

CONF-960158--4

TASK SUMMARY

DEVELOPMENT AND TESTING OF INORGANIC SORBENTS MADE BY THE INTERNAL GELATION PROCESS FOR RADIONUCLIDE AND HEAVY METAL SEPARATIONS*

B. Z. Egan, J. L. Collins, K. K. Anderson, and C. W. Chase

Chemical Technology Division
Oak Ridge National Laboratory
Post Office Box 2008
Oak Ridge, Tennessee 37831-6223

RECEIVED
FEB 05 1996
OSTI

November 29, 1995

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Prepared for the
DOE Office of Science and Technology
Efficient Separations and Processing Crosscutting Program
Technical Exchange Meeting
January 1996
Gaithersburg, Maryland

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

*Research sponsored by the U.S. Department of Energy under contract DE-AC05-84OR21400 with the Lockheed Martin Energy Systems, Inc.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED ✓R

MASTER

DEVELOPMENT AND TESTING OF INORGANIC SORBENTS MADE BY THE INTERNAL GELATION PROCESS FOR RADIONUCLIDE AND HEAVY METAL SEPARATIONS

Task Description

The objectives of this task are to develop, prepare, and test microspheres and granular forms of inorganic ion exchangers to remove radionuclides and heavy metals from waste streams occurring at various sites. Several inorganic materials, such as hexacyanoferrates, titanates, phosphates, and oxides have high selectivities and efficiencies for separating and removing radionuclides such as uranium, technetium, cesium, and strontium, and metals such as cobalt, silver, zinc, and zirconium from aqueous waste streams. However, these sorbents frequently exist only as powders and consequently are not readily adaptable to continuous processing such as column chromatography. Making these inorganic ion exchangers as microspheres or granular forms improves the flow dynamics for column operations and expands their practical applications. Microspheres of several materials have been prepared at ORNL, and the effectiveness of zirconium monohydrogen phosphate and hydrous titanium oxide microspheres for removing radionuclides from hot cell waste solutions has been demonstrated.

Technology Needs

Inorganic ion exchange materials, such as hexacyanoferrates, titanates, phosphates, and hydrous metal oxides have high selectivities and efficiencies for separating and removing fission products (e.g., cesium, europium, cerium, ruthenium, zirconium, and strontium), actinides, and other elements (such as silver, lead, mercury, nickel, zinc, chromium, and fluoride) 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 processing such as column chromatography. 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. The binders tend to block pores and passageways to the exchange sites within the structures and adversely affect the loading and kinetic behavior of the exchangers. Preparation of inorganic ion exchangers as microspheres improves the flow dynamics for column operations and expands their practical applications. One disadvantage of many of the inorganic ion exchangers that are made as powders, granular material, or as pellets 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. These same materials, when made by the internal gelation process, are more 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.

Scientific Background

Inorganic ion exchangers, such as hydrous titanium oxide, hydrous zirconium oxide, hydrous iron oxide, hydrous aluminum oxide, hydrous cerium oxide, potassium cobalt hexacyanoferrate, titanium phosphate, zirconium phosphate, polyantimonic acid, ammonium molybdochosphate, manganese dioxide, sodium titanate, and many others could be useful for treating supernate solutions, low-level liquid wastes, contaminated groundwater, contaminated surface water (including acid mine drainage), and soil leachates. Some specific site applications include (1) removing cesium from acid solutions (Idaho), (2) removing strontium, technetium, and cesium from tank supernatants (Hanford, Oak Ridge), (3) treating contaminated wastewater (all sites) to remove uranium, technetium, cobalt, lead, zinc, etc., (4) removing radioisotopes from groundwater (all sites), (5) removing actinides and fission

products from waste sludge leachate (Idaho, Hanford, Oak Ridge, Savannah River), (6) removing heavy metals from acid mine drainage runoff (mine tailings, non-DOE sites), (7) removing radio-nuclides such as Eu, Ce, and Pr from organic streams (solvent extraction processes, analytical wastes), (8) removing fluoride from waste streams, and (9) removing radionuclides, Cs, Co, Eu, etc., from liquid wastes generated in hot cell operations, to convert them to a more transportable, storable waste. In addition to these applications, these inorganic sorbents also have high potential as *in situ* barrier materials to prevent the migration of metals and radionuclides from burial grounds, leaking tanks, and other sources of contamination.

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.

Technical Approach

In general, this program involves the preparation of inorganic ion exchangers in the form of micro-spheres and also microspheres in which the ion exchanger powders are homogeneously dispersed throughout the microspheres, to produce materials that would be more useful for continuous processing of contaminated streams.

The most promising inorganic sorbents for application to the specific waste streams will be selected, and sufficient quantities of microspheres will be prepared for testing. Initial candidates include ammonium molybdate phosphate (AMP), sodium silicotitanate (SST), and polyantimonic acid (PAA). It is likely that AMP, PAA, and SST would be incorporated into microspheres to produce more column-usable forms. The matrix material of the microspheres would be either a hydrous metal oxide of titanium or zirconium, or a monohydrogen or monosodium phosphate form of these elements. These phosphates are insoluble in relatively strong acid. AMP is very effective in removing cesium from streams over a range of acidity and with high salt content. PAA has been shown to be effective in removing cesium, strontium, zirconium, and americium from certain streams at very low pHs. SST can exist in many crystalline forms and can be effective in removing cesium and strontium from alkaline streams containing high salinity.

The prepared sorbents will be tested in batch experiments for the removal of radionuclides and metals from simulated waste or contaminated solutions. The most promising materials, based on the batch studies, will be selected for column chromatography studies. Bench-scale studies will determine the radionuclide and metal removal efficiency, maximum loading, etc., in a continuous process.

Accomplishments

This is a new program. However, microspheres of several materials have already been developed and prepared at Oak Ridge National Laboratory (ORNL) by the internal gelation process. Hydrous titanium oxide and titanium monohydrogen phosphate microspheres and microspheres of both of these materials embedded with very fine particles of potassium cobalt hexacyanoferrate were used successfully for removing highly radioactive fission products from hot cell waste solutions. In small batch tests the mixed microspheres were also effective in removing cesium and strontium from supernatant taken from the Melton Valley Storage Tank facility at ORNL.

Benefits

The internal gelation process was originally developed as a process for preparing UO₂ 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.

Technology Transfer

Information developed by this task will be submitted to the DOE Program Manager for dissemination. Results will be presented to Waste Management personnel at other DOE sites, and researchers at other sites will be kept informed of progress. Results will be presented at DOE workshops, program reviews, and technical meetings.

Making inorganic ion-exchangers in a more usable form as microspheres using the internal gelation process is amenable to commercialization. The large-scale engineering of the internal gelation process has already been developed for nuclear fuels. The same equipment designs with minor modifications could be used to make large quantities of the ion exchange microspheres. Private industry has expressed interest in licensing and expanding the use of the technology.

References

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.

J. L. Collins, B. Z. Egan, B. B. Spencer, C. W. Chase, K. K. Anderson, G. E. Jernigan, and J. T. Bell, "Treatment of Radioactive Wastes from DOE Underground Storage Tanks," *Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management - Spectrum '94*, August 14-18, 1994, pp.813-818.

J. L. Collins, D. J. Davidson, C. W. Chase, B. Z. Egan, D. D. Ensor, R. M. Bright, and D. C. Glasgow, *Development and Testing of Ion Exchangers for Treatment of Liquid Wastes at Oak Ridge National Laboratory*, ORNL/TM-12315, Oak Ridge National Laboratory, March 1993.

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, 121-34 (1987).

Keywords

Supernate, tank waste, microspheres, gelation, ion exchange, separations.

For further information, please contact:

B. Z. Egan
Lockheed Martin Energy Systems
Oak Ridge National Laboratory
P. O. Box 2008
Oak Ridge, Tennessee 37831-6223
(423) 574-6868
Email: eganbz@ornl.gov

J. L. Collins
Lockheed Martin Energy Systems
Oak Ridge National Laboratory
P. O. Box 2008
Oak Ridge, Tennessee 37831-6221
(423) 574-6689