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Crystalline Silicotitanates—New Ion Exchanger for Selective Removal of Cesium and Strontium From Radwastes

R. G. Dosch, E. A. Klavetter, H. P. Stephens, N. E. Brown, R. G. Anthony

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Albuquerque, New Mexico 87185 and Livermore, California 94550
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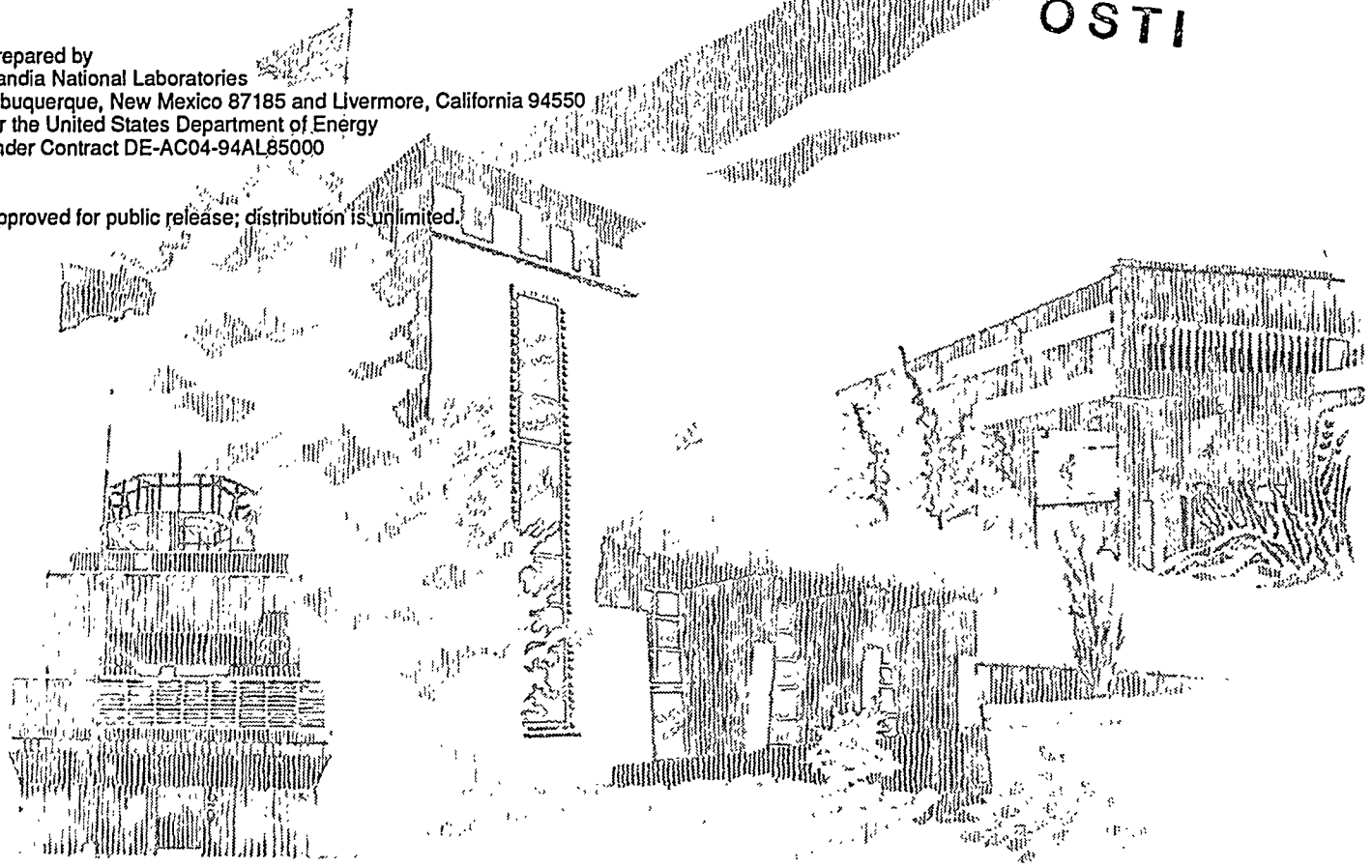

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R. G. Dosch, E. A. Klavetter, and H. P. Stephens
Process Research Department

N. E. Brown
Hanford Environmental Technology Department

Sandia National Laboratories
Albuquerque, New Mexico 87185

R. G. Anthony
Texas A&M University
College Station, Texas 77843

Abstract

A new class of inorganic ion exchange material called crystalline silicotitanates (CST) has been developed for radioactive waste treatment in a collaborative effort between Sandia National Laboratories and Texas A&M University. The Sandia National Laboratories Laboratory Directed Research and Development program provided the initial funding for this effort and this report summarizes the rapid progress that was achieved. A wide range of compositions were synthesized, evaluated for cesium (Cs) removal efficiency, and a composition called TAM-5 was developed that exhibits high selectivity and affinity for Cs and strontium (Sr). Tests show it can remove parts per million concentrations of Cs^+ from highly alkaline, high-sodium, simulated radioactive waste solutions modeled after those at Hanford, Oak Ridge, and Savannah River. In experiments with solutions that simulate highly alkaline Hanford defense wastes, the crystalline silicotitanates exhibit distribution coefficients for Cs^+ of greater than 2,000 ml/g, and distribution coefficients greater than 10,000 ml/g for solutions adjusted to a pH between 1 and 10. In addition, the CSTs were found to exhibit distribution coefficients for Sr^{2+} greater than 100,000 ml/g and for plutonium of 2,000 ml/g from simulated Hanford waste.

Procedures for synthesis of the CST powder were scaled up from lab quantities to 800 grams per lot with material performance comparable to developmental materials. The technology for preparing TAM-5 CST was transferred through a Cooperative Research and Development Agreement to UOP, Des Plaines, IL. With minimal changes to the synthesis process, UOP scaled up the synthesis and produced a commercial 1,800-pound lot with ion exchange and chemical properties comparable to lab-prepared materials.

The CST crystal structure was determined and positions of individual atoms identified using x-ray and neutron diffraction. The structural information has permitted identification of the ion exchange sites and provided insights into the strong effect of pH on Cs ion exchange. Information on the synthesis, composition, and structure of CST is considered proprietary and is not discussed in this report.

BACKGROUND

Within the Department of Energy (DOE) complex, there are hundreds of tanks used for processing and storing radioactive waste by-products generated by weapons material production facilities. These tanks contain tens of millions of gallons of highly radioactive supernatant liquid containing molar concentrations of sodium (Na^+) in a highly alkaline solution (pH>14), along with solid salt cake (primarily $NaNO_3$ and $NaNO_2$), and sludge that is a complex mixture of insoluble metal oxides and hydroxides. Most of the highly soluble cesium salts and small amounts of strontium salts are present in the liquid supernatant. Cesium (Cs) and strontium (Sr) removal is important because they are strong gamma and beta emitters and the decay energy is a major contribution to the heat generation in the radwastes.

Cesium is a fission by-product and consists of several isotopes: stable Cs-133, Cs-134 with a half-life of 2.065 years, Cs-135 with a half-life of 3×10^6 years, and Cs-137 with a half-life of 30.17 years. Since most wastes are at least 20 years old, essentially all of the Cs-134 has decayed, leaving Cs-137 as the major radiation source with low activity due to the Cs-135. The total Cs concentration in the Hanford and other DOE wastes is 3 to 4 times higher than the concentration measured as Cs-137 activity. This is important because ion exchange processes remove all Cs isotopes equally and the total concentration reflects the amount of Cs to be removed by this process.

At present, demonstrated processes for removal of Cs from the highly alkaline, high Na^+ wastes are limited, and extensive studies are in progress to develop more efficient and less complex processes. 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 and solution decontamination factors of many orders of magnitude can be achieved in columns. (3) Ion exchange processes and equipment are simple, compact, and a mature technology that can be used for either plant or mobile waste treatment. (4) The processes introduce no hazardous organic solvents into the waste stream. Use of inorganic (in contrast to organic resins) ion exchange materials also offers the advantage of improved chemical and physical stability in the presence of intense radiation. Regenerable organic ion exchangers require extensive processing equipment to handle the exchanger, the regeneration liquids, the eluant with the dissolved Cs, and disposal of the spent exchanger after its performance is degraded by radiation and chemical reactions.

The use of a once-through inorganic ion exchanger avoids many of these potential issues. Zeolites, inorganic ion exchangers used at Three Mile Island and the West Valley Nuclear Services facility, slowly decompose and dissolve in alkaline solutions with a pH>12 and are not useful in solutions with pH>13. Titanate ion exchangers are stable in the highly alkaline solutions encountered in defense waste processing, but do not sorb Cs. This report summarizes the development of crystalline silicotitanates that are highly selective for both Cs and Sr from highly alkaline wastes. Once separated from the radwastes, the use of inorganic ion exchangers as an interim, or possibly long-term radwaste storage form is possible.

Amorphous hydrous titanium oxide (HTO) materials were developed at Sandia National Laboratories in the 1960s and 1970s for use in preparing electroactive ceramic materials for defense applications. They were investigated for use in stabilizing radioactive wastes because of their ion exchange properties and their potential for conversion to a stable ceramic form (4-7). Work with HTO ion exchange materials in the context of nuclear waste processing began at Sandia National Laboratories in 1975 and focused on conversion of high-level waste (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 absorbed most cationic radionuclides but had essentially no affinity for highly soluble and radioactive Cs. This program was carried to the point of obtaining spent reactor fuel, reprocessing it with a bench-scale Purex process, absorbing the radioactive waste on the HTO using an ion exchange column, and hot pressing the radwaste-loaded HTO into a monolithic ceramic. The effort was carried out at Oak Ridge National Laboratory 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 National Laboratories and Hanford showed the HTO materials to be extremely effective in removing Sr^{2+} and plutonium (Pu) from dissolved salt cake and salt cake simulants; however, Cs^{+} remained in solution and was not removed in an ion exchange column. Samples of the HTO material were also supplied to the Savannah River site for evaluation with their wastes. Sr removal data from Savannah River agreed with the observations at Sandia and Hanford. A 500 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 the HTOs could be produced using commercial suppliers and existing equipment. About 1980, the Sandia program to develop amorphous HTO ion exchangers for application to nuclear wastes was concluded after the DOE selected glass and not ceramics as the baseline wasteform. As a result of this work at Sandia National Laboratories and Savannah River, HTO materials were tested and are being used for in-tank precipitation of Sr and Pu at the Savannah River site (10-12). Further development of HTO materials at Sandia National Laboratories for use as catalysts for coal liquefaction and other applications was continued through funding by DOE Fossil Energy Program (13-17). A new class of ion exchangers called crystalline silicotitanates (CSTs) was prepared in this catalyst program.

Testing at Sandia showed that this new class of ion exchangers had a high affinity for Cs^{+} under neutral conditions. Funding from the Laboratory Directed Research and Development (LDRD) program permitted us to study the Cs^{+} ion exchange characteristics and to dramatically improve properties in high pH solutions. Improved compositions were systematically prepared and evaluated for Cs ion exchange, and the Cs ion exchange performance was dramatically improved.

In the following sections of this paper we present a status report on the development of CST ion exchangers that was supported by Sandia National Laboratories and the LDRD program. Because of highly promising test results, additional funding was obtained from the DOE Office of Environmental Restoration and Waste Management (EM-50) and subsequently from the DOE Richland Operations Office. The last year of the LDRD program supported the initial phase of

the Cooperative Research and Development Agreement (CRADA) with UOP (A joint venture company of Union Carbide and Allied Signal Corporations), Des Plaines, IL, to commercialize the CST powder. In a later stage of the CRADA, the CST powder was converted by UOP to a granular material suitable for column ion exchange processing of radwastes.

Synthesis and Characterization

The CST materials are prepared (20, 21) by a combination of sol-gel chemistry and hydrothermal synthesis, in contrast to the amorphous HTO ion exchangers, which are prepared solely by sol-gel chemistry. CST materials are prepared by reacting alkyl titanates, alkyl silicates, and other materials 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 also be used.

The CST materials have been examined by a host of chemical and material characterization methods, including a preliminary characterization of their structure by x-ray diffraction (XRD), transmission electron microscopy (TEM) and other analytical 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. A patent application on CST technology has been jointly submitted by Sandia National Laboratories and Texas A&M University (TAMU).

The crystallinity of CST materials is illustrated in Figure 1, which shows a transmission electron micrograph of one CST formulation powder. Lattice fringe patterns in Figure 1 clearly show lattice planes in the 20 to 30-nm cuboidal crystallites. Figure 2 shows the XRD pattern of one of the CST formulations. The XRD pattern is typical of an ordered crystalline material. In contrast, Figure 3, an XRD pattern of an amorphous HTO ion exchanger, exhibits no crystallinity. It has been found that the interplanar d-spacings of the CST materials can be modified by synthesis techniques. Materials with d-spacings over the range of 0.78 to 1.5 nm have been prepared and evaluated for ion exchange performance. This group of materials includes members with minor crystal structure modifications as well as quite different structures.

Figure 1. Transmission electron micrograph of a crystalline silicotitanate ion exchange material

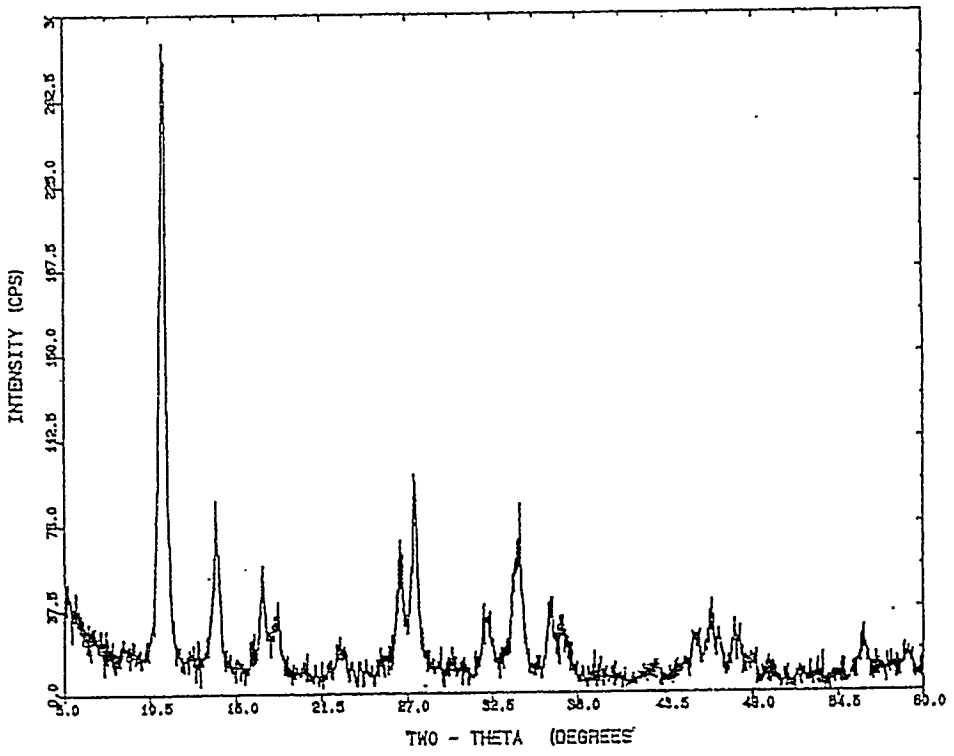

Figure 2. X-ray powder diffraction pattern of a crystalline silicotitanate ion exchange material

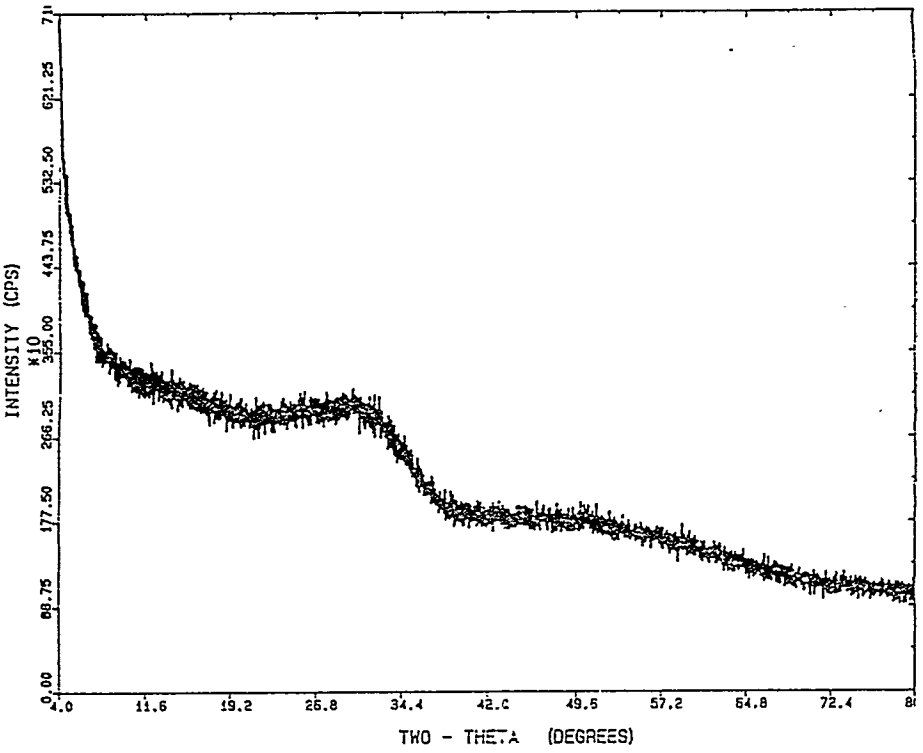

Figure 3. X-ray powder diffraction pattern of amorphous hydrous titanium oxide ion exchanger

Ion Exchange Studies

Studies have been performed to assess CST affinity for Cs by measuring batch distribution coefficients (K_d). The distribution coefficient is a quantitative measure of a material's capability to remove an ion from solution and is the ratio of the amount of the ion adsorbed by the ion exchange material to the amount of the ion remaining in solution.

$$K_d = \frac{(Co-C_1)}{C_1} \cdot \frac{V}{M}$$

In this formula, C_o is the initial solution concentration, C_1 is the solution concentration after contact, V is the solution volume in milliliters (usually 10 ml) and M is the mass of the ion exchanger, (usually 0.010 g). Although initial tests have focused on Cs, limited measurements have been performed to characterize its affinity for strontium and plutonium.

The ion exchange capacity of the CSTs is measured by contacting the sodium form of CST (Na-CST) with strong acid resulting in the replacement of Na^+ with H^+. The Na^+ concentration was measured by atomic absorption spectroscopy (AAS). The ion exchange capacity of the materials was 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 neutral solution of 100 ppm (7.5×10^{-4} M) Cs in 3 M $NaNO_3$ was used to measure the Cs^+ K_d. A 0.01-g quantity of the CST was gently agitated with 10 ml of the test solution for 24 hours, filtered, and the concentration of Cs^+ measured by AAS or inductively coupled plasma/mass spectrometry (ICP/MS) techniques. The Cs distribution coefficients (K_d, ml/g) were correlated with the largest d-spacing measured by XRD for each material as shown in Figure 4.

As can be seen in Figure 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. These measurements were made in 3 M $NaNO_3$ with a pH in the range of 6-8 using 100 ppm Cs. It was concluded from these measurements that the affinity of the CST for Cs^+, and possibly other aqueous cations, can be tailored by modification of the crystal structure. CST materials characterized by the 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 nonhydrated Na^+ and Cs^+ ions. It is reported (18) that although the nonhydrated ionic radius of Cs^+ is larger than that of Na^+, the hydrated radius of Na^+ is larger than that of Cs^+. Although the ion exchange mechanism is not known, it involves diffusion of the nonhydrated Na^+ out of the CST lattice and replacement by a Cs^+ ion in the interstitial spaces of the CST lattice.

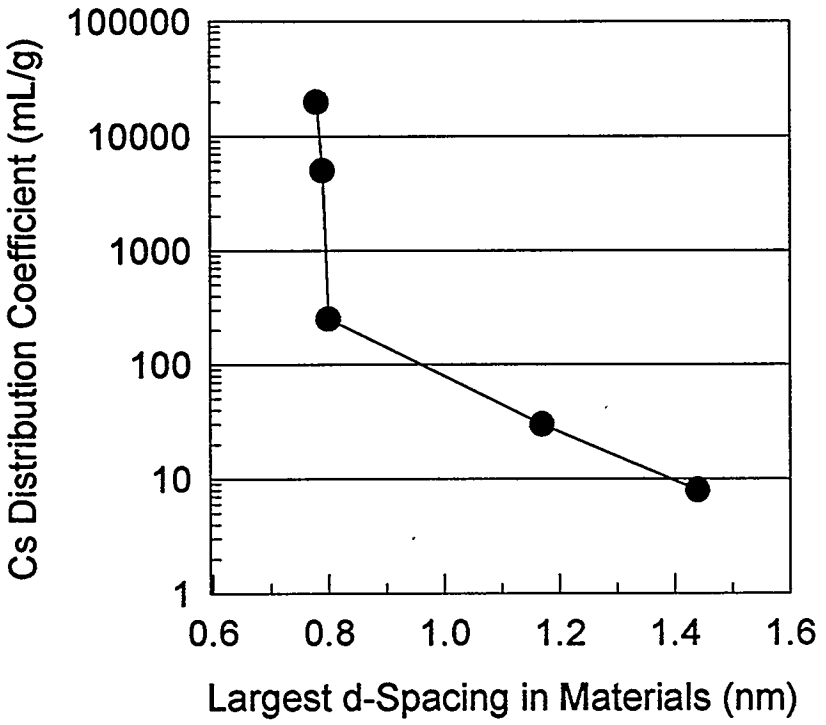

Figure 4. Plot of Cs^+ K_d as a function of the largest d-spacing for several crystalline silicotitanates

Following these experiments in neutral solutions, distribution coefficients for the CST ion exchanger giving the best performance, called TAM-5, were determined over a wide pH range from 1 M HNO_3 to 2.5 M 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 0.6 M. Several experiments were also performed to determine the distribution coefficients for strontium in neutral and alkaline solutions containing 20 ppm Sr^{2+} in 5.7 M Na^+. It was determined that the K_d for Sr^{2+} increased from 780 ml/g at a pH of 7 to 4000 ml/g in 0.6 M OH^- with a pH close to 14.

Extensive studies were conducted to assess the effect of compositional modifications on Cs ion exchange performance in highly basic solutions comparable to those found in the radwaste storage tanks. Details of these investigations are an important part of the development of CSTs and are protected by a proprietary agreement. The studies have yielded a second-generation CST material that has Cs^+ distribution coefficients greater than 1,500 ml/g in solutions containing 100 ppm Cs^+, 5.7 M Na^+ and 2.5 M OH^-. These same materials exhibit Cs^+ distribution coefficients greater than 24,000 ml/g in neutral solutions of 3.2 M $NaNO_3$, and 2,400 ml/g in 1 M HNO_3.

Tests with Simulated Wastes

In addition to the ion exchange studies performed at Sandia National Laboratories, 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. Table 1 shows a representative composition of the simulated DSSF waste. It can be seen that these tests were performed with 3.9 M Na^+, 7×10^{-5} M Cs^+ ($Na^+/Cs^+ = 5.6 \times 10^4$), and 1.3 M OH^-. Cs^+ distribution coefficients were determined by radioisotopic tracer techniques. For several tests 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 placed in contact with the simulated waste solution for an extended time to determine the stability of the material.

TABLE 1 Composition of Simulated Double Shell Slurry Feed (DSSF) Waste

Species	Concentration (M/L)
Na^+	3.9
K^+	0.09
Rb^+	8.56×10^{-5}
Cs^+	7.0×10^{-5}
Al^{3+}	0.34
OH^- (total)	2.7
NO_2^-	0.34
NO_3^-	1.23
SO_4^{2-}	0.12
CO_3^{2-}	0.16
F^-	0.07

The results of these evaluations (19) confirm that the CST ion exchange materials have an excellent ability to remove Cs^+ from DSSF waste solutions. The second-generation CST material exhibited Cs^+ distribution coefficients of 2,400 ml/gram at 25°C in the simulated DSSF waste solutions. Cesium distribution coefficients exceeding 8,000 ml/g for first-generation materials and 20,000 ml/g for second-generation materials were observed after adjusting the pH of the simulated DSSF solutions to 10.8 by carbon dioxide addition. This suggests that use of CST materials, with partial neutralization of waste solutions by a reagent such as CO_2, could result in an even more efficient ion exchange process for removal of Cs^+. The tests 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 placed in contact 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

With the LDRD initial funding, we have prepared, characterized, and tested a new class of inorganic ion exchanger called crystalline silicotitanates (CST) for selective removal of Cs and Sr from defense radwastes. As a result of ion exchange distribution coefficient tests with CSTs, it is concluded that these newly developed materials exhibit significant potential for application to the treatment of aqueous nuclear waste solutions, especially highly alkaline, high-sodium defense wastes. In experiments with alkaline solutions that simulate defense waste compositions, the CSTs were found to have high affinities for Cs^{+}, Sr^{2+}, and Pu. The high affinity of CSTs for Cs in acidic solutions is also being investigated for use at Idaho National Engineering Laboratory and the Savannah River Site. The extremely high affinity for Cs in neutral solutions indicates a possible use for decontaminating fuel cooling pools, groundwater treatment, and for retarding the migration of Cs and Sr by groundwater. Inorganic CST ion exchange materials also offer the advantage of much higher radiation stability than is exhibited by organic ion exchange resins. 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. The last major hurdle remaining for CSTs is the conversion of the small particle size CST powder to a CST engineered form for use in ion exchange columns. This effort is being pursued by UOP through the CRADA that is described in the Appendix.

ACKNOWLEDGMENTS

This work was supported by the U. S. Department of Energy at Sandia National Laboratories under contract DE-AC04-94AL85000. The authors express their appreciation to Lane Bray, Battelle Pacific Northwest Laboratories, for measuring and providing measurements of the distribution coefficients for CST materials contacted with DSSF simulated waste solutions.

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APPENDIX

List of Publications Resulting from the LDRD Project

R. G. Dosch, N. E. Brown, H. P. Stephens, and R. G. Anthony, "Treatment of Liquid Nuclear Wastes with Advanced Forms of Titanate Ion Exchangers," in *Waste Management 93*, pp. 1751-1754, 1993.

E. A. Klavetter, N. E. Brown, D. E. Trudell, R. G. Anthony, D. Gu, and C. Thibaud-Erkey, "Ion-Exchange Performance of Crystalline Silicotitanates for Cesium Removal from Hanford Tank Waste Simulants," in *Waste Management 94*, pp. 709-713, 1994.

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R. G. Anthony, R. G. Dosch, D. Gu and C. V. Philip, "Use of Silico-Titanates for Removing Cesium and Strontium from Defense Waste," *I&EC Research*, 33 (11), 2702-2705, 1994.

Presentations Resulting from the LDRD Project

R. G. Dosch, R. G. Anthony, N. E. Brown, J. L. Sprung, and H. P. Stephens, "Advanced Forms of Titanate Ion Exchangers for Chemical Pretreatment of Nuclear Wastes," American Chemical Society, Washington, DC, August 23-28, 1992.

R. G. Dosch, N. E. Brown, H. P. Stephens, and R. G. Anthony, "Treatment of Liquid Nuclear Wastes with Advanced Forms of Titanate Ion Exchangers," Waste Management 93, February 28-March 3, 1993, Tucson, Arizona.

E. A. Klavetter, N. E. Brown, D. E. Trudell, R. G. Anthony, D. Gu, and C. Thibaud-Erkey, "Ion-Exchange Performance of Crystalline Silicotitanates for Cesium Removal from Hanford Tank Waste Simulants," Waste Management 94, February 27-March 3, 1994, Tucson, Arizona.

E. A. Klavetter, N. E. Brown, D. E. Trudell, R. G. Anthony, D. Gu, and C. Thibaud-Erkey, "Performance of Crystalline Silicotitanates for Cesium Removal from Hanford Tank Waste Simulants," American Chemical Society Meeting, Washington, DC., August 1994.

List of Invention Disclosures Resulting from the Project

One

List of Patents (applied for or issued) Resulting from the Project

Two; one is a continuation-in-part of the original application

Information regarding Employee Recruitment as a Result of the Project

Two personnel were hired at Sandia to work on this project in Department 6212.

Information Regarding Involvement of Students in the Project

Texas A&M University is a co-inventor of the CSTs and has played an important role in the development of the CSTs. Funding to TAMU from Sandia National Laboratories supported two Research Scientists and six students.

Information Regarding Follow-on Work (New activities, projects, sponsors)

Office of Environmental Management (EM)
As a result of rapid progress on this LDRD project, subsequent funding was obtained in FY93, FY94, and FY95 from the Office of Environmental Management, Office of Technology Development, EM-53, Teresa Fryberger. The funding was directed toward understanding the chemical and physical properties that are responsible for cesium and strontium selectivity of the crystalline silicotitanates in radwastes found at the various DOE facilities. Tests were also conducted on stability toward Co-60 radiation with doses up to $1x10^9$ rads (Si).

Department of Energy, Richland Field Office
Funding was also obtained from the Department of Energy, Richland Field Office in FY93 to develop a granular form of the CST and to assess its performance under conditions found at the Hanford Site. Funding continued in FY94 and FY95 from the Pacific Northwest Laboratory Technology Development Program Office (TDPO) and the Tank Waste Remediation System (TWRS) as a continuation of the FY93 funding.

CRADA
To further develop the crystalline silicotitanate materials for use in radionuclide ion exchange separation processes, scale up of the CST to a commercial scale and conversion of the small particle size CST powder into a suitable engineered form was necessary. Sandia National Laboratories, in conjunction with Texas A&M University, decided to pursue a cooperative research and development agreement (CRADA) with an industrial corporation with expertise in the area of ion exchange materials.

To facilitate interactions with a CRADA partner, TAMU assigned Sandia National Laboratories all patent rights for the CST materials for radwaste processing. Sandia and TAMU have submitted a joint patent on the CST materials that is pending in the U.S. Patent and Trademark Office. The TAMU license was agreed to in principle in early 1993 and executed on March 8, 1994. Sandia National Laboratories therefore became the lead organization in commercializing

the CST materials, with TAMU under contract to Sandia to support that commercialization and further development of the materials.

A solicitation was published in the *Commerce Business Daily* on March 23, 1993 requesting responses from companies interested in development and commercialization of the CST materials for radionuclide separations and other purposes. Thirty-three responses were received and an information package was distributed. Respondents were contacted and information was requested on their organization's technical and marketing capabilities, primarily in the area of ion exchange materials and process development. Sandia formed an evaluation team composed of both technical and technology transfer personnel that ranked the information packages received. Representatives from Sandia, Texas A&M, and DOE visited the two highest ranked companies. On September 7, 1993, Sandia National Laboratories and UOP, a joint venture company of Union Carbide Corporation and Allied-Signal Corporation, mutually agreed to pursue a CRADA and license. The CRADA and license were executed at UOP, Des Plaines, IL on March 2, 1994.

The CRADA provided for UOP and Sandia National Laboratories, with support from TAMU, to achieve commercialization capability for the CST materials by September 2, 1995. In the scope of work, Task 1 was to validate the Sandia/TAMU synthesis of the CST material phase suitable for cesium removal from radionuclide waste streams. Task 2 was scale up of the CST powder synthesis process to a viable commercial process. That task was completed ahead of schedule in August 1994, and a commercial batch of 1,800 pounds of CST powder was successfully produced in September 1994. Task 3 included development of a granular form of the CST material suitable for use in ion exchange column operations for cesium removal at the Hanford Site. That task is on schedule. Task 4 involves the characterization and documentation of the CST materials produced.

The Sandia-UOP license gives UOP the rights to produce and sell the CST material phase developed for cesium removal and radwaste processes. In exchange, Sandia will receive royalties based on the sales of the CST material and an annual fee for the license, with the annual fee dependent upon the royalties received. In the Sandia-TAMU license, Sandia agreed to pay TAMU a portion of the royalties received from CST sales.

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Dr. R. G. Anthony
Department of Chemical Engineering
Texas A&M University
College Station, TX 77843

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