids no Tc uptake was observed.



Cancrinite formed in 7 days at 90°C

Sandia National Laboratories

Artificial sludges aged at 90°C for 30 to 90 days contained many phases found in actual tank sludges. Many wastes were concentrated by boiling so ageing artificial sludges in this manner was representative.

IV How do the trace constituents behave in sludges?

What will govern the long-term release of radionuclides from “cleaned” tanks?

Problem: Sluicing of tanks will leave a residuum of insoluble, radionuclide-bearing iron hydroxides and phosphate minerals that constitute a potential long-term source of radiotoxicity to the underlying soil and groundwater. If subsequent leaching by fresh recharge is predicted to be significant, further stabilization of tank residuum may be required.

Approach:

1. Measure radionuclide desorption rates from iron hydroxides,
2. Determine dissolution rates of radionuclide-bearing phosphates,
3. Use measurements to estimate long-term export of radionuclides.

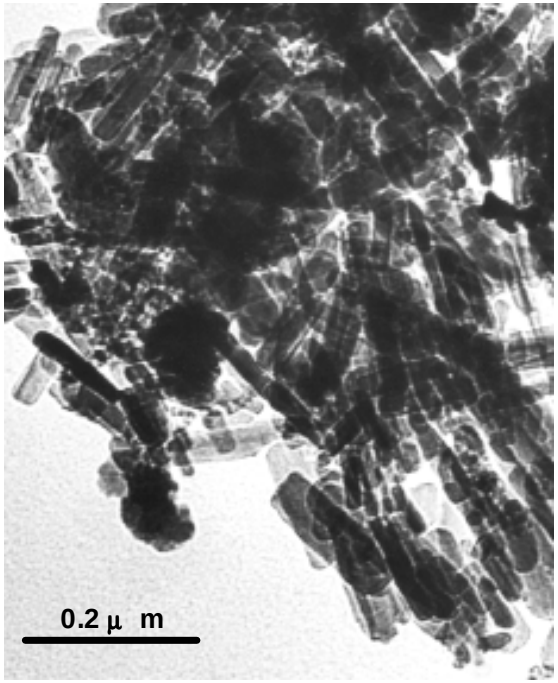
Determine Ca-Phosphates Dissolution Rates

Background: Hydroxyapatite - $Ca_5(PO_4)_3OH$ exists in a number of the tanks and contains impurities of ^{90}Sr, and possibly uranium isotopes as well. The release rates of these isotopes to the biosphere is envisioned to ultimately be limited by the rate at which the hydroxyapatite host dissolves into fresh recharge.

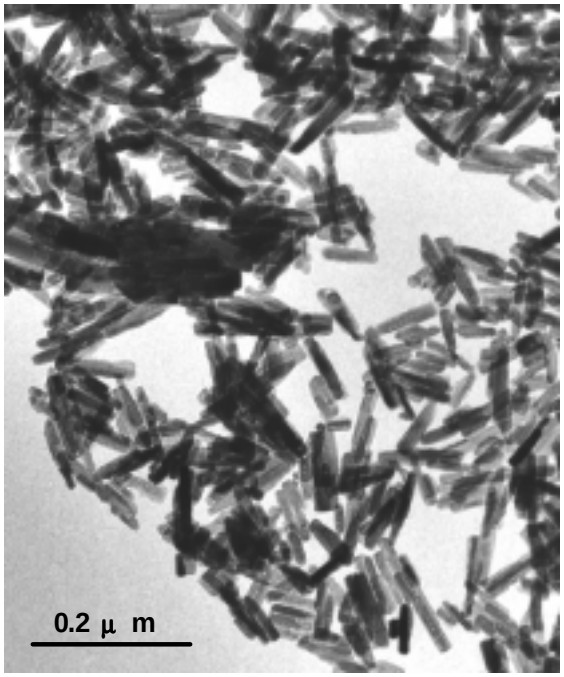
Research Plan: Synthesize hydroxyapatite and measure dissolution rates using a flow-through reactor.

Artificial and Tank Sludge Apatite Crystals

Calcium phosphate (Hydroxyl apatite, HAP) is a common insoluble mineral in tank waste. Artificial HAP was prepared under tank waste conditions.



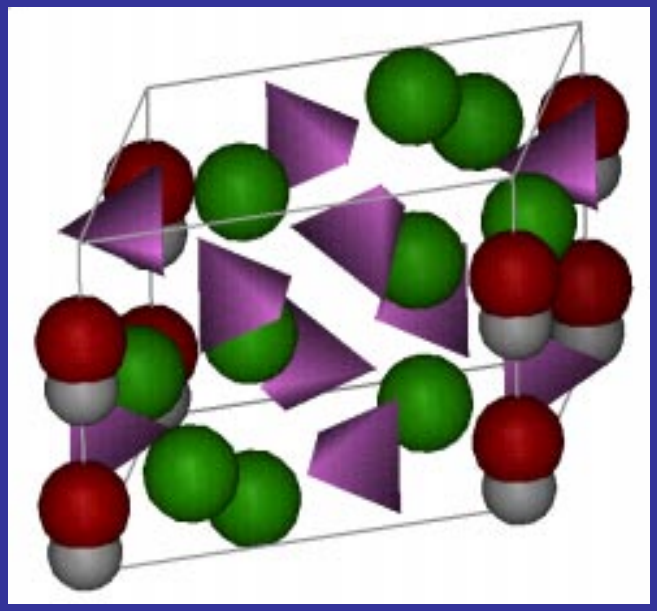
HAP in tank waste (B201, BY110, T111, U110, etc.)



Artificial HAP prepared under tank waste conditions

Jun Liu, PNNL, Richland

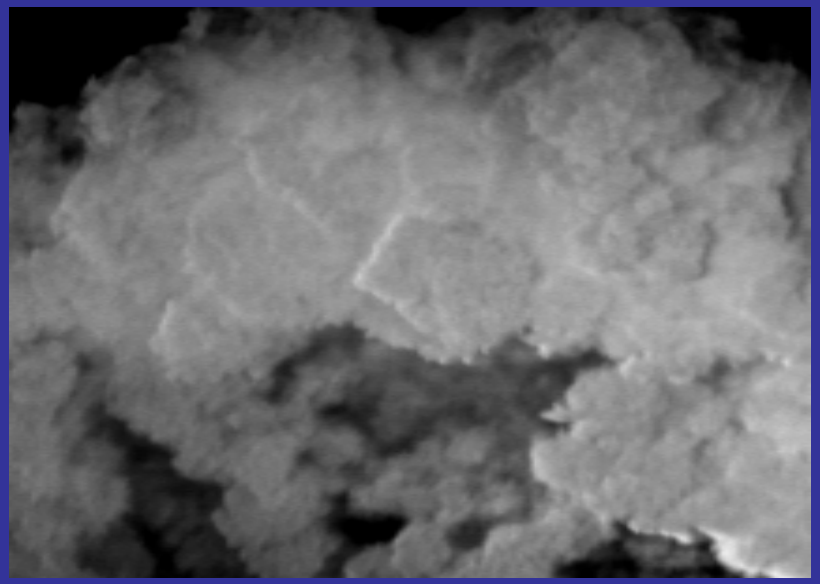
HAP Synthesis

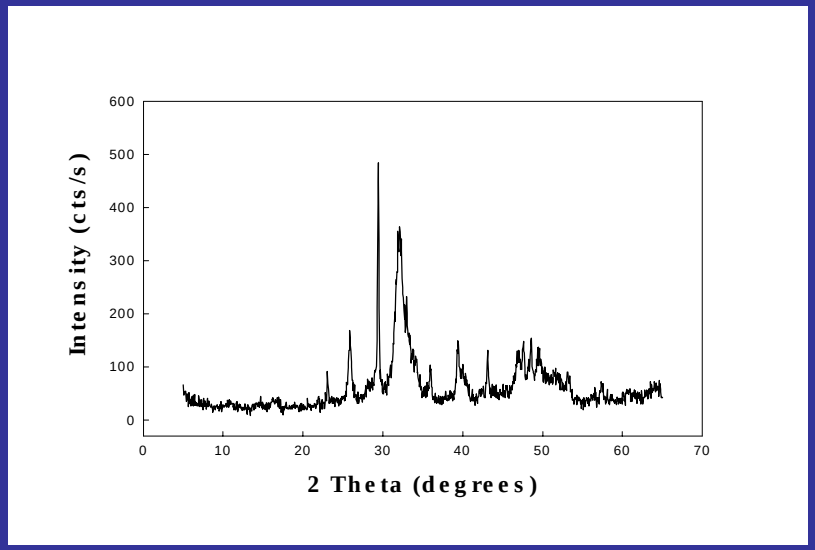


$Ca_5(PO_4)_3OH$

A = 250 ml 10M $NaNO_3$+
30g NaOH +
4.013g $Na_2HPO_3 \cdot 7H_2O$
+B = 0.132M $CaCl_2$

Time = 7-14d
Temp = 25°C





Sandia National Laboratories

Measure Fe-hydroxides Desorption Rates

<u>Background:</u> Iron hydroxides tend to sorb metal cations such as uranyl. We expect recrystallization of ferrihydrite (the primary phase in the tanks) to goethite (typically the most stable phase in arid soils) once dilute solutions encounter the ferrihydrite. Desorption of radionuclides sorbed cannot be predicted but must be measured if an accurate prediction of long-term release is to be made.

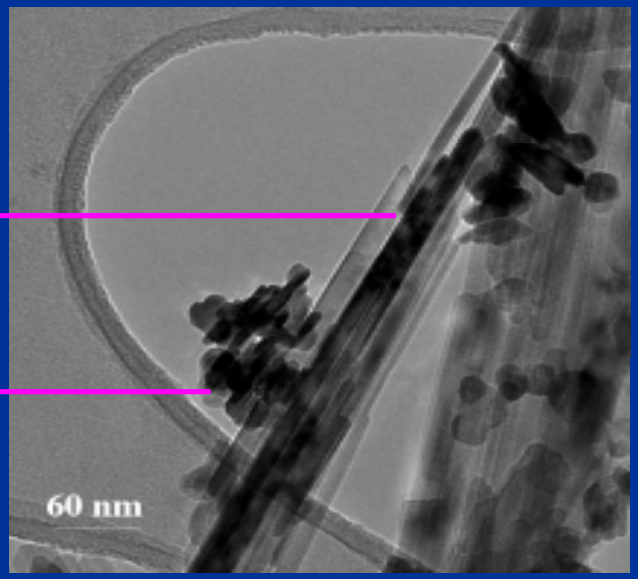
<u>Research Plan:</u> Measure uptake (rates and total capacity) of uranyl (and other radionuclides) by goethite and measure desorption rates into dilute solutions.

Sandia National Laboratories

Future Condition of The Sludge

Goethite Crystals

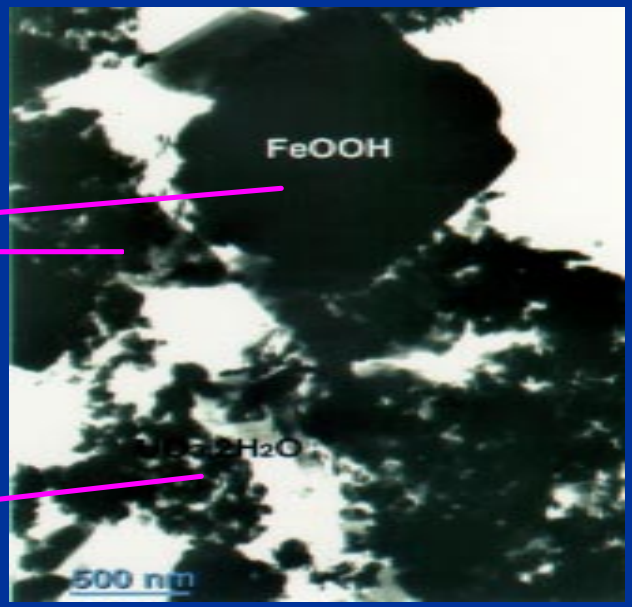
U-Rich Particles



Present Condition of The Sludge

Poorly Crystalized Iron Hydroxide

U-Rich Particles



1. Uranyl desorption rates decrease over time.
2. Several models can fit the data.

Data shold form linear trends if the desorption model is valid.

First-order equation

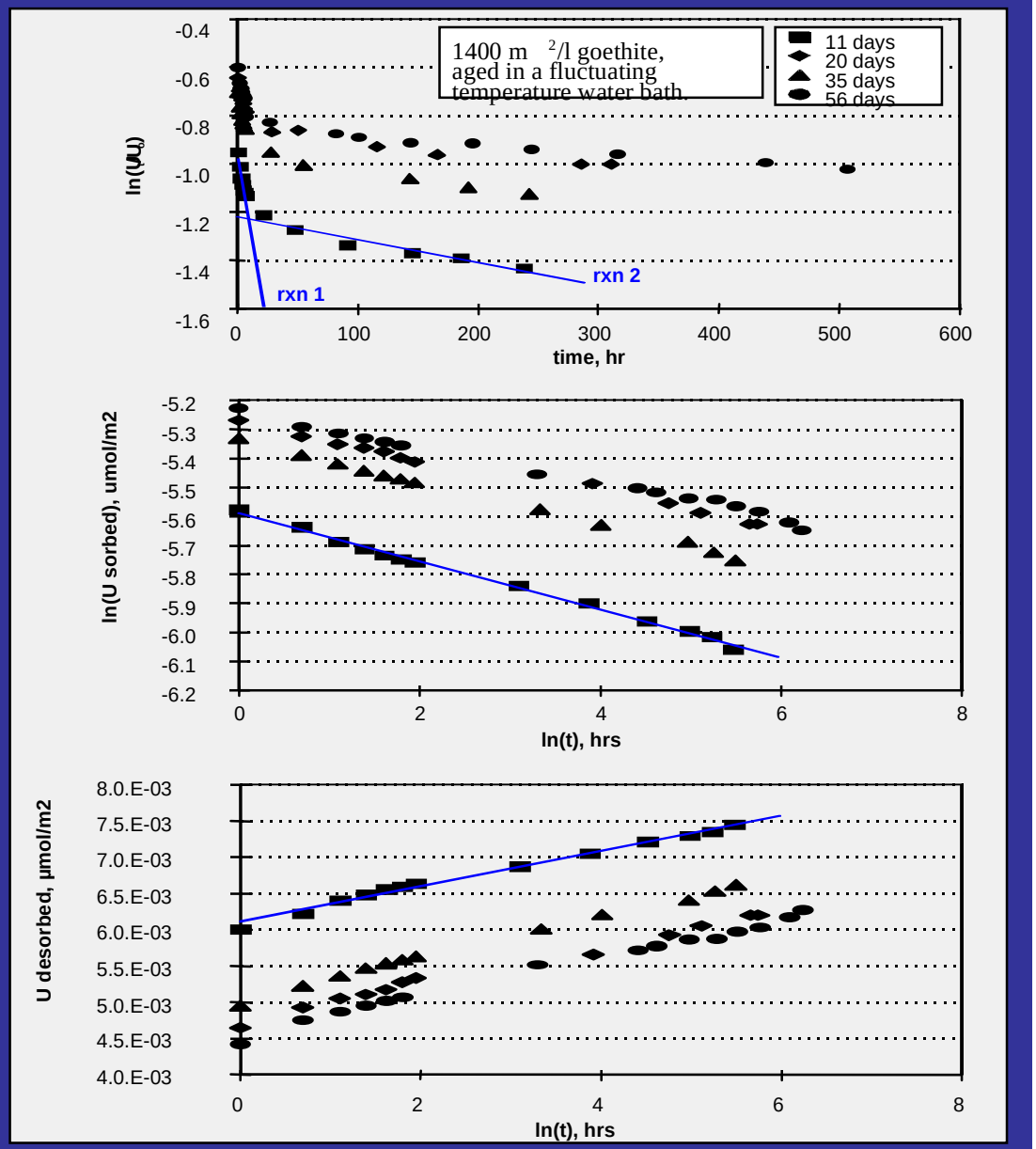
$$\ln (C_A/C_{Ao}) = - k_A t$$

Two-constant rate equation

$$\ln C_A = \ln a + b \ln t$$

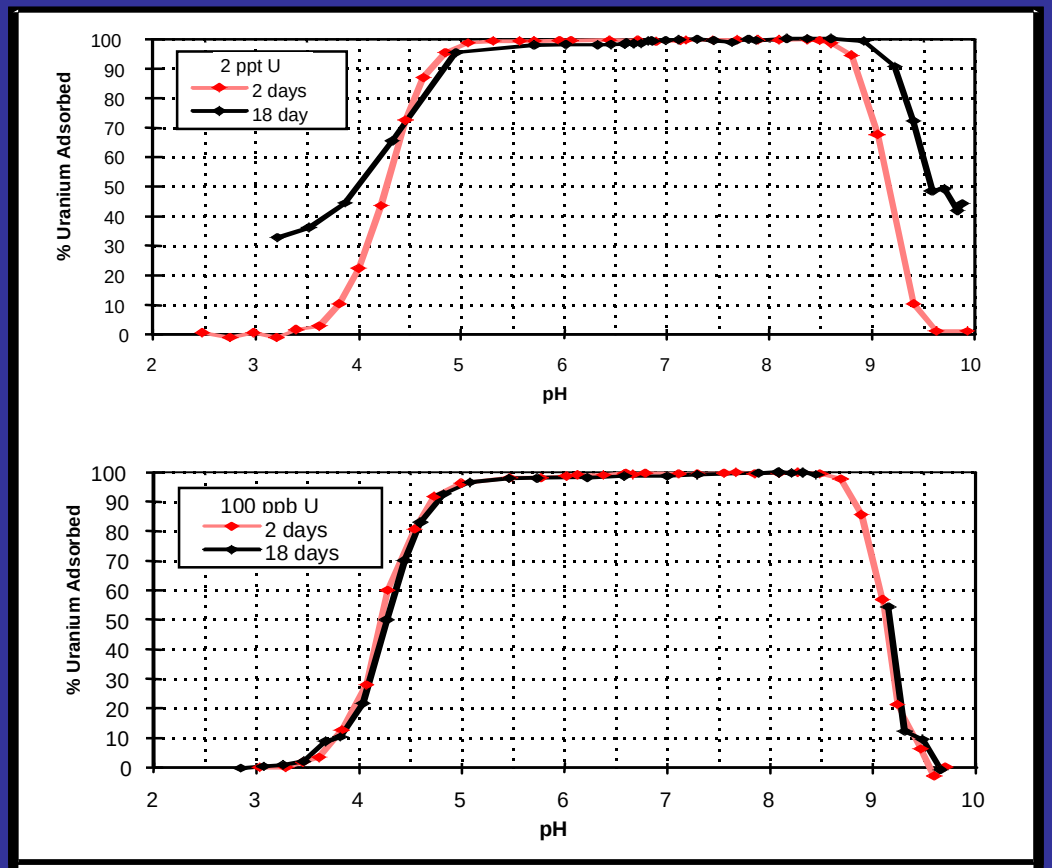
Modified Elovich equation

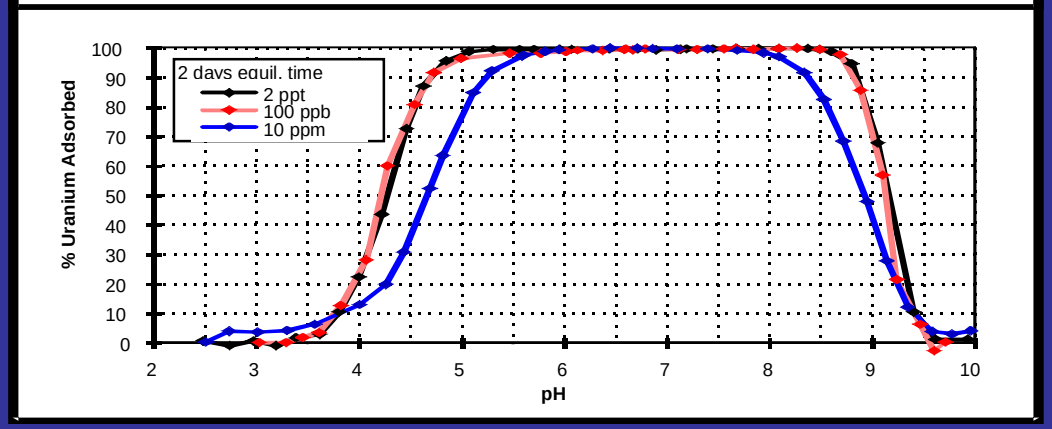
$$C_A = (1/Y) \ln (XY) + (1/Y) \ln t$$



Sandia National Laboratories

Uranyl Adsorption and Time





1. Uptake increases with time at low loadings (ppt).

2. Uptake is constant with time at high loadings (>ppt).

3. Uptake is proportional to fluid concentrations at all levels.

Sandia National Laboratories

Where does waste stream chemistry matter?

Neutralizing acid wastes from all five processes removed Ba, Cd, Co, Nd(Am), Pb and Sr quantitatively from solution.

Heating to 90° C only released a small amount of the Pb from the $BiPO_4$, TBP and REDOX waste stream precipitates.

For anions waste chemistry matters: Se, Tc and Re were not removed for $BiPO_4$, TBP or Zr-rich PUREX sludges. REDOX and Al-Clad PUREX sludges did remove a fraction of the Se, Tc, and Re.

	Re(ppm)	Tc(ppm)	Se(ppm)
REDOX	40 to 27 ppm	1 to 0.8 ppm	40 to 31 ppm
Al-PUREX	40 to 29 ppm	1 to 0.6 ppm	40 to 26 ppm

Heating to 90°C freed 50% to 100% of the sorbed Tc but not the sorbed Re.

Impact of Closure On Radionuclide Mobility

Reducing grout is the leading technology for tank closure. An artificial reducing grout was prepared using Portland cement, ferrous ammonium sulfate and manganous chloride. The mix water was spiked with Se, U, Re and Tc. After hydration and exposure to air:

* **Se fell from 50 ppm to 0.6 ppm and remained low.**
* **U fell from 50 ppm to below the detection limit (0.02 ppm).**
* **Re concentrations never decreased.**
* **Tc initially fell from5 ppm to 0.05 ppm. But, in a week half the Tc was back in solution due to oxidation by the air.**

Conclusion: Phases formed during closure may impact Se and U (plus other actinides) mobility, *but not that of Tc*.

Sludge phases are excellent sinks for many RCRA metals and radionuclides.

Tc and Se are notable exceptions. Since anions (TcO_4^-, $SeO_3^=$, and $SeO_4^=$) are not readily sorbed at high pH this result was expected.

Conclusions

1. A few phases make up the bulk of most sludges.

2. Phases in synthetic sludges are similar to those in actual tank wastes.

3. Most sludge phases probably formed within 90 days of neutralizing the primary waste stream.

4. Differences in waste stream chemistry impact radionuclide removal and retention

5. Representative artificial sludges can be synthesized and tested at relatively low cost.

Future research will focus on radionuclide release rates, phase chemistry, and ageing of:

	Subsystem	*Impurities of Concern*
1.	Hydrous iron oxides	Cr, Ni, Mn, Si, Al, Pb, Cd, U
2.	Apatite (F and OH)	Sr, Ba, Actinides
3.	Hydrotalcite, AlOOH	Tc (Re), Se
4.	$BiPO_4$,OH	Fe, Si, +4 Actinides
5	$UO_2(OH)_2$	Other Actinides

These studies will provide a credible source term for tank closure performance assessments.

TEM (Transmission Electron Microscopy) Study of Tank Waste Sludges and Artificial Tank Waste Samples*

Jun Liu, Pacific Northwest National Laboratory, Richland, WA 99353
(509-375-2616, Jun.Liu@pnl.gov)

TEM provides information on the composition, morphology, particle size and distribution, agglomerate structure, and phase distribution of the minerals in tank wastes.

This information is critical to tank waste processing (predicting of viscosity, dissolution and precipitation behavior in enhanced washing, sedimentation efficiency, etc.

This information is also critical in performance assessment for predicting the long term leach rate of radionuclides.

* Artificial tank waste samples were prepared at Sandia National Laboratory

Sandia National Laboratories

Abstracts