Phosphate Separation by Leaching and Precipitation

GJ Lumetta, JC Braley, JC Carter, MK Edwards, PJ MacFarlan, AR Felmy, and O Qafoku

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

Problem Statement

- The U.S. Department of Energy (DOE) is responsible for environmental remediation at the Hanford Site in Washington State.
- Retrieving, processing, immobilizing, and disposing of the 2.2×10^5 m^3 of radioactive wastes stored in the Hanford underground storage tanks dominates the overall environmental remediation effort at Hanford.
- The Hanford Tank Waste Treatment and Immobilization Plant (WTP) is the cornerstone of the tank waste remediation effort.
- Capacity of the WTP for treating and immobilizing the Hanford tank wastes is such that completion of the mission in the time frame required by the Tri-Party Agreement is questionable.
- For this reason, DOE is pursuing supplemental treatment options for selected wastes to route certain components of those wastes to processing and disposition pathways outside of WTP, accelerating the overall Hanford tank waste remediation mission.
- One waste component of particular concern is phosphorus. There is a relatively low tolerance for P in the high-level waste (HLW) melter in the WTP.

Process for Separating Phosphate

- Mainly aimed at processing of bismuth phosphate sludge (Group 1)
- Intended for implementation in the Hanford tank farm
- Phosphorus removed from the HLW solids by caustic leaching
  - Prior tests with actual waste showed phosphate readily removed from bismuth phosphate sludge solids by treatment with caustic under mild conditions
- Phosphate-containing leachate solution treated with lime (CaO)
  - Phosphate incorporated into very stable hydroxyapatite phase
  - Well suited for disposal in cementitious waste form (as LAW)
- Sodium hydroxide regenerated in the liquid phase as phosphate precipitates
  - Recycle of NaOH to front end of the process

Caustic Leach

$FePO_4(s) + 3NaOH(aq) \rightarrow Fe(OH)_3(s) + Na_3PO_4(aq)$

Lime Treatment

$3Na_3PO_4(aq) + 5CaO(s) + 5H_2O \rightarrow Ca_5(OH)(PO_4)_3(s) + 9NaOH(aq)$

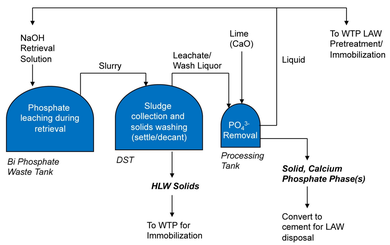
FY 2010 Accomplishments

- Developed bismuth phosphate sludge simulant
  - Used for process optimization and testing
- Completed parametric leaching tests with the simulant
- Updated thermodynamic phosphate solubility models
  - Models will guide flowsheet development and testing
- Completed initial tests of lime treatment to remove phosphate from the caustic leachate solution

A Hanford tank farm under construction

What's inside

Hanford WTP, May 2010



Example Deployment Option

Advantageous features:

1. The leaching of phosphate from the sludge solids is achieved during the retrieval operation.
2. The slurry containing the dissolved sodium phosphate and the high-level wastes (HLW) solids is transferred to an existing double-shell tank (DST) where the solids are allowed to settle by gravity.
3. The liquid phase containing the sodium phosphate is transferred and processed through a small, dedicated processing tank. Because no HLW solids would be processed through this tank, it is possible that the facility containing this tank could be designed and operated as a radiological facility rather than a nuclear facility (the primary radionuclides present would be ^{137}Cs and ^{99}Tc).
4. No heating equipment is required.
5. Relies on simple unit operations.

Bismuth Phosphate Sludge Simulant

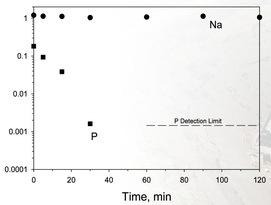
- Two approaches taken
  - Mimic of Hanford plant operations
  - Precipitation of iron(III) phosphate
    - Variables examined: pH, temperature, Fe concentration, presence of Bi
- FTIR was used as rapid screening tool to determine how close the simulants matched the actual waste
- Best simulant obtained by adding 1 M $Fe(NO_3)_3$ solution to a 0.5 M Na_3PO_4 solution adjusted to pH 12.5 at ambient temperature
  - Air-dried solids were ground and passed through a 0.45-µm sieve

Parametric Leaching Experiments

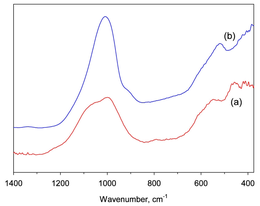
- Leaching with variable [NaOH] at ambient temperature indicated that 0.5 M NaOH is as effective as 2.0 M NaOH in removing phosphate
- Leaching with 0.5 M NaOH at variable temperature (25, 40, 60°C) showed no significant temperature effect
  - Near quantitative removal of P within 15 min in all cases

Phosphate Removal with Lime: Initial Scoping Experiments

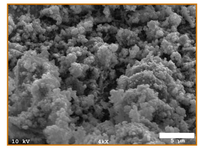
- 0.15 to 0.2 M Na_3PO_4 solutions in 1 M NaOH treated with CaO
- Only 70 to 75% of P removed from solution when treated with CaO at Ca:P = 2
- But quantitative P removal achieved at Ca:P =4
- FTIR and Raman spectra of the solids suggest the formation of hydroxyapatite
- Only 2 moles of hydroxide ion released per mole of phosphate removed from solution
  - This is less than the 3 moles OH^-/mole PO_4^{3-} expected for formation of hydroxyapatite
  - The reason for this is not entirely clear

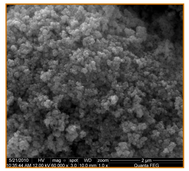


Sodium and phosphorus concentrations as a function of time during treatment of 0.18 M Na_3PO_4/1 M NaOH with CaO; Ca:P = 4

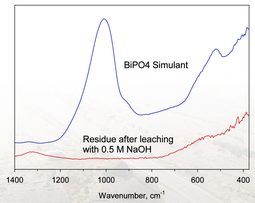


Comparison of FTIR Spectra of Actual $BiPO_4$ Waste (a) and the Simulant (b)





SEM Indicates Qualitative Similarity Between Actual Waste (left) and Simulant (right)



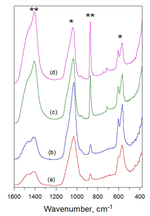
FTIR spectrum simulant simulant solids before and after caustic leaching indicating phosphate removal

Sequential Leaching/Lime Treatment Experiment

- Four conditions examined
  - All leached at 0.5 M NaOH
- Slightly higher P removal from the simulant at 60°C
  - Cases 2 and 4: 93 to 94% P removed
  - Cases 1 and 3: 82 and 89% P removed, respectively
- For all leachate solutions, quantitative P removal achieved by treatment with CaO at Ca/P = 4
- 2.0 to 2.4 mole OH^- liberated per mole P precipitated
  - Again, a value of 3 is expected for formation of hydroxyapatite, but this result is consistent with the earlier scoping experiment
- Analysis of calcium/phosphate product indicates the presence of hydroxyapatite [$Ca_5(OH)(PO_4)_3$], portlandite [$Ca(OH)_2$], and calcite ($CaCO_3$).

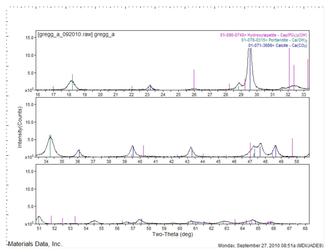
Case	Salts Added?	T, °C	Leachate Vol./g $FePO_4 \cdot xH_2O$, mL/g
1	No	22	33
2	No	60	33
3	Yes	22	202
4	Yes	60	83

In cases 3 and 4, $NaNO_3$, NaF, and Na_2SO_4 were added to simulate "unwashed" sludge conditions.



FTIR Spectra of Solid Residuals Remaining After Treatment of Phosphate-Containing Leachate Solutions With CaO: a) No Nitrate Added, Leached at Ambient Temperature, b) No Nitrate Added, Leached at 60°C, c) Nitrate Added, Leached at Ambient Temperature, and d) Nitrate Added, Leached at 60°C

** Assigned to hydroxyapatite*
*** Assigned to calcium carbonate*



XRD pattern of Solid Residual Remaining After Treatment of Phosphate-Containing Leachate Solution With CaO (No Nitrate Added, Leached at Ambient Temperature), showing the presence of hydroxyapatite, portlandite, and calcite ($CaCO_3$)

Conclusions and Recommendations

- Results to date indicate that caustic leaching followed by treatment of the phosphate-rich leachate solution with lime is a feasible method to avoid processing of high phosphate material in WTP
- The process could be implemented in a number of ways; an engineering evaluation must be done to determine the optimal approach. Factors to consider include:
  - Caustic leaching during retrieval or in a dedicated tank
  - Calcium strike in an existing double shell tank, or in smaller dedicated near-tank facility
  - Operating temperature: trade-off between higher solution volumes at ambient temperature versus more process complexity (i.e., heating equipment) at higher temperatures
  - Choice of solid/liquid separation
- The following specific issues are to be investigated in FY 2011:
  1. *Understanding the distribution of ^{137}Cs and ^{99}Tc in the process.* Ideally, these radionuclides will remain in the liquid phase after the CaO strike so that they are routed back to the tank farm (and ultimately to WTP).
  2. *Assessing the extent to which NaOH can be recycled in the process.* NaOH recycle might be constrained by buildup of ^{137}Cs and/or sodium salts (e.g., $NaNO_3$) upon repeated recycling.
  3. *Determining a suitable waste form for the calcium phosphate product.* The calcium phosphate solid formed upon treating the caustic leachate solution with CaO to removed phosphate will be a LAW material. Studies must be conducted to determine the best waste form option for this material. (And subsequently, use of this waste form must be negotiated with the regulators.)
  4. *Testing with actual tank waste.* It is critical that testing with actual tank waste material be performed to verify that the observations made with the simulant are also realized with the actual tank waste material.

U.S. DEPARTMENT OF ENERGY

Acknowledgement
This work was funded by the U.S. Department of Energy Office of Environmental Management, through the Office of Waste Processing, EM-31.

About Pacific Northwest National Laboratory
The Pacific Northwest National Laboratory, located in southeastern Washington State, is a U.S. Department of Energy Office of Science laboratory that solves complex problems in energy, national security and the environment, and advances scientific frontiers in the chemical, biological, materials, environmental and computational sciences. The Laboratory employs 4,000 staff members, has a $760 million annual budget, and has been managed by Ohio-based Battelle since 1965.

For more information, please contact:
Gregg J Lumetta,
Pacific Northwest National Laboratory
P.O. Box 999, MSIN P7-25 • Richland, WA 99352
(509) 376-6911 • Gregg.lumetta@pnl.gov

www.pnl.gov

Print

Close