ORNL/CP-96463

TASK SUMMARY

CONF-980335--

DEVELOPMENT AND TESTING OF SPHEROIDAL INORGANIC SORBENTS*

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MAR 06 1998
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January 29, 1998

Prepared for the
DOE Office of Science and Technology
Efficient Separations and Processing Crosscutting Program
Technical Exchange Meeting
March 1998
Augusta, Georgia

19980406 132

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*Research sponsored by Oak Ridge National Laboratory managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy under contract DE-AC05-96OR22464.

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DEVELOPMENT AND TESTING OF SPHEROIDAL INORGANIC SORBENTS

J. L. Collins and K. K. Anderson

Technology Needs

Inorganic ion exchange materials have high selectivities and efficiencies for separating and removing fission products, actinides, and other elements from aqueous waste streams. However, in most cases, these sorbents are commercially available only as fine powders or as unstable granular particles that are not readily adaptable to continuous processes. Some of these powders are also made as pellets by using binding materials. However, the binders tend to lessen the number of exchange sites that are available for use by blocking pores and passage ways to the exchange sites within the structures. Therefore, the loading and kinetic behavior of the exchangers are adversely affected. Another disadvantage of many of the inorganic ion exchangers is the lack of reproducibility as sorbents. These materials are prepared in batch processes in which chemical and physical gradients can occur that cause variances in the crystal morphology and compositions of the products.

The internal gelation technology being developed in this task provides a means of preparing many inorganic ion exchange materials as microspheres which can improve the flow dynamics for column operations and expand the practical applications of these materials. Preparations of the microspherical sorbents are very reproducible. Furthermore, in a few cases, the densities and porosities of an exchanger made as microspheres can be tailored by varying the chemical and physical process parameters; this allows some control over the selectivity and loading behavior of the exchanger.

Technology Description

The general objectives of this task are to develop, prepare, and test spheroidal inorganic ion exchangers made by the HMTA (hexamethylenetetramine) internal gelation process to remove radionuclides and heavy metals from waste streams occurring at the various DOE sites. Inorganic ion-exchange materials, such as sodium silicotitanate, sodium titanate, ammonium molybdophosphate, phosphotungstic acid, hexacyanoferrates, titanium monohydrogen phosphate, hydrous titanium oxide, polyantimonic acid, magnesium oxide, etc. have high selectivities and efficiencies for separating and removing radionuclides (e.g., cesium, strontium, technetium, iodine, europium, cerium, ruthenium, and zirconium), actinides, and other elements (such as lead, mercury, silver, nickel, zinc, chromium, and fluoride) from aqueous waste streams.[1-4]

The initial task of this program, which was initiated in March 1996, involved the development of sodium titanate (ST) sorbents as microspheres by the HMTA internal gelation process. Sodium titanate is a very good sorbent material for removing the strontium from alkaline supernatant of high ionic strength. Several preparations of composite microspheres of hydrous titanium oxide (HTiO) and titanium monohydrogen phosphate (TiHP), which were embedded with very fine particles of sodium titanate, were made. The optimum amount of sodium titanate powder that could be embedded in these sorbents to obtain maximum strontium loading was determined. These composite microspheres were chosen for development because both matrix materials (hydrous titanium oxide and titanium monohydrogen phosphate), as well as the sodium titanate, are good sorbents for removing strontium from alkaline supernatants.

Two chemical conversion methods were also developed for making pure sodium titanate microspheres; both required the use of hydrous titanium oxide gel spheres made by the HMTA internal gelation process. One method involved the hydrothermal conversion of hydrous titanium oxide gel spheres with sodium hydroxide and sodium salts. The other method utilized an alkoxide conversion process for converting hydrous titanium oxide gel spheres to a pure sodium titanate. As part of the optimization process, the prepared sorbents were tested in batch experiments for the removal of strontium from simulated Melton Valley Storage Tank (MVST) W-29 supernatant. For comparison, commercial sodium titanate sorbents and other strontium-selective sorbents were also tested. The microspherical sorbents worked as well as or better than the commercial engineered forms of sodium titanate in removing the strontium.

The development of cesium specific spherical sorbents for treatment of acidic, high-salt waste solutions was initiated in FY 1998. Acid-side treatment is important at INEEL and could become important if acidic sludge washing were to become a treatment option at Hanford, Savannah River, or Oak Ridge. Zirconium monohydrogen phosphates (ZrHP) embedded with ammonium molybdophosphate (AMP) was the cesium selective inorganic sorbent chosen for making microspheres. AMP is known to be a very effective sorbent for removing cesium from waste streams over a wide range of acidity and salinity, and it has very rapid loading kinetics. The cesium can also be eluted from AMP with ammonium salt solutions. AMP cannot be used as a sorbent at pHs above 7 because it decomposes. In the pH range of 1 to 7, ZrHP is also a very effective sorbent for removing Cs, Sr, Th, U(VI), Pu (IV), Am(III), Hg, and Pb from streams of lower ionic concentrations.

Benefits

The HMTA internal gelation process was originally developed as a process for preparing UO_2 microspheres and nuclear fuels for Light Water and Fast Breeder Reactors. Making inorganic ion exchangers as microspheres by the internal gelation process is a "spin-off" of these highly-developed fuel technologies. The major benefit of this program is to further develop the technology for use in making inorganic ion exchangers more usable for large scale column use. These materials could have several advantages in treating a variety of waste streams.

Numerous inorganic ion exchangers are being or have the potential of being used in treating supernatants, low-level liquid wastes, contaminated groundwater, contaminated surface water (including acid mine drainage), and soil leachates.

Some specific site applications include:

- removing cesium from acid solutions (Idaho),
- removing strontium, technetium, and cesium from tank supernatants (Hanford, Oak Ridge, Savannah River),
- treating contaminated wastewater to remove uranium, technetium, cobalt, lead, zinc, etc. (all sites),
- removing radioisotopes from groundwater (all sites),
- removing actinides and fission products from waste sludge leachate (Idaho, Hanford, Oak Ridge, Savannah River),
- removing heavy metals from acid mine drainage runoff (mine tailings, non-DOE sites),
- removing radionuclides such as Eu, Ce, and Pr from organic streams (solvent extraction processes, analytical wastes), and
- removing radionuclides such as Cs, Co, Eu, etc. from liquid wastes generated in hot cell operations and converting them to a more transportable, storable waste.

The loaded inorganic ion exchangers might be appropriate as a final waste form or more amenable to incorporation into other inorganic waste forms such as glass, ceramics, or grouts. The inorganic ion exchangers are more resistant to ionizing radiation, high temperatures, and harsh chemical environments than the more common organic polymeric materials.

Technology Transfer

A patent application entitled *Method for Preparing Hydrous Titanium Oxide Spherules and Other Gel Forms Thereof* was filed with the United States Patent and Trademark Office on November 1, 1996. In January of 1998, the ORNL Office of General Patent Counsel received the Notice of Allowance for this patent. In June of 1997, Eichrom Industries, Inc. obtained a license with exclusive rights in the specific fields of use claimed in the patent. Patent applications for several other spheroidal hydrous metal oxide sorbents will also be filed. Part of our FY 1998 task is to work with Eichrom to transfer the technology. Another task is to write additional patent applications for the other spheroidal sorbents and catalysts that have been developed.

Scientific Background

The chemistry of the HMTA internal gelation process is described in detail in a report by J. L. Collins et al.[5] The results of those studies showed that there were four principal reactions involved in the hydrolysis and precipitation of uranyl nitrate hexahydrate and that the kinetics and equilibria of these reactions varied with temperature. The chemical behavior observed in that study should hold true for making microspheres of other hydrous metal oxides by the HMTA internal gelation process. The four reactions for making hydrous titanium oxide can be shown as follows:

complexation/decomplexation,

$$2CO(NH_2)_2 + Zr^{4+} \rightleftharpoons Zr[CO(NH_2)_2]_2^{4+}, \tag{1}$$

hydrolysis,

$$Zr^{4+} + xH_2O \rightleftharpoons Zr(OH)_4 \bullet yH_2O\downarrow + 4H^+ \text{ and} \tag{2}$$
$$ZrO^{2+} + xH_2O \rightleftharpoons ZrO(OH)_2 \bullet yH_2O\downarrow + 2H^+,$$

HMTA protonation,

$$(CH_2)_6N_4 + H^+ \rightleftharpoons (CH_2)_6N_4 \bullet H^+, \text{ and} \tag{3}$$

HMTA decomposition,

$$(CH_2)_6N_4 \bullet H^+ + 3H^+ + 6H_2O \rightleftharpoons 4NH_4^+ + 6CH_2O. \tag{4}$$

The major constituents of a broth for making microspheres of hydrous metal oxide are hexamethylenetetramine, urea, and the metal salt. Urea serves as a complexing agent for the metal (reaction 1) and at certain concentrations allows for stable broths to be prepared at 0°C that remain clear and free of gelation or precipitation for reasonable periods of time. As the temperature of the broth droplets rises in the hot organic medium, decomplexation occurs (reaction 1) and permits the hydrolysis of the titanium to begin (reaction 2). HMTA, a weak organic base, drives the hydrolysis reaction to

completion. At first the HMTA molecules are singularly protonated (reaction 3). Once most of the HMTA molecules (≥ 95%) are protonated, they begin to decompose (reaction 4) into ammonia molecules, which make the system even more basic. Each protonated HMTA molecule can effectively remove three additional hydrogen ions. The reaction products are ammonium salt and formaldehyde. In addition to being a complexing agent, urea also functions as a catalytic agent in the decomposition of protonated HMTA molecules.

Technical Approach

The procedure for making hydrous zirconium oxide microspheres by this process involves first mixing formulated amounts of HMTA, urea, and zirconium at temperatures near 0°C to form a broth. Broth formulations that remain clear and free of gel for reasonable periods of time (≥1 h) at the temperature used. To make the HZrO/AMP microspheres, a predetermined amount of AMP is also mixed into the broth. It is added as slurry of very fine AMP particles. While being mixed the broth is injected as droplets via a flat-tipped, stainless steel hypodermic needle into a flowing stream of heated organic medium. Broth formulations with short gel times (8 to 12 s) are used. The droplets flow through a heated gel-forming apparatus and then through a long serpentine tube. The droplets become solid microspheres and are collected in a stainless steel-wire mesh, collection basket. The microspheres are then aged for about 10 to 30 m in a reservoir of hot organic medium. The reaction impurities are removed from the microspheres by washing them several times with dilute NH_4OH and then with deionized water.

Optimization of the composite microspheres involves empirically determining the amount of AMP that can be embedded to obtain maximum cesium loading from acidic supernatant with high salt concentrations. Although ZrHP is ineffective in removing cesium from this type stream, it is an excellent sorbent for removing cesium from waste streams of low ionic strength in the pH of 1to 7 range. The ZrHP/AMP microspheres should be effective in treating a broad range waste streams.

As part of the optimization development, the prepared sorbents are being tested in batch experiments to determine their effectiveness in removing cesium from acidified MVST supernatant. Samples of the best ZrHP/AMP microspheres, based on the batch tests, are to be sent to D. J. Wood and T. A. Todd at INEEL for testing. (The work at INEEL is sponsored by the Tank Focus Area,)

Accomplishments

Batch test results comparing the effectiveness of the microspherical sorbents that were developed with commercial sorbents for removing strontium from simulated MVST W-29 supernatant are given in Table 1. The composition of the supernatant was as follows: 3.9 *M* $NaNO_3$, 1.0 *M* NaOH, 0.14 *M* Na_2CO_3, 0.1 *M* NaCl, 0.25 *M* KNO_3, 1.0×10^{-4} *M* $CaCO_3$, and 1.1×10^{-5} *M* Sr (1 ppm). Strontium was added as strontium nitrate which was traced with the gamma-emitter, ^{85}Sr ($t_{1/2}$ = 64.8 d). Each test was conducted by mixing about 0.025 g of exchanger (either an air-dried mass or a mass of sorbent that would yield 0.025 g if it were air-dried) with ~5 mL of simulated supernatant for 24 h. The best of the air-dried microspheres that were prepared by hydrothermal conversion and the best composite hydrous titanium oxide microspheres that were embedded with about 23% sodium titanate powder and dried at 110°C removed 98.5 to 98.8% of the strontium, which was similar to 98.3% removed by granular sodium titanate obtained from Allied Signal. The distribution ratios ranged from 12,600 to 17,300 mL/g. Composite hydrous titanium oxide microspheres that were embedded with about 23% sodium titanate powder and not dried worked the best removing about 99.9% of the strontium. The $D_{24\,h}$ was

101,000 mL/g. Pure hydrous titanium oxide microspheres and granular hydrous titanium oxide obtained from DuNord worked equally well in removing about 95.5% ($D_{24\,h}$ = 4,300 mL/g) of the strontium which was better that the 92.2% ($D_{24\,h}$ = 2,400 mL/g) removed by granular IONSIV® IE-911 which was obtained from UOP. The sodium titanate microspheres prepared by an alkoxide conversion method worked only little better than the hydrous titanium oxide microspheres.

Table 1. Removal of strontium from simulated MVST W-29 supernatant by sorbents.

Sorbent[a]	D[b] (mL/g)	% R
IONSIV® IE-911 (gr),UOP	2,400	92.2
HTiO (gr), DuNord	4,300	95.5
NaTi (gr), Allied-Signal	12,600	98.3
HTiO ϕ[c]	4,300	95.5
NaTi ϕ[c,d]	5,600	96.4
NaTi ϕ[c,e]	14,000	98.5
(23% NaTi/HTiO) ϕ[f]	17,300	98.8
(23% NaTi/HTiO) ϕ[g]	101,000	99.9

[a]ϕ = microspheres; (gr) = granular or engineered form
[b]mixing time = 24 h; supernatant/sorbent ratio = ~200
[c]air-dried
[d]prepared by alkoxide conversion method
[e]prepared by hydrothermal conversion method
[f]dried at 110°C
[g]not dried

Batch tests with microspheres prepared by the hydrothermal conversion method were also conducted with a 0.1 *M* $NaNO_3$ solution with a strontium concentration of 100 ppm. The pH of the solution was adjusted to 12 with sodium hydroxide. The Ds for the microspheres ranged from 150,000 to 700,000 mL/g for tests with mixing times of 24 h. The Ds obtained for Allied Signal's granular sodium titanate were ~200,000 mL/g. The percentages of strontium that was removed by the microspheres ranged from 99.8 to 99.9%.

Experimental work was initiated to develop a microspherical sorbent of zirconium monohydrogen phosphate embedded with fine particles of ammonium molybdophosphate, which is currently being optimized for the removal of cesium from acidic supernatants with high salt concentrations such as the ones found at INEEL.

For the purpose of making ZrHP/AMP microspheres, it is advantageous to be able to add the fine particles of AMP as a wet slurry to the broth used in the internal gelation process because it is easier to keep the AMP particles in suspension. With that goal in mind, preparations of AMP were prepared by two different methods with the hope that one of these materials would sorb cesium as well as the commercially prepared AMP powder obtained from Bio-Rad Laboratory, Inc. Cesium removal batch tests were conducted with samples of these AMP materials for comparison. Real supernatant from MVST W-27 was used which was acidified with nitric acid to a pH of 0.8. The major constituents of the acidified supernatant were Na (4.86 *M*), K (0.26 *M*), and NO_3^- (5.34 *M*). Cold cesium was also added to increase the cesium concentration from about 1 mg/L to 100 mg/L. The concentration of ^{137}Cs about 8.5 mCi/L. The tests were conducted using a volume (mL) of supernatant to mass of sorbent (g) ratio (V:m) of 200 and a mixing time of ~24 h. The average distribution ratio for the best of the prepared AMP samples was ~6,000 mL/g. About 92.2% the cesium was removed. The average D for the Bio-Rad AMP was ~17,000 mL/g with 98.8% of the cesium removed. In each case ~19 mg of cesium was loaded per gram of AMP.

Six preparations of hydrous zirconium oxide microspheres which were embedded with fine particles of AMP were made. Afterwards, the microspheres were treated with phosphoric acid solutions to convert the hydrous zirconium oxide to acid-insoluble zirconium monohydrogen phosphate. The amount of AMP used was varied to provide samples of microspheres with a dry weight percentages in the range of 30 to 60. Batch tests with samples of wet and air-dried microspheres from each preparation are being conducted with the acidified MVST W-27 supernatant (described above) to determine their cesium loading potential. A V:m ~ 200 and a mixing time of ~24 h are being used. For comparison, similar tests are being conducted with a composite sorbent (AMP-PAN) which was developed by F. Sebesta at the Czech Technical University in Prague, Czech Republic. This sorbent is composed of AMP powder bound in an organic polymer of polyacrylonitrile (PAN). It has already been shown at INEEL to be an effective sorbent in removing cesium from acidic supernatants.

Keywords

ammonium molybdophosphate, cesium, hydrous titanium oxide, hydrous zirconium oxide, ion exchange, internal gelation, microspheres, separations, sodium titanate, sorbents, strontium, supernatant, tank waste, titanium monohydrogen phosphate, strontium, zirconium monohydrogen phosphate

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TTP Number: OR16C342

References

1. A. K. De and A. K. Sen, "Synthetic Inorganic Ion-Exchangers," *Separation Science and Technology*, **13**(6), 517-540, 1978.
2. A. Clearfield, ed., *Inorganic Ion Exchange Materials*, CRC Press, 1982.
3. E. W. Hooper, B. A. Phillips, S. P. Dagnall, and N. P. Monckton, *An Assessment of the Application of Inorganic Ion Exchangers to the Treatment of Intermediate Level Wastes*, AERE-R-11088, Atomic Energy Research Establishment, Harwell, 1984.
4. J. L. Collins, B. Z. Egan, K. K. Anderson, C. W. Chase, J. E. Mrochek, J. T. Bell, and G. E. Jernigan, *Evaluation of Selected Ion Exchangers for the Removal of Cesium from MVST W-25 Supernate,* ORNL/TM-12938, April 1995.
5. J. L. Collins, M H. Lloyd, and R. L. Fellows, "The Basic Chemistry Involved in the Internal-Gelation Method of Precipitation of Uranium as Determined by pH Measurements," *Radiochimica Acta*, **42**, 121-134 (1987).

M98004055

Report Number (14) ORNL/CP--96463
CONF-980335--

Publ. Date (11) 19980129
Sponsor Code (18) DOE/EM, XF
UC Category (19) UC-2000, DOE/ER

DOE