

TREATMENT OF LIQUID NUCLEAR WASTES WITH ADVANCED FORMS OF TITANATE ION EXCHANGERS

R. G. Dosch, N.E. Brown and H. P. Stephens
Sandia National Laboratories
Albuquerque, New Mexico

R. G. Anthony
Texas A&M University
College Station, Texas

ABSTRACT

A new class of inorganic ion exchange materials that can separate low parts per million level concentrations of Cs^+ from molar concentrations of Na^+ has recently been developed as a result of a collaborative effort between Sandia National Laboratories and Texas A&M University. The materials, called crystalline silicotitanates, show significant potential for application to the treatment of aqueous nuclear waste solutions, especially neutralized defense wastes that contain molar concentrations of Na^+ in highly alkaline solutions. In experiments with alkaline solutions that simulate defense waste compositions, the crystalline silicotitanates exhibit distribution coefficients for Cs^+ of greater than 2,000 ml/g, and distribution coefficients greater than 10,000 for solutions adjusted to a pH between 1 and 10. Additionally, the crystalline silicotitanates were found to exhibit distribution coefficients for Pu and Sr^{2+} of greater than 2,000 and 100,000 respectively. Development of these materials for use in processes to treat defense waste streams is currently being pursued.

BACKGROUND

Within the Department of Energy complex, there are hundreds of tanks used for processing and storing radioactive waste byproducts generated by weapons material production facilities. These tanks contain tens of millions of gallons of highly radioactive supernate liquid containing molar concentrations of Na^+ along with solid salt cake and sludge. Treatment and disposal of these wastes can be facilitated by separation of gamma-emitting Cs radioisotopes from the supernate liquid and soluble salt cake portions of the wastes.

Ion-exchange processes offer several advantages for performing this separation. 1) The processes are versatile in that both continuous flow systems (ion-exchange columns) or batch processing (in-tank) can be used, 2) ion exchange is efficient-- decontamination factors of many orders of magnitude can be achieved, 3) ion exchange processes and equipment are simple and compact, allowing mobile in-tank or near-tank treatment, and 4) the processes introduce no residual wastes, such as hazardous organic solvents, into the waste stream. Use of inorganic (in contrast to organic resins) ion-exchange materials, such as the titanates, offers the advantage of improved stability in the presence of intense radiation. Also, titanate ion-exchangers are stable in the alkaline solutions encountered in defense waste tanks, a property that suggests their use as an interim or temporary waste form. In contrast, zeolites--widely used inorganic ion exchangers--slowly decompose and dissolve in alkaline solutions.

Work with amorphous hydrous titanium oxide (HTO) ion-exchange materials in the context of nuclear waste remediation began at Sandia National Laboratories in 1975 and was directed toward the conversion of high level waste (defined as waste obtained by reprocessing spent commercial reactor fuel using the flowsheet developed for the Barnwell facility in South Carolina) to a stable, ceramic form (1-3). The HTO materials were developed several years earlier for use in preparing electroactive ceramic materials for defense applications, and were attractive for use in radioactive waste stabilization because of their ion exchange properties and their potential for conversion to a stable ceramic form (4-7). This program was carried to the point of obtaining spent reactor

fuel, reprocessing it with a bench scale Purex process, absorbing the waste on the HTO using an ion exchange column, and hot pressing the radwaste-loaded HTO to a monolithic ceramic. The effort was performed at Oak Ridge National Laboratories in collaboration with Sandia National Laboratories.

The program to develop amorphous bulk HTO for radioactive waste isolation was redirected after 1977 to studies involving wastes at the Hanford site (8,9). Tests conducted at Sandia and Hanford showed the HTO materials to be extremely effective in removing Sr^{2+} and Pu from dissolved salt cake and salt cake simulants. Samples of the HTO material were also supplied to Savannah River Laboratories for evaluation with their wastes. The results from Savannah River with regard to Sr removal agreed with the observations at Sandia and Hanford. A five hundred pound batch of HTO ion exchanger was prepared by Cerac, Inc. in Milwaukee, Wisconsin and part of this batch was converted to extrudates by Norton Co. in Akron, Ohio. This work was performed to demonstrate that these materials could be produced using commercial suppliers and existing equipment. At this point, the Sandia program to develop amorphous HTO ion exchangers for application to nuclear wastes was concluded. The initial effort at Sandia and Savannah River has led to large scale use of HTO materials for in-tank waste remediation at the Savannah River Site (10-12). Subsequent development of HTO materials at Sandia was continued through funding by DOE Fossil Energy for use as catalysts for coal liquefaction and other applications (13-17).

A limitation to the use of amorphous HTO ion-exchangers for treatment of defense waste was their low affinity for Cs^+ in solutions containing high concentrations of Na^+ . Because radioisotopes of Cs^+ are the predominate gamma source, and Cs^+ has a high mobility in the biosphere, this left a substantial gap in the remediation of defense wastes with HTO ion exchangers. This problem has now been solved by the development of new, advanced forms of titanate ion-exchange materials, called crystalline silicotitanates (CST), that have been shown to be efficient in absorbing Cs^+ from solutions containing high concentrations of Na^+ . This class of materials was recently developed at Sandia and Texas A&M

University for use as catalyst supports for DOE Fossil Energy projects. In the following sections of this paper we present a status report on the development of CST ion exchangers for application to processing nuclear wastes, an effort that is supported by the DOE Office of Environmental Restoration, Waste Management, and the DOE Richland Operations Office, and Sandia Laboratory Directed R&D funds.

DEVELOPMENT OF CRYSTALLINE SILICOTITANATES

Synthesis and Characterization

In contrast to the amorphous HTO ion exchangers, which are prepared by sol-gel chemistry, the CST materials are prepared by a combination of sol-gel chemistry and hydrothermal synthesis. Presentation of the details of the synthesis of crystalline silicotitanate ion-exchangers is awaiting a pending patent. Briefly, they are prepared by reacting alkyl titanates, alkyl silicates, and other modifiers with aqueous and/or methanol solutions of alkali metal hydroxides and alkylammonium hydroxides and bromides, followed by hydrothermal treatment. Although the CST ion exchangers are usually prepared in the sodium form, other exchangeable counter ions, such as potassium, can be used.

The CST materials have been examined by a host of methods, including a preliminary characterization of their structure by X-ray diffraction (XRD), transmission electron microscopy (TEM) and other techniques. From exhaustive literature searches and comparisons of the characterization data with those of possible analogous materials, we have concluded that the CST ion exchangers are a new class of inorganic materials. The crystallinity of CST materials is illustrated in Figs. 1 and 2, which show a powder XRD pattern and a transmission electron micrograph of one CST formulation. The XRD pattern is typical of an ordered crystalline material. In contrast, Fig. 3, a XRD pattern of an amorphous HTO ion exchanger, exhibits no crystallinity. Electron diffraction patterns in the TEM (Fig. 2) clearly show lattice planes in the 20 to 30 nm cuboidal crystallites. It has been found that the interplanar d-spacings of the CST materials can be modified by synthesis techniques. Materials with maximum d-spacings over the range of 0.78 to 1.5 nm have been prepared.

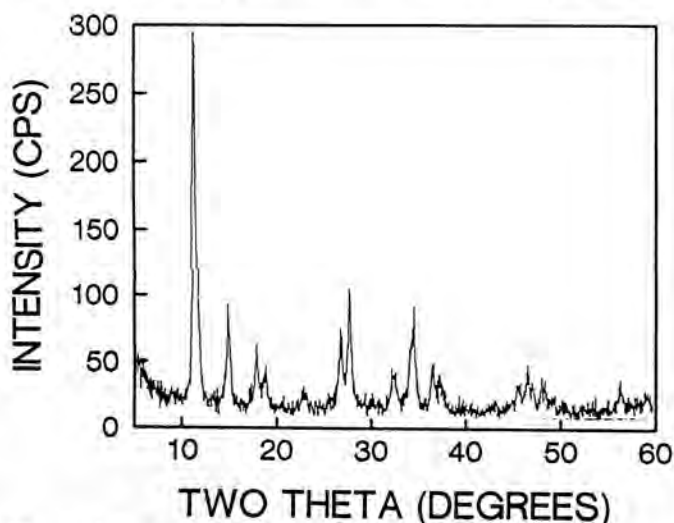


Fig. 1. X-ray powder diffraction pattern of a crystalline silicotitanate ion-exchange material.

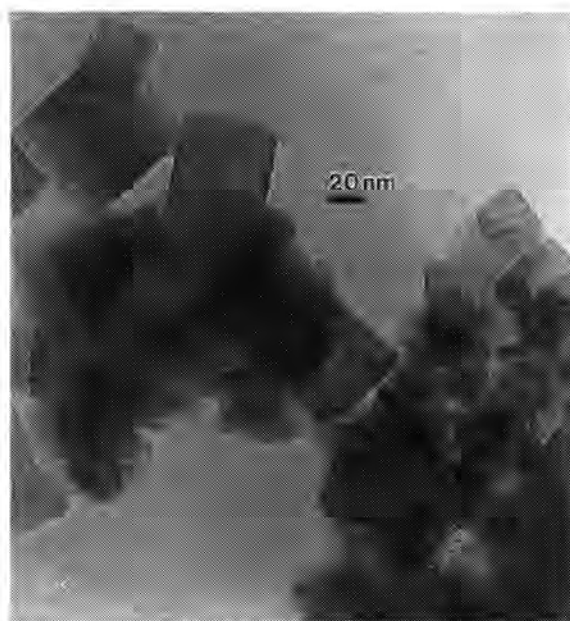


Fig. 2. Transmission electron micrograph of a crystalline silicotitanate ion-exchange material.

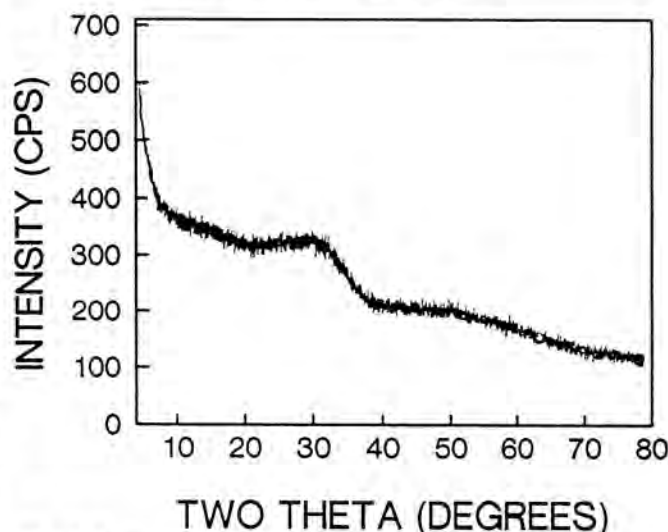


Fig. 3. X-ray powder diffraction pattern of an amorphous hydrous titanium oxide ion-exchange material.

Ion-Exchange Studies

Studies have been performed to ascertain the ion-exchange capacity of the CST materials, and determine the distribution coefficients, by batch evaluation techniques, for several aqueous species. Although initial efforts have focused on Cs^+ , several measurements have been performed to characterize the affinity for strontium and plutonium.

Contact of the sodium form of CST (Na-CST) with acid results in the replacement of Na^+ with H^+ . Experiments in which the Na^+ was quantitatively exchanged with acid were used to determine the ion-exchange capacity of the materials, found to range from 4 to 5 meq/g. This ion-exchange capacity range is nominally the same as that determined for the amorphous HTO materials (8,15).

The relationship of the structure of CST ion exchangers to their affinity for Cs^+ adsorption in the presence of Na^+ was investigated by synthesizing a series of the materials, then

measuring the K_d for Cs^+ . A solution of 100 ppm ($7.5 \times 10^{-4} \text{M}$) Cs in 3M NaNO_3 was used for the measurement of the Cs^+ K_d . A 0.1g quantity of the CST was contacted (with agitation) with 10 ml of the test solution, and the concentration of Cs^+ , at equilibrium, was measured by atomic absorption spectroscopy or inductively coupled plasma/mass spectrometry techniques. The Cs^+ distribution coefficients (K_d , ml/g), calculated as the Cs concentration in the CST (g-Cs/g-CST) divided by the concentration in the solution at equilibrium (g Cs/ml solution), were correlated with the largest d-spacing measured by XRD for each material, as shown in Fig. 4.

As can be seen in Fig. 4, the affinity of the CST ion exchanger for Cs^+ increases by over three orders of magnitude, from 10 to 20,000 ml/g, as the largest d-spacing approaches a value of 0.78 nm. It is concluded from this observation that the affinity of the CST for Cs^+ , and other aqueous cations, can be tailored by modification of the crystal structure. CST materials characterized by a largest d-spacing of about 0.8 nm are postulated to contain channels that can accept hydrated Cs^+ , while excluding hydrated Na^+ . This is consistent with the trends in the ionic radii of hydrated and non-hydrated Na^+ and Cs^+ ions. It is reported (18) that although the non-hydrated ionic radius of Cs^+ is larger than that of Na^+ , the hydrated radius of Na^+ is larger than that of Cs^+ . Although the exact mechanism is not known, it is possible that while non-hydrated Na^+ can migrate out of the CST lattice, the hydrated Na^+ --of larger diameter--is excluded. However, hydrated Cs^+ is of small enough diameter to exchange for non-hydrated Na^+ in the interstitial spaces of the CST lattice.

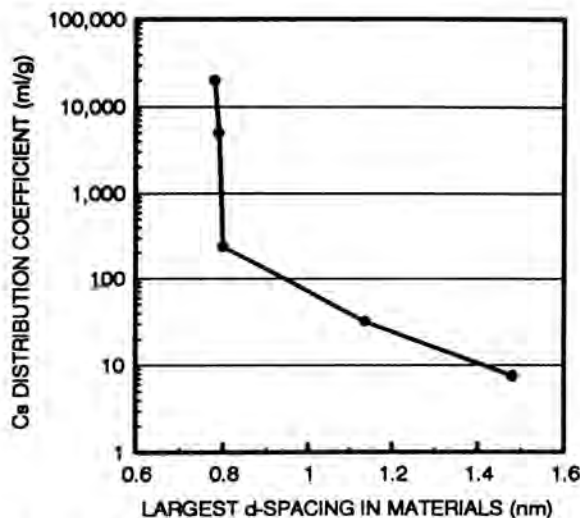


Fig. 4. Plot of Cs^+ K_d as a function of the largest d-spacing for the crystalline silicotitanate.

Following these experiments, performed in neutral solutions, distribution coefficients for the CST ion exchangers were determined over a wide range of hydrogen ion concentrations, from 1M HNO_3 to 2.5M NaOH . It was found that at pH values above approximately 10, the K_d for these first-generation CST materials decreased substantially, from 20,000 ml/g at a pH of 7 to approximately 100 at OH^- concentrations above 0.6M. Several experiments were also performed to determine the distribution coefficients for strontium in neutral and alkaline solutions containing 20 ppm Sr^{2+} in 5.7M Na^+ . It was found that in contrast to Cs^+ , the distribution

coefficient for Sr^{2+} increased with increasing pH, from a value of 780 ml/g at a pH of 7 to 4000 ml/g at 0.6M OH^- .

Modifications in synthesis techniques and CST material composition have recently been employed to prepare second-generation CST materials that have Cs^+ distribution coefficients greater than 1500 ml/g in solutions containing 100 ppm Cs^+ , 5.7M Na^+ ($\text{Na}^+/\text{Cs}^+ = 7575$) and 2.5M OH^- . These same materials exhibit Cs^+ distribution coefficients greater than 24,000 ml/g in neutral solutions, and 2,400 in 1M HNO_3 .

Tests with Simulated Wastes

In addition to the ion-exchange studies performed at Sandia, several samples of first- and second-generation CST materials were sent to L. Bray, Battelle, Pacific Northwest Laboratories (PNL) for confirmation of the ion-exchange properties using simulated wastes. Test solutions used at PNL were formulated to represent Hanford waste from double shell slurry feed (DSSF) tanks. From Table I, a representative composition of the simulated DSSF waste used, it can be seen that these experiments were performed with 3.9M Na^+ , $7.0 \times 10^{-5} \text{M Cs}^+$ ($\text{Na}^+/\text{Cs}^+ = 5.6 \times 10^4$), and 1.3M OH^- . Cs^+ distribution coefficients were determined by radioisotopic tracer techniques. For several experiments with first-generation CST materials, tracer amounts of radioisotopes of Sr and Pu were also used to determine the distribution coefficients for these elements. In addition, one of the first CST samples (first-generation material) to be sent to PNL was contacted with the simulated waste solution for an extended time to determine the stability of the material.

TABLE I
Composition of Simulated Double Shell Slurry Feed (DSSF) Waste

| Species | Concentration (M) |
|----------------------|-----------------------|
| Na^+ | 3.9 |
| K^+ | 0.09 |
| Rb^+ | 8.56×10^{-5} |
| Cs^+ | 7.0×10^{-5} |
| Al (total) | 0.34 |
| SO_4^{2-} | 0.12 |
| OH^- (free) | 1.3 |
| CO_3^{2-} | 0.16 |
| F^- | 0.07 |
| NO_2^- | 0.34 |
| NO_3^- | 1.23 |

Results of these evaluations (19) have shown that the CST ion-exchange materials have an excellent capacity to remove Cs^+ from DSSF waste solutions. The second-generation CST material exhibited Cs^+ distribution coefficients at 25°C of 2,400 in the simulated DSSF waste solutions. Coefficients exceeding 8,000 for first generation materials and 20,000 for second-generation materials were observed after adjusting the pH of the simulated DSSF solutions to 10.8 by bubbling carbon dioxide through them. This suggests that use of CST materials, with partial neutralization of waste solutions by an inexpensive reagent such as CO_2 , could result in an even more efficient ion-exchange process for removal of Cs. The experiments with first-generation CST materials and tracer

amounts of Sr^{2+} and Pu in the DSSF waste simulants yielded distribution coefficients of 2700 for Pu and greater than 100,000 for Sr^{2+} (based on detection limits for Sr). In addition, the first-generation CST material that was contacted with the simulated DSSF waste at 40°C for a period of 16 weeks has shown no degradation in performance with respect to retention of Cs^+ .

CONCLUSION

As a result of ion-exchange batch distribution coefficient experiments with crystalline silicotitanates, it is concluded that these newly-developed materials exhibit significant potential for application to the treatment of aqueous nuclear waste solutions, especially neutralized defense wastes that contain molar concentrations of Na^+ in highly alkaline solutions. In experiments with alkaline solutions that simulate defense waste compositions, the crystalline silicotitanates were found to have high affinities for Cs^+ , Sr^{2+} , and Pu. Use of inorganic crystalline silicotitanate ion-exchange materials also offers the advantage of improved stability, in comparison with organic resins, in the presence of intense radiation. Crystalline silicotitanate ion-exchangers are stable in the alkaline solutions encountered in defense waste tanks, a property that suggests their use as an interim or temporary waste form. Development of these materials for use in processes to treat defense waste streams is currently being pursued.

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