

Use of Titanium-Treated Zeolite for Plutonium, Strontium, and Cesium Removal from West Valley Alkaline Wastes and Sludge Wash Waters

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Summary

Zeolite (IONSIV IE-96) treated with a titanium (Ti) solution will extract traces of plutonium (Pu), strontium (Sr), and cesium (Cs) found in the West Valley Nuclear Services Co., Inc. (WVNS) alkaline supernatant and alkaline sludge water washes. Small ion exchange columns containing Ti-treated zeolite have been successfully tested at WVNS and at Pacific Northwest Laboratory (PNL) for the removal of Pu. Full-scale ion exchange processing of sludge wash solutions is now being developed at WVNS for use in FY 1992. Commercial manufacturing options for the production of the Ti-treated zeolite were investigated. The Ti-treated zeolite may have application at Hanford and at other U.S. Department of Energy (DOE) sites for the removal of low-level concentrations of Cs, Sr, and Pu from alkaline waste streams.

Introduction

West Valley Nuclear Services Co., Inc. (WVNS), a wholly owned subsidiary of Westinghouse Electric Corp., has implemented the West Valley Demonstration Project (WVDP) for the U.S. Department of Energy (DOE) and New York State Energy Research and Development Authority (NYSERDA) to remove high-level waste (HLW) from storage tanks and solidify it in a form suitable for transportation to a federal repository for final disposal (Krauss 1986). The HLW resulted from the commercial reprocessing of reactor fuels using the PUREX separation

process. The HLW in Tank 8D-2 contains two fractions, an alkaline waste (supernatant) solution containing $\sim 6 \text{ M Na}^+$, and a sludge layer of iron hydroxide and fission product solids.

The Supernatant Treatment System (STS) has been used to separate Cs (^{137}Cs) from $\sim 300,000 \text{ kg of Na}^+$ in the $2 \times 10^6 \text{ L}$ of alkaline waste solution in Tank 8D-2. The ^{137}Cs content is removed from the liquid by passing a water-diluted solution ($\sim 2 \text{ M Na}^+$) through a series of ion exchange columns. The resulting effluent is concentrated to 6 M Na^+ , mixed with concrete, and stored as low-level waste. The Pu content in the cement matrix is approximately 21 nCi/g , and no actinide treatment of the alkaline supernatant has been required. The STS consists of four 3-ft-diameter x 11-ft-long ion exchange columns in series, suspended in the top of a spare underground storage tank (Carl and Braunscheidel 1986). The ion exchange process has utilized the inorganic ion exchanger IE-96, made by UOP. (UOP is the name of the joint venture company operated between Union Carbide and Allied Signal. UOP was operated solely by Union Carbide until 1990.) IE-96 was chosen for Cs recovery (Bray et al. 1984a) due to its high exchange capacity and decontamination factor (DF) values, and because it can be incorporated with glass formers and washed sludge to form borosilicate glass. Tests at PNL on the laboratory-scale ion exchange column (IE-96) predicted Cs DFs in excess of 10,000 (Bray et al. 1984b). After processing 78% of Tank 8D-2 alkaline supernatant ($1.6 \times 10^6 \text{ L}$) to recover 5,135 kCi ^{137}Cs , the STS has produced waste supernatant for final cementation with an average Cs DF of $>40,000$. In the fall of 1991, the next phase of the process will be initiated. Current plans are to

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remove soluble sulfate from the sludge layer in Tank 8D-2 using four water additions to the tank. During these water additions, the sludge will be mobilized to wash the soluble salts (notably sulfate) from the sludge prior to sludge vitrification as well as to remove the remaining supernatant.

In 1988, PNL washed a small sample of WVNS alkaline sludge from Tank 8D-2 and reported that ~20% of the Pu transferred to the water wash. In 1989, the WVNS Analytical Laboratory confirmed this observation. WVNS found that ~23% of the Pu and ~96% of the U in the sludge transferred to the water phase during washing, due to the high carbonate/bicarbonate content in the pH 10 waste. Subsequent WVNS and PNL studies showed that washing the sludge with caustic water, adjusted with NaOH to a pH of 12.5, significantly reduced the U and Pu content in the water fraction. However, the Pu content at pH 12 still represented approximately 5% of the Pu in the tank, exceeding the actinide limit in the concrete waste form of <100 nCi/g of waste. A method for Pu removal from sludge water washes was required.

PNL has been investigating several methods for the removal of actinides as well as the ^{137}Cs from alkaline sludge wash solutions. WVNS has stipulated that the actinide removal method selected must not affect the STS Cs recovery operation, must not require additional processing equipment, and must not affect the WVNS waste vitrification operation. Zeolite (IE-96) treated with Ti solution has been developed by PNL within these constraints for the recovery of Pu, Sr, and Cs from alkaline sludge water washes. The commercial production of Ti-treated zeolite has been investigated, and the manufacturing technology was successfully transferred to UOP.

Titanate Chemistry

The chemistry of hydrous oxide-type materials has been explained by Amphlett (1964, pp. 88-92) "on the basis of ion exchange involving surface hydroxyl groups." Studies have been made of the ion exchange properties of quadrivalent metal oxides such as SiO_2 , SnO_2 , TiO_2 , ThO_2 , and ZrO_2 . According to Amphlett, "In principle the quadrivalent metal oxides may behave either as cation or anion exchangers, depending upon the basicity of

the central metal atom and the strength of the metal-oxygen bond relative to that of the oxygen-hydrogen bond in the hydroxyl group." Thus, Ti acts as a cation exchanger in alkaline solutions.

Sandia National Laboratory (Lynch et al. 1975) described ion exchange materials of the hydrous oxide type that were developed for solidifying aqueous radioactive wastes. Ion exchange solids were prepared by reacting metal alkoxides (i.e., $\text{Ti}[\text{OC}_3\text{H}_7]_4$) with a base in a nonaqueous solution (alcohol). Dosch (1978) described the development of a commercial source of sodium titanate powder and its preparation using titanium isopropoxide ($\text{Ti}[\text{OC}_3\text{H}_7]_4$), NaOH, acetone, and methanol. Both Sr and Pu were removed with high efficiency from alkaline wastes using this ion exchanger.

Column plugging was seen as a potential problem because of the relatively fine powders formed during the preparation of the sodium titanate ion exchanger. Two methods were tested: inclusion in a porous substrate, and consolidation of the sodium titanate powder with binder materials. Inclusion into a porous substrate involved soaking the substrate in alcohol of tetraisopropyl titanate and sodium hydroxide, washing with methanol, and then soaking in an acetone-water mixture to hydrolyze the material within the pores. Sodium titanate was also introduced into a strong base anion macroreticular ion exchange resin by a similar method. W. W. Schulz (1978) successfully tested both the sodium titanate powder and 34 wt% sodium titanate-loaded macroreticular resin in the decontamination of Hanford Pu reclamation facility salt waste solution. M. A. Ebra (1981) evaluated the use of sodium titanate resin for Sr removal in the Defense Waste Processing Facility. The 40 wt% $\text{NaTi}_2\text{O}_5\text{H}$, 40-60 mesh, organic resin was prepared by Cerac, Inc., of Milwaukee, Wisconsin, using anion exchange resin (AG MP-1) obtained from Biorad, Inc., of Richmond, California. Excellent results were obtained for the removal of Sr from alkaline wastes.

Results and Discussion

Laboratory studies at PNL were completed to determine the effect of treating IE-96 zeolite with a titanium solution to remove traces of Pu from alkaline supernatant and sludge wash solutions.

The IE-96 was treated to contain 1 to 5 wt% Ti expressed as TiO_2 . Several treatment approaches were investigated. Batch distribution studies and ion exchange column tests using treated and untreated zeolite were used to show the effectiveness of the added Ti. The results show that Ti-treated zeolite will effectively remove Pu, Cs, and Sr from alkaline supernatant and water wash wastes. These tests were followed by studies at WVNS using actual Tank 8D-2 alkaline supernatant and sludge wash water to verify the use of Ti-treated zeolite. The results confirm the PNL studies, and WVNS has asked UOP to prepare Ti-treated zeolite for plant operation.

PNL also conducted ion exchange column studies using Ti-treated zeolite. Multiple ion exchange columns (A, B, and C) were connected

in series and used to test Ti-treated zeolite for the removal of Pu from alkaline sludge wash water. The three columns each had a capacity of 2 mL of exchanger to accommodate the limited volume of actual waste available. WVNS could then use the same column design to confirm the results using actual wastes versus synthetic feeds. The results show that Ti-treated zeolite will effectively remove Pu from solution as compared to untreated zeolite (Figures 1 and 2).

Acknowledgments

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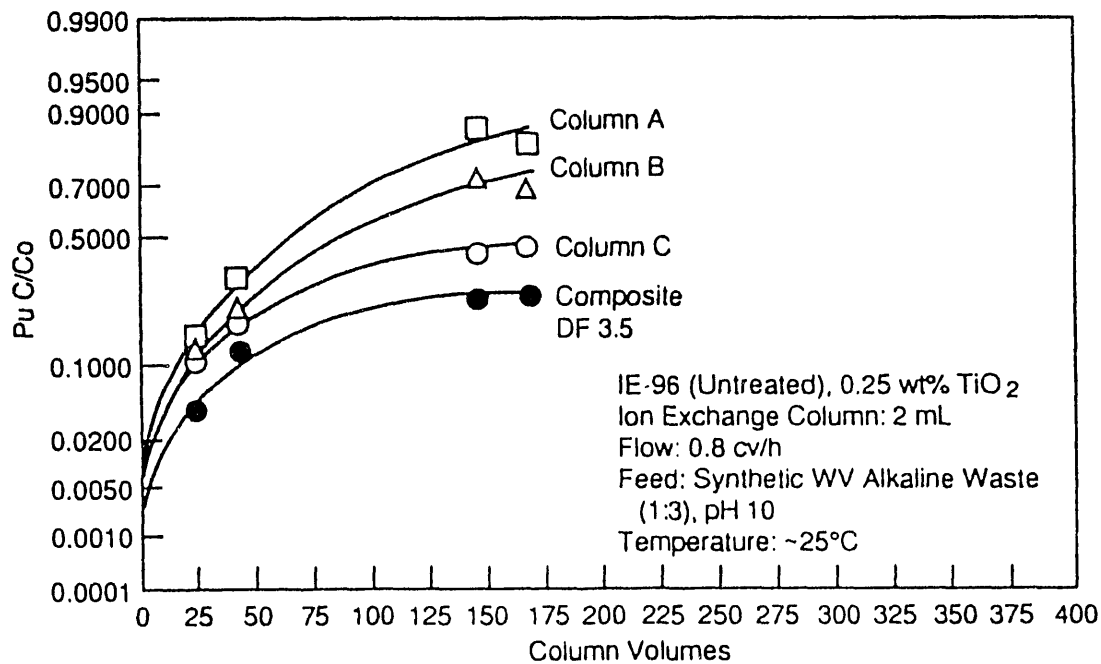


Figure 1. Recovery of Plutonium from Synthetic Alkaline Waste - IE-96

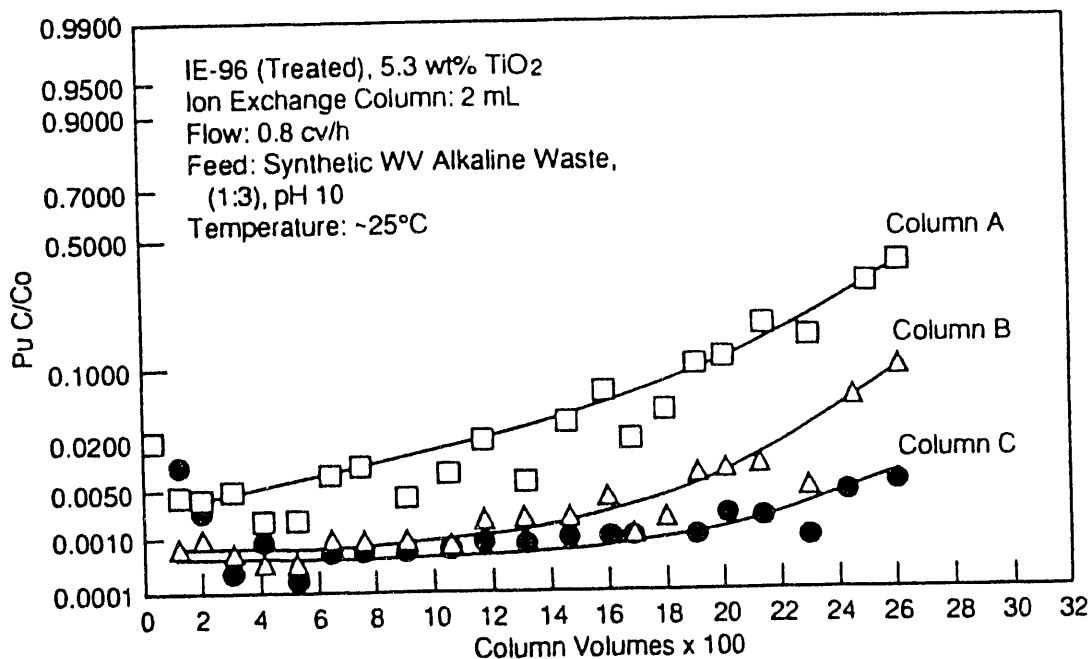


Figure 2. Recovery of Plutonium from Synthetic Alkaline Waste - 5.3 wt% TiO_2

References

- Amphlett, C. B. 1964. *Inorganic Ion Exchangers*, pp. 88-92. Elsevier Publishing Company, New York.
- Bray, L. A., L. Holton, J. M. Pope, D. E. Carl, and B. Wise. 1984a. "Selection of a Reference Process for Treatment of the West Valley Alkaline Waste." Presented at the American Nuclear Society International Meeting on Fuel Reprocessing and Waste Management, Jackson, Wyoming. PNL-SA-12283, Pacific Northwest Laboratory, Richland, Washington.
- Bray, L. A., L. K. Holton, T. R. Myers, G. M. Richardson, and B. M. Wise. 1984b. *Experimental Data Developed to Support the Selection of a Treatment Process for West Valley Alkaline Supernatant*. PNL-4969, Pacific Northwest Laboratory, Richland, Washington.
- Carl, D. E., and M. J. Braunscheidel. 1986. "Design and Installation of the West Valley Supernatant Treatment System." Presented at the American Nuclear Society International Topical Meeting, Waste Management and Decontamination and Decommissioning, Niagara Falls, New York.
- Dosch, R. G. 1978. *The Use of Titanates in Decontamination of Defense Wastes*. SAND78-0710, Sandia National Laboratory, Albuquerque, New Mexico.
- Ebra, M. A. 1981. *Evaluation of Sodium Titanate Resin for Sr^{2+} Removal in DWPF Stage 2*. DPST-81-411, Savannah River Laboratory, Aiken, South Carolina.
- Krauss, J. E. 1986. "The West Valley Demonstration Project." Presented at the American Nuclear Society International Topical Meeting, Waste Management and Decontamination and Decommissioning, Niagara Falls, New York.
- Lynch, R. W., R. G. Dosch, B. T. Kenna, J. K. Johnstone, and E. J. Nowak. 1975. *The Sandia Solidification Process - A Broad Range Aqueous Waste Solidification Method*. IAEA-SM-207/75, Sandia National Laboratory, Albuquerque, New Mexico.
- Schulz, W. W. 1978. *Decontamination of Hanford Plutonium Reclamation Facility Salt Waste Solution*. RHO-SA-23, Rockwell Hanford Operations, Richland, Washington.



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