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PNNL-SA-27105

Proceedings of the

Efficient Separations and Processing Crosscutting Program 1996 Technical Exchange Meeting

January 16-19, 1996
Gaithersburg, Maryland

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Office of Technology Development
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Prepared by
Pacific Northwest National Laboratory
Richland, Washington

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Summary

This document contains summaries of technology development presented at the 1996 Efficient Separations and Processing Crosscutting Program (ESP) Technical Exchange Meeting. The ESP is sponsored by the U.S. Department of Energy's Office of Environmental Management (EM), Office of Technology Development.

The meeting is held annually to promote a free exchange of ideas among technology developers, potential users (e.g., within EM focus areas and at DOE sites), and other interested parties within the EM community. During this meeting, developers of ESP-funded technologies describe the problems and needs addressed by their technologies; the technical approach, accomplishments, and resolution of issues; the strategy and schedule for commercialization; and evolving potential applications.

Presenters are asked to address the following areas:

- target waste management problem, waste stream, or data need
- scientific background and technical approach
- technical accomplishments and resolution of technical issues
- schedule and strategy for commercializing and *implementing* the technology or acquiring needed data
- any potential alternate applications of the technology or data, including outside DOE/EM.

This meeting is not a program review of the individual tasks or subtasks, but instead focuses on the technical aspects and implementation of ESP-sponsored technology or data. The meeting is also attended by the ESP Technical Review Team, who have the opportunity to review the ESP as a whole.

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Presenters: Teresa Fryberger, DOE/EM-53; Bill Kuhn, Pacific Northwest National Laboratory

Introduction

The U.S. Department of Energy (DOE) established the Office of Technology Development (OTD, EM-50) as part of the Office of Environmental Management (EM) in November 1989. EM manages remediation of all DOE sites and wastes from current operations. The goal of the EM program is to minimize risks to human health, safety, and the environment and to bring all DOE sites into compliance with federal, state, and local regulations by the year 2019. EM-50 is charged with developing new technologies that are safer, faster, more effective, and less expensive than current methods.

To focus resources and address opportunities, EM-50 has targeted five major remediation and waste management problem areas within the DOE complex for action based on risk, prevalence, or need for technology development to meet environmental requirements and regulations. Other areas may be added or current areas further partitioned to ensure that research and technology development programs remain focused on EM's most pressing remediation and waste management needs. These major problem areas, termed "Focus Areas," are described here.

- **High-Level Waste Tank Remediation.** Across the DOE complex, hundreds of large storage tanks contain hundreds of thousands of cubic meters of high-level mixed waste. Primary concerns are deteriorating tank structures and consequent leakage of their contents. Research and technology development activities must focus on developing safe, reliable, and cost-effective methods for characterization, retrieval, treatment, and final disposal of the wastes.
- **Contaminant Plume Containment and Remediation.** Contaminant plumes at DOE sites are estimated to include nearly 2 billion gallons of contaminated groundwater and more than 55 million cubic yards of contaminated soils. There is insufficient information at most sites about the contaminants' distribution and concentration. Migration of some contaminants threatens water resources and, in some cases, has already adversely affected the offsite environment. Many current characterization, containment, and treatment technologies are ineffective or too costly. Improvements are needed in characterization and data interpretation methods, containment systems, and in situ treatment.
- **Facility Transitioning, Decommissioning, and Final Disposition.** Current estimates are that as many as 7000 DOE-owned facilities are contaminated with radioactive species on surfaces and inside equipment. These must be decontaminated and decommissioned over the next 30 years. While building and scrap materials at the sites are a potential resource with significant economic value, current regulations lack clear standards for releasing the equipment for other uses. This indirectly discourages the recovery, recycling, and/or reuse of these resources. Development of enhanced technologies to decontaminate these materials and effective communication to the public of the low relative risks involved will help enable the recovery, recycle, and/or reuse of these resources. Improved material removal, handling, and processing technologies are also needed to enhance worker safety and reduce cost.
- **Mixed Waste Characterization, Treatment, and Disposal.** DOE has site inventories of more than 300,000 cubic meters of mixed waste—hazardous chemical components contaminated with radioactive components. DOE faces major technical challenges in the management of this waste. Conflicting regulations and a lack of definitive mixed-waste treatment standards hamper treatment and disposal.

The capacity nationwide for mixed-waste disposal is also limited and expensive. DOE spends millions of dollars annually to store mixed waste because of the lack of accepted treatment technology and disposal capacity. In addition, currently available waste management practices require extensive, and therefore costly characterization, retrieval, handling treatment, and disposal of mixed waste.

- **Landfill Stabilization.** DOE sites have large volumes of solid and other wastes in landfills. Because some waste contaminants are migrating, interim containment is required before final remediation. Materials buried in retrievable storage containers pose another problem. Evolving regulations dictate that some landfills must be stabilized to prevent contamination of groundwater and ensure control over contaminants in the waste. Retrieval systems must be developed to minimize worker exposure and quantities of secondary waste. Another high-priority need are in situ methods for containment and treatment.

In addition to these Focus Areas, EM has established Crosscutting Areas that cut across the Focus Areas by providing technologies in chemical and physical separations and treatment, characterization, and robotics.

The Efficient Separations and Processing Crosscutting Program

The Efficient Separations and Processing Crosscutting Program (ESP) was created in 1991 to identify, develop, and perfect chemical and physical separations technologies and chemical processes to treat wastes and address environmental problems throughout the DOE complex. The ESP funds several multiyear tasks that address high-priority waste remediation problems involving high-level, low-level, transuranic, hazardous, and mixed (radioactive and hazardous) wastes. The ESP supports applied research and development (R&D) leading to the demonstration or use of these separations technologies by other organizations within DOE-EM.

The ESP fosters future expertise in separations technologies by encouraging university participation. Where possible, the program transfers separations technologies developed by DOE to U.S. industry. The ESP is organized as a crosscutting program under DOE-EM's Office of Research and Development.

A key goal of the ESP is to apply ESP-sponsored technologies in all Focus Areas regardless of the intended application. The ESP emphasizes innovation and proof-of-principle in its tasks and will accept higher risks because of the greater probability of payoff when averaged over all Focus Areas. Focus Area staff help decide whether specific ESP tasks begin or continue. For example, Focus Area representatives reviewed FY 1995 ESP proposals.

Technology Needs

A wide range of wastes and associated environmental problems exists at more than 100 contaminated installations in 36 states and territories because of half a century of nuclear processing activities undertaken by DOE and its predecessors. The cost of cleaning up this legacy is estimated to be hundreds of billions of dollars. The ESP was begun because billions of dollars could be saved if new separations technologies and processes could produce even marginal cost savings. Treating essentially all DOE defense wastes requires separation methods that concentrate the contaminants and/or purify waste streams for release to the environment or downgrade the waste to a form that requires less difficult and expensive disposal.

Initially, ESP R&D efforts focused on treatment of high-level waste from underground storage tanks because of the potential for large reductions in disposal costs and hazards. As other separations needs have become clearer and as waste management and environmental restoration priorities have changed, the program has evolved to encompass broader waste management and environmental remediation problems.

Scope of Separations

The ESP provides the following categories of separations:

- removal of dilute radionuclides from aqueous phases
- removal of dilute toxic materials from aqueous phases
- removal of bulk constituents from waste streams to minimize the volume of waste to be disposed or to recover chemicals for recycle
- destruction of complexants, bulk anions, and toxic organic compounds.

Current Program

The ESP conducts primarily laboratory research to create new chemical separations technologies and processes. These technologies must be able to scale up economically, without introduction of major new technical problems, to treat wastes in the volumes and at the rates required by regulatory requirements. The most important category of work is the development of new separations processes.

The program also sponsors development of improved chemical processes when needed, research on chemical reactions that enhance chemical separations or eliminate a separations step by destroying a contaminant, and development of innovative waste forms if required to carry out new separations strategies.

The ESP currently funds 31 multiyear tasks that address high-priority waste remediation problems. Fifty percent of these tasks include university staff; 75% have outside collaboration.

Additional efforts in these technical areas will be funded only if there are conspicuous advantages (cost, timeliness, probability of the technology's success, capability of staff, etc.) relative to current ESP projects, but such funding is possible. Funding for new tasks is normally $200K to $500K per year. Table 1 shows ESP's funding profile. These data describe funding disbursed by ESP and are adjusted to reflect funding cuts imposed during the fiscal years.

Table 1. Funding Profile for Efficient Separations and Processing Crosscutting Program, FY 1992-1996.

FY 1992	FY 1993	FY 1994	FY 1995	FY 1996
$1.6M	$11.4M	$14.0M	$10.2M	$14.2M

For this proceedings document, the ESP technologies have been put into the following product lines:

- short-lived radionuclides
- long-lived radionuclides
- heavy metals
- waste processing and treatment.

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Short-Lived Radionuclides

- ☐ Crystalline Silicotitanates for Cesium/Strontium Removal
- ☐ Separation Technologies for the Treatment of Idaho National Engineering Laboratory Wastes
- ☐ Evaluation of Improved Techniques for Removing Strontium and Cesium from Process Wastewater and Groundwater
- ☐ Separation of Tritiated Water from Water Using Composite Membranes

Crystalline Silicotitanates for Cesium/Strontium Removal

Presenters: Norm Brown and Jim Miller, Sandia National Laboratories[1]; John Sherman, UOP Molecular Sieves

EM Focus Areas: high-level waste tank remediation; contaminant plume containment and remediation

Task Description

A new class of inorganic ion exchangers called crystalline silicotitanates (CST) has been developed that exhibits very high selectivity for cesium and strontium in the highly alkaline radioactive wastes at the Hanford Site and other DOE sites. Tests have also shown that CSTs have high selectivity for cesium in acidic and neutral solutions. The ESP is supporting an effort at Sandia National Laboratories and Texas A&M University to further develop and characterize the important chemical and physical properties that will determine the applicability of CST to radioactive waste treatment at Hanford and other DOE facilities.

Technology Needs

In March 1994, a Cooperative Research and Development Agreement (CRADA) was executed with UOP Molecular Sieves, Mt. Laurel, New Jersey, to scale up the synthesis of CST and convert the fine powder into an engineered form. UOP prepared a 1800-lb batch of CST powder in September 1994 that is commercially available as UOP IONSIV® IE-910. During the past year, the main CRADA goal has been to convert the fine CST powder into an engineered form, called IONSIV® IE-911, suitable for use in ion exchange columns in highly alkaline conditions such as those found at Hanford, Oak Ridge National Laboratory (ORNL), and Savannah River.

Sandia and UOP obtained guidance on the required performance characteristics of the engineered form from Westinghouse Hanford Company (WHC) and Pacific Northwest National Laboratory (PNNL). Based on this input, the design basis is high capacity for cesium and strontium, a particle size in the -30 to + 60 mesh range, and hydraulic properties and attrition resistance comparable or superior to IONSIV® TIE-96.

Technical Approach

The experimental approach to characterize CST materials has been to measure batch distribution coefficients (K_d, mL/g) under conditions that simulate potential processing conditions. Extensive work has been conducted on W-27 simulants from ORNL, double-shell slurry feed-5 (DSSF-5) from Hanford, THOREX wash solutions from West Valley Nuclear Services, Inc., and groundwater from Idaho National Engineering Laboratory's (INEL) Test Area North (TAN). A typical K_d measurement would involve contacting 0.10 g of CST with 10 mL of the simulant for 24 hours with gentle agitation at ambient temperature. Batch kinetic K_d measurements were made on developmental engineered forms with contact times ranging from 20 minutes to 72 hours. After filtration and sample preparation, nonradioactive cesium and strontium concentrations are measured to part-per-billion levels using inductively coupled plasma/mass spectroscopy.

Attrition resistance was measured by the standard UOP industrial shaker test on fresh samples and those exposed to a waste simulant for 7 days at ambient temperature. The best materials were tested under flow conditions in a 1-cm-diameter column with flow rates of 1 to 3 column volumes (CV) per hour.

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[1] This work was supported by the U.S. Department of Energy at Sandia National Laboratories under Contract DE-AC04-94AL85000.

Samples were collected until at least the 70% breakthrough point was achieved. No shrinkage, swelling, gas evolution, or void formation was observed in the IONSIV® IE-911.

Accomplishments

Batch tests with the West Valley THOREX solutions (0.9 *M* Na^+, pH 12) and a developmental IONSIV® IE-911 resulted in K_d values of >10,000 mL/g. A column test with a flow rate of 0.8 CV/h was conducted at Sandia with simulated waste, and no cesium was measured up to 450 CV. Based on these results, an actual waste test was conducted at West Valley. The test lasted 14 days and 225 CV of waste was treated at 10°C at an average flow rate of 0.65 CV/h. A decontamination factor (DF) of 10^6 was measured for cesium, 10^4 for strontium, and 100 for both uranium and plutonium. As expected, anionic technetium was not retained by the CST.

Batch tests with ORNL W-27 simulant (4.77 *M* Na^+, 4.85 *M* NO_3^-, pH = 12.5) were conducted with developmental IONSIV® IE-911 materials. K_d values of 530 mL/g were measured and Lot 38 B was selected for column tests. A 1-cm-diameter x 10-cm-long column was tested with W-27 simulant at a flow rate of 3 CV/h. Cesium concentrations were measured and the 50% breakthrough volume was found to be 500 CV, which was in good agreement with that predicted from the batch K_d measurement. A test using W-27 actual waste was conducted at ORNL using a 1 cm (d) x 6 cm (l) column containing 10 g of Lot 38B, and the 50% breakthrough point was determined to be 350 CV. Analysis of the W-27 waste revealed a pH of 12.8 and a slightly higher Na^+ and NO_3^- concentration than that used in the simulant test. The Texas A&M ion exchange model predicts these compositional changes would decrease the K_d about 30%. Hence, there is good agreement between the actual waste and simulant tests. Detailed W-27 waste test results will be presented by ORNL.

Extensive testing has been conducted on IONSIV® IE-911, Lot 38B, in DSSF-5 solutions. Average K_d measurements are about 500 mL/g. These data have been used by UOP to further the development of IONSIV® IE-911. A column experiment at 3.75 CV/h with 10 ppm cesium indicated a 50% breakthrough point of 500 CV. Detailed test results will be reported by PNNL. Development of IONSIV® IE-911 has continued at UOP since the preparation of lab sample Lot 38B. Improved kinetics and capacity have been achieved and the most recent data will be presented.

Tests to remove cesium and strontium from groundwater simulating that found at INEL's TAN have been conducted using IONSIV® IE-911 Lot 38 B. The composition is about 450 ppm dissolved solids with significant concentrations of Na^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Cl^-, SO_4^{2-} and HCO_3^-. Batch K_ds of >10^4 mL/g for cesium and 2 x 10^5 mL/g for strontium were measured. A column test was conducted at 10 CV/h to 4550 CV. During the test, no cesium breakthrough and only slight strontium breakthrough was measured. The DF for cesium was >500 and strontium was >1600.

Samples of IONSIV® IE-910 and IONSIV® IE-911 were loaded with cesium and irradiated to 10^8 and 10^9 Rads (Si) under a range of test solutions and conditions. The samples were examined by X-ray diffraction, and cesium concentrations were measured in solution. Preliminary conclusions are that no significant degradation was observed under all test conditions.

A thermodynamic equilibrium model that estimates cesium K_d has been developed for solutions with pH >1 to <14. The model includes the competitive exchange of H^+, Na^+, K^+, Rb^+ and Cs^+. Distribution coefficients estimated by the model for Hanford, ORNL, and other waste simulants such as DSSF, neutral current acid waste, and W-27 correspond with experimental data within 10%. This model will find use in anticipating changes in ion exchange performance as solution parameters change. A model to predict the breakthrough behavior of ion exchange columns is being developed and applied to estimate the effect of flow rate on W-27 wastes at ORNL.

Benefits

Based on these and other test results, IONSIV® IE-911 has many potential benefits over competing ion exchangers. It has high capacity for cesium over a pH range from 14 to 0 and excellent capacity for strontium over a pH range from 14 to neutral. The kinetics are very good at 3 CV/h and will be evaluated at higher flow rates as development continues. Because it is nonregenerable and would be used once, significant cost savings will be possible due to less complex processing equipment and a smaller facility.

The cesium-loaded exchanger has excellent radiation stability to 10^9 Rads (Si) and studies are in progress to assess its use as a potential cesium interim or final waste form. Direct incorporation into glass appears to be feasible based on PNNL tests that show the historical 1% TiO_2 in glass limit is very conservative and TiO_2 concentrations up to 5% or higher are possible. Commercial samples of IONSIV® IE-911 will be available early in 1996 to confirm these test results with actual wastes at the various DOE facilities.

Technology Transfer/Collaboration

UOP Molecular Sieves
Texas A&M University

Acknowledgments

Additional funding for this work was provided by Westinghouse Hanford Company's Tank Waste Remediation System Program in FY 1995. UOP development efforts have been fully funded by UOP.

Keywords

cesium, strontium, alkaline, groundwater, acid, ion exchanger, radioactive waste, TWRS, ORNL, PNNL, INEL, Sandia

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TTP Number: AL26C311

Separation Technologies for the Treatment of Idaho National Engineering Laboratory Wastes

Presenters: Terry Todd and Scott Herbst, Idaho National Engineering Laboratory[1]

EM Focus Areas: high-level waste tank remediation; contaminant plume containment remediation; mixed-waste characterization, treatment, and disposal

Task Description

The Idaho National Engineering Laboratory (INEL) is collaborating with several DOE and international organizations to develop and evaluate:

- Technologies for the treatment of acidic high-level radioactive wastes. The focus on the treatment of high-level radioactive wastes is on the removal of cesium and strontium from wastes typically 1 to 3 *M* in acidity.
- Technologies to treat groundwater contaminated with radionuclides and/or toxic metals.
- Technologies to remove toxic metals from hazardous or mixed waste streams, for neutral pH to 3 *M* acidic waste streams.

Technology Needs

The INEL reprocessed spent nuclear fuel from 1953 to 1992 to recover fissile uranium. The high-level raffinates from reprocessing were temporarily stored in underground storage tanks until they were solidified in a fluidized-bed calciner. The solid calcine is stored in stainless-steel bins within concrete vaults.

In April 1992, DOE discontinued reprocessing of spent nuclear fuel and shifted the focus of the Idaho Chemical Processing Plant (ICPP) to management and disposition of accumulated radioactive wastes. Currently ~1.8 million gallons of acidic, radioactive liquid waste, which is not amenable to calcination, and ~3800 m^3 of calcine exist at the ICPP. Legal drivers and agreements exist that obligate the INEL to develop, demonstrate, and implement technologies for treatment and interim storage of the radioactive liquid and calcine wastes. Per these agreements, all high-level radioactive waste must be treated and removed from INEL by the year 2035.

Remediation efforts will begin in FY 1997 to remove volatile organic compounds (VOCs) and radionuclides (cesium and strontium) from groundwater located at INEL's Test Area North (TAN) facility. A plume of VOCs and radionuclides has spread from the former TSF-05 injection well, and a Comprehensive Environmental Response, Compensation, and Liability Act remediation action is under way.

A Record of Decision was signed in August 1995 that commits the INEL to remediate the plume from TSF-05. Removal of strontium and cesium from the groundwater using commercially available ion-exchange resins has been unsuccessful at meeting maximum contaminant levels (MCLs), which are 119 pCi/L and 8 pCi/L for cesium and strontium, respectively.

Removal of toxic metals, such as mercury, lead, and chromium(VI), and partitioning of these materials from radioactive elements will be investigated in the laboratory on simulated wastes. Removing these metals from liquid wastes could render the liquids non-hazardous from a Resource Conservation and Recovery Act standpoint; that is, they become radioactive waste instead of mixed waste. Mixed waste is a particular problem for most DOE sites because appropriate treatment methodologies have not been approved.

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[1] This work was supported by the U.S. Department of Energy under Contract DE-AC07-94ID13223.

Background and Approach

In FY 1993 a joint development program was established within the ESP to evaluate technologies currently under development in the former Soviet Union for treating high-level radioactive waste. This joint program between the Khlopin Radium Institute of St. Petersburg, Russia, and INEL has been developing and testing two technologies for the removal of radionuclides from INEL acidic waste. The two solvent extraction technologies are a phosphine oxide derivative process for removing actinides and technetium and a cobalt dicarbollide derivative process for the simultaneous removal of cesium and strontium from acidic waste.

Both Russian process flowsheets have been modified to enhance extraction performance and to improve the safety characteristics of the processes. Current FY 1996 work scope includes testing the modified cobalt dicarbollide process with actual waste in centrifugal contactors at the INEL.

Removal of cesium from acidic waste streams is less developed than for alkaline wastes. Several ion-exchange technologies have been recently developed within the ESP program for acid-side cesium removal. Recently, several ion-exchange materials became available on engineered supports including crystalline silicotitanates (CST), composite ammonium molybdophosphate/polyacrilonitrile (AMP-PAN), nickel hexaferrocyanide/polyacrilonitrile (NiFC-PAN), and composite copper hexaferrocyanide/silica (CuFC). Most of these technologies were tested previously using simulated INEL waste.

Testing of the engineered form of these technologies with actual waste is planned for FY 1996 in conjunction with the producers of these materials, namely UOP Molecular Sieves/Sandia National Laboratories for the CSTs, the Czech Technical University for the PAN composites, and the Institute of Physical Chemistry, Moscow, Russia, for the CuFC/silica composite, provided material is available for testing.

A joint 3M/PNNL/INEL effort demonstrated removal of cesium and strontium from contaminated groundwater using 3M Empore™ technology. The 3M technology removes radionuclides efficiently from the groundwater in a system that can be easily designed for high throughput, simple cartridge change out, and reduced waste disposal costs. Additional testing at the TAN facility using a slip stream of contaminated injection well water is planned. This test will provide final system performance verification before transfer of the technology to EM-40 is recommended.

Accomplishments

We completed testing of the modified cobalt dicarbollide process, which incorporated a non-aromatic diluent and the phosphine oxide derivative processes in centrifugal contactors using simulated INEL acidic liquid waste. The testing was conducted jointly with Khlopin Radium Institute scientists at the INEL. Cesium and strontium removal efficiencies of 98.9% and 99.89%, respectively, were achieved using 24 stages of centrifugal contactors. The centrifugal contactors were specifically designed for the TRUEX process, which has different hydrodynamic properties than the cobalt dicarbollide process. Specifically, the centrifugal contactors were designed for a less-dense organic phase. The cobalt dicarbollide solvent is more dense than the aqueous waste. In addition, phase disengagement properties of the TRUEX and cobalt dicarbollide processes are quite different. The flexibility of the centrifugal contactors to operate under a very wide range of conditions, and the effectiveness of the cobalt dicarbollide process to remove fission products under less than ideal conditions was demonstrated.

A comprehensive literature review and report on the use and application of copper ferrocyanide sorbents for the removal of cesium from acidic solutions was published. Testing of the commercial Russian sorbent on simulated INEL acidic tank waste was performed in batch contacts and column tests. The cesium distribution coefficient obtained was $K_d = 3000$ and the maximum sorbent capacity measured was 144 g Cs/kg resin. Results of dynamic column tests with simulated waste spiked with ^{137}Cs indicate that greater than 99.5% of the cesium can be removed with two columns in series at 5% breakthrough. A report was issued summarizing the results of the tests with INEL simulant.

Efficient removal of cesium and strontium from TAN contaminated groundwater was demonstrated using 3M web technology. Approximately 1250 gallons of contaminated water were pumped at 1 L/min through two prefilters (2-µm and 0.1-µm), then through a strontium-specific cartridge that incorporated AlliedSignal sodium titanate, and finally through a cesium-specific cartridge that incorporated cobalt hexaferrocyanide in the web. Strontium breakthrough (50%) was achieved after processing 800 gallons of water, and no cesium was detected (<9 pCi/L) from the system effluent for the entire duration of the test. The system ran for nearly 80 hours continuously without operational problems.

Benefits

The radionuclide content of the INEL wastes is less than 1 wt% with the remainder comprised of inert metals from fuel cladding, soluble neutron poisons used in the dissolution process, sodium from decontamination and solvent wash activities, and calcium added to control corrosion in the calciner. With the proper selection/combination of technologies, it is possible to decontaminate the INEL wastes sufficiently to achieve Nuclear Regulatory Commission Class A low-level waste for the bulk constituents and the high-level waste volume resulting from the separations process would be significantly less than the original waste volume. This would result in lower facility and processing costs associated with the low-level waste stream and the much lower throughput high-level waste stream. It would also save considerable cost for interim storage and final geologic disposal of the high-level waste fraction.

A economically viable technology for the removal of cesium and strontium from contaminated groundwater has not been implemented to date. The testing performed with the 3M web technology on samples of TAN water from the TSF-05 injection well demonstrated a simple alternative for removal of these radionuclides.

Collaboration\Technology Transfer

Khlopin Radium Institute, St. Petersburg, Russia
Institute of Chemical Technology, Moscow, Russia
Czech Technical University
Pacific Northwest National Laboratory
UOP Molecular Sieves
Sandia National Laboratories
AlliedSignal, Inc.
3M
Parsons Environmental Services

Keywords

dicarbollide, extraction, phosphine oxide, actinides, centrifugal contactors,ferrocyanide, ion exchange, acidic waste, cesium, strontium, INEL, toxic, groundwater

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TTP Number: ID76C311

Evaluation of Improved Techniques for Removing Strontium and Cesium from Process Wastewater and Groundwater

Presenter: Debbie Bostick, Oak Ridge National Laboratory[1]

EM Focus Area: contaminant plume containment and remediation

Task Description

The goal of this task is to evaluate new sorbent materials, ion-exchange materials, or other processes for groundwater and process wastewater decontamination that will be more selective for the removal of ^{90}Sr and ^{137}Cs than standard treatment methods. Laboratory studies will strive to obtain a quantitative understanding of the behavior of these new materials and to evaluate their sorption efficiency in reference to a standard benchmark treatment technique.

Testing of the new materials will begin by conducting scoping tests where new treatment materials are compared with standard, commercially available materials in batch shaker tests. Sorption tests will be performed under various treatment conditions (e.g., pH, temperature, simulant waste composition) for the most promising materials. Additional testing with actual wastewater will be conducted with two or three of the most effective treatment methods. Once batch testing of a treatment method is completed, dynamic column tests will be performed using the most successful sorbents, to obtain the defining column operating parameters.

Technology Needs

Most DOE sites manage very large volumes of dilute liquid wastes that must be treated before being discharged to the environment. The waste is composed principally of contaminated groundwater and cooling water. Wastewater generated from research operations, reactors, and radiochemical production facilities also contribute to the overall waste inventory. The principal contaminants of the waste are ^{90}Sr and ^{137}Cs with trace quantities of heavy metals and organics..

The current treatment processes for these wastes generate large amounts of solid secondary waste that must be disposed of as radioactive waste. Handling and disposal of these secondary wastes is very expensive. Therefore, new processes are needed that will minimize the volume of secondary waste produced.

Scientific Background

A number of sorbents, ion exchangers, and advanced extractants are currently being developed for removing strontium and cesium from highly alkaline waste. These same sorbents may hold promise for the treatment of contaminated groundwater and process wastewater. Materials and processes that have demonstrated a high efficiency for nuclide removal from alkaline, and in some cases neutral, wastes include selective molecular recognition sorbents that have been immobilized on permeable membranes by 3M; the resorcinol-formaldehyde resin developed at Savannah River Technology Center (SRTC); engineered silicotitanates developed at Sandia National Laboratories; and sodium titanates, pillared clays, and micas developed by Texas A&M University and AlliedSignal, Inc.

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[1] Managed by Lockheed Martin Energy Research Corp., for the U.S. Department of Energy under contract DE-AC05-96OR22694.

Technical Approach

Testing of these new materials will be initiated by first preparing a standard wastewater simulant, and then selecting natural chabazite zeolite sorption as the baseline treatment technology against which the new materials will be tested. Testing procedures will then be standardized so that sorption behavior of the newly developed materials can be evaluated under comparable experimental conditions. The most promising materials will then be tested under dynamic flow conditions in small column tests and also will be used to treat actual wastewater samples.

Accomplishments

Batch sorption studies using treated zeolite in the wastewater simulant have been completed; radionuclide sorption on the zeolite was determined to fit the Freundlich sorption model. Zeolite sorption efficiency was observed in the presence of the major cations present in wastewater (e.g., sodium, calcium, potassium, and magnesium). Chabazite zeolite was also used to decontaminate batch samples of actual process wastewater and groundwater. The sorption characteristics of small zeolite column were determined using a wastewater simulant; 50% breakthrough of strontium and cesium from a 3.85-mL zeolite column occurred at 15,000 and 50,000 bed volumes, respectively.

After the sorption characteristics of baseline zeolite sorbent had been determined, testing of emerging sorption materials began. The resorcinol-formaldehyde (R-F) resin was selected as the first in the series of new sorbents that will be tested under this task. Although the resin was initially developed for the removal of cesium in highly alkaline waste streams, the material has demonstrated promise in removing both cesium and strontium from wastewater simulant. Batch-wise testing of the R-F resin was conducted to determine the optimum conditions for nuclide removal in the simulant.

Sorption results from several resin pretreatment methods were compared to sorption isotherms developed using the resin as received. Optimum resin performance was achieved by washing the resin with ultra-pure water. The cesium sorption isotherm on the resin is linear for simulant containing 10^{-9} to 10^{-4} meq/L cesium; the cesium sorption ratio in the linear range is 28,000 L/kg. The cesium sorption capacity in the wastewater simulant was similar to that found using the chabazite zeolite treatment, approximately 0.1 meq/kg.

The strontium sorption isotherm has two inflection points, possibly indicating a multilayer sorption mechanism. The sorption capacity, therefore, is dependent on the ratio of sample volume-to-mass of resin used in the batch test. If this ratio is less than 0.5 mL per mg resin, the strontium sorption capacity on the resin is 600 meq/kg. If the sample volume-to-resin mass ratio is greater than 2 mL/mg, the strontium sorption capacity in the simulant is only 4 meq/kg. In comparison, the strontium sorption capacity from the same simulant using pretreated zeolite is 30 meq/kg.

The effect of elevated sodium, potassium, magnesium, and calcium concentration on strontium and cesium sorption was studied. Strontium sorption on the resin is significantly more effected by the presence of interfering cations, as compared to that observed with the zeolite. With the addition of 4 meq/L interfering cation to the wastewater simulant, the strontium sorption ratio is reduced to 0.3% of its original value. The cesium sorption is reduced by 50% for the same increase in cation concentration.

A column study has been initiated to determine the breakthrough characteristics of strontium and cesium from R-F resin. The column is sized similarly to that of the zeolite column test so that direct comparison of column behavior can be made.

Samples of crystalline $Na_4Ti_9O_{20}$ powder and pellets were received from AlliedSignal and are currently being evaluated with the same procedures used to characterize the zeolite and R-F resin.

Benefits

This task will perform evaluations of ESP separation technologies for removing strontium and cesium from process wastewater and contaminated groundwater. Successful tests of these processes may lead to full-scale demonstrations as part of the Tank Focus Area. These technologies may eventually be deployed by the Tank Waste Remediation System program or similar waste remediation operations at Savannah River, Oak Ridge, and Idaho that may generate large volumes of secondary, slightly contaminated process, ground, or surface waters.

Technology Transfer/Collaborations

New sorbent materials have been obtained through collaboration with 3M, AlliedSignal, Boulder Scientific Company, and Pacific Northwest National Laboratory. Formulations of wastewater and groundwater simulants, representing water at Oak Ridge, have been forwarded to IBC Advanced Technologies, 3M, and Texas A&M University to aid in the development of new sorbents for wastewater applications. Sorption results using chabazite zeolite have been forwarded to Parsons Engineering Science, Inc., ORNL Waste Treatment Plant staff, and Westinghouse Electric Corporation for guidance in the treatment of contaminated wastewater.

Keywords

strontium, cesium, zeolite, resorcinol-formaldehyde resin, sodium nonatitanate, process wastewater, groundwater, sorption, ion exchange

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TTP Number: OR16C312

Separation of Tritiated Water from Water Using Composite Membranes

Presenters: Jim Duncan, Westinghouse Hanford Company; Dave Nelson, Pacific Northwest National Laboratory[1]

EM Focus Areas: contaminant plume containment and remediation; facility transitioning, decontamination, decommissioning, and final disposition

Task Description

Polymeric composite membranes are being developed to remove tritium from contaminated water at DOE sites. Industrial membrane systems are being developed that have proven to be energy efficient, and membrane technologies such as reverse-osmosis have been well developed for desalination and other industrial/municipal applications. Aromatic polyphosphazene membranes are being investigated because they have excellent radiological, thermal, and chemical stability. The FY 1996 effort is directed toward delineating a potential mechanism, providing a statistical approach to data acquisition, refining a mass balance, and designing a staged array module.

Technology Needs

Although processes to remove tritiated water (HTO) are available (e.g., combined electrolysis-catalytic exchange), most require intensive capital or energy expenditures. Thus, the proposed remediation of HTO from DOE sites frequently involves migration with time through geologic formations. Although this is logical because of tritium's short half-life (12.3 years), regulatory agencies have requested more emphasis on separation technology because of concerns about groundwater movement; that is, the rapid groundwater flow that allows a plume of HTO quicker access to a river and ultimately to human and animal ingestion. Sites currently having either a point source or groundwater containing HTO are Hanford, Savannah River, Idaho National Engineering Laboratory (INEL), Lawrence Livermore National Laboratory (LLNL), Brookhaven National Laboratory (BNL), and Mound Laboratory.

Scientific Background

During earlier studies of barrier materials for hydrogen isotopes,[1] it was observed that tritium had a lower permeability through brominated acrylonitrile-butadiene copolymer than deuterium or hydrogen. The authors proposed that this difference was a result of tritium's lower diffusivity by virtue of its larger molecular mass. Hollow fiber polyimide membranes have been used to separate tritium from moist air in support of fusion research.[2] Cellulose acetate membranes have been used to separate deuterium oxide (D_2O; 200 ppm enriched) from light water (H_2O) under pervaporation conditions (reduced pressure at the downstream).[3] Pervaporation was more effective (a = 1.08) at lower temperatures and pressures (20°C and 6 torr). Transition to an ultrafiltration mechanism was proposed for higher temperatures and pressures.

A similar change in mechanism was shown to occur with the separation of 50% D_2O from H_2O with downstream pressures of 260 torr and temperatures of 65°C.[4] An extension of this research used polytetrafluoroethylene (PTFE) membranes for both hydrogen/deuterium and $^{16}O/^{18}O$ separations within water.[5] Separation of the oxygen isotopes was greater than those for the hydrogen isotopes, which suggests different mechanisms for the pervaporation processes. For similar temperatures and pressures, the hydrophobic membrane gave enhanced separation

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[1] Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

compared to a cellulose acetate membrane. Preliminary engineering calculations have been reported for the separation of D_2O from H_2O using the PTFE membranes in counter-current cascades.[6]

In the current investigation, polyphosphazenes were chosen as the polymeric material for the membranes because they have been shown tobe isothermally stable to 320°C,[7] and selected types, especially poly[bis(phenoxy)phosphazene] (PPOP), were permeable to alcohol.[8] Furthermore, these polymers are chemically resistant to various solvents and are film-forming thermoplastics.[9] Polyphosphazenes with aryloxy side groups provided very low scission or cross-linking yields when exposed to gamma-radiation,[10] especially if no halogen or alkyl-groups were substituted on the aryl-group.

Technical Approach

In FY 1995, we showed that the poly[bis(phenoxy)-phosphazene]-based membrane can consistently achieve 30% reduction in a single pass, from 3 µCi/L (K-East Basin water). The FY 1996 work is directed primarily at a basic understanding of the HTO separation. Thus, a series of mass balance experiments will be conducted to confirm the preliminary FY 1995 results. Experiments will follow statistically designed parameters. The designed experiments will examine factors that might impact the HTO separation, such as pH, ion type/concentration, and temperature.

Staff at the University of Idaho and the University of Washington will provide spectroscopic data on the possible mechanism of the HTO separation. SpinTek Membrane Systems (Huntington Beach, California) will assist in the study of water permeation through the membranes. Several critical factors must be determined if the system is to be implemented. We expect to examine N-Basin water (39 µCi/L) during FY 1996 as well as water with a much higher tritium content. Experiments with water in the milliCurie per liter or higher range will require coordination with regulatory and technical personnel and possibly other DOE sites. The data from this experiment are crucial because they will allow us to determine further design parameters for the staged array system. Once most of the mechanism information and membrane property data are obtained, we will calculate the hypothetical separation of the HTO from water in the cascade.

Accomplishments

The major milestones of this project are directed at several issues, including a statistical approach to experimental design and mass balances, calculations from a designed module staged array, and a determination of the mechanism of the HTO separation. A statistical design of experiments has been completed, and work toward providing the necessary information is under way. Thus far, we have deionized and distilled 10 gallons of K-East Basin water (3 µCi/L) and used this as a source of HTO for initial experiments. Twenty gallons of N Basin water (39 µCi/L) will also be prepared for similar use.

Experiments were conducted with 10% carboxylated poly(diphenoxy)phosphazene and poly(diphenoxy)phosphazene, unannealed, using distilled K-East Basin water (3 µCi/L). The experiments indicated that HTO separation is quite variable and reached 18% depletion with only one carboxylated membrane under deionized water conditions. This confirms the variability from many previous experiments with unannealed membranes. The annealed membranes have also been examined under similar conditions (4°C and distilled K-East Basin water), but the scintillation results indicate little, if any, HTO depletion. However, the pressure stability required to maintain permeation with the annealed membranes was more consistent in contrast to the continual pressure fluctuations needed for the unannealed membranes.

The same set of experiments (two membranes and 4°C) was performed with distilled K-East Basin HTO containing 0.001 M Na_2SO_4. Both membrane types provided HTO separation, with the carboxylated membrane showing up to 17% HTO depletion, after 4 hours of operation. We are currently conducting membrane experiments with 0.01 *M* and 0.1 *M* Na_2SO_4 solutions as well as with similar calcium salt concentrations. Although the initial experiments have not been completed, the current data suggest that hydration shell involvement may be a significant part of the HTO separation mechanism.

Liumar Technologies Corporation of Ottawa, Ontario, is determining the coating conditions of the poly-(diphenoxy)phosphazene with material from Ethyl Corp. They are also attempting to establish the nanofiltration characteristics of the membrane using various molecular weight polyethylene oxides. We are collaborating with the University of Idaho and the University of Washington (Center for Process Analytical Chemistry) to help further define the HTO separation mechanism spectroscopically.

Benefits

Waters containing unacceptable tritium concentrations (above environmental release limits or drinking water standards) are released at DOE sites, including Hanford, Savannah River, INEL, LLNL, BNL, and Mound. One example involves the C-O_{18}H Treatment Facility at Hanford (to treat 242-A evaporator wastewater), which will discharge 1.4 million gallons of treated condensate containing tritium averaging 6.3 µCi/mL through the year 2015. Currently, water from some test wells at Hanford contain tritium concentrations approaching 6×10^7 pCi/L. The Tri-Party Agreement requires the HTO in the K-East Basin (spent nuclear fuel storage) be treated or relocated. There are no currently acceptable removal options for tritium remediation other than migration with time through geologic formations. This work will reduce the risk to the environment and public, reduce the costs for ultimate disposal for the tritium-containing water, and provide a way to recover the tritium in a concentrated form for disposal or use.

Tritium is also found in nuclear power plants in Canada and the U.S., as well as at the Savannah River Site, as a result of neutron capture within the heavy water moderator/coolant. Light water coolant also contains increasing concentrations of tritiated water (HTO and related species) in a similar ppm range due to neutron emission/capture (uranium fission). This technology would go far to mitigate HTO as a point source pollutant for light water reactors. Also, there is a possibility that this membrane separation process would be of use in the future fusion effort.

Technology Transfer/Collaborations

This work is a collaborative effort between Pacific Northwest National Laboratory (PNNL), Westinghouse Hanford Company, and SpinTek Membrane Systems. Atomic Energy Canada, Limited, has also expressed interest in the membrane process and has entered into a proprietary agreement with PNNL. Two meetings with Ontario Hydro personnel have been conducted.

PNNL has expanded the involvement of interested industries, including collaboration with Desalination Systems, Inc., during FY 1995. Liumar Technologies Corporation has examined the polyphosphazene membranes for their proprietary applications and continue to provide us information about aqueous permeation. Separation Systems Technology, Inc., (San Diego, California) has also provided us considerable information concerning membrane properties needed for module design. SEG/Oak Ridge has discussed their need for this technology for application to commercial nuclear power facilities.

We have obtained information concerning deuterium and tritium physical properties from both the All Russian Institute of Chemistry/Murmansk and the Association of Advanced Technologies/Minatom (Russia). To promote interest in this technology, we have presented the work before the Canadian Nuclear Society,[11] the American Nuclear Society,[12] and have a major publication in press.[13] A patent was also issued.[14]

Keywords

tritiated water, membrane, polyphosphazene, cross-flow, aqueous separation

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Long-Lived Radionuclides

- ☐ High-Temperature Vacuum Distillation Separation of Plutonium Waste Salts
- ☐ Water-Soluble Chelating Polymers for Removal of Actinides from Wastewater
- ☐ Advanced Integrated Solvent Extraction and Ion Exchange Systems
- ☐ Thermally Unstable Complexants/Phosphate Mineralization of Actinides
- ☐ Selective Sorption of Technetium from Groundwater
- ☐ Solvent Extraction of Radionuclides from Aqueous Tank Waste
- ☐ Electrically Controlled Cesium Ion Exchange
- ☐ Sequestering Agents for the Removal of Actinides from Waste Streams

High-Temperature Vacuum Distillation Separation of Plutonium Waste Salts

Presenter: Ed Garcia, Los Alamos National Laboratory

EM Focus Area: facility transitioning, decommissioning, and final disposition

Task Description

In this task, high-temperature vacuum distillation separation is being developed for residue sodium chloride-potassium chloride salts resulting from past pyrochemical processing of plutonium. This process has the potential of providing clean separation of the salt and the actinides with minimal amounts of secondary waste generation. The process could produce chloride salt that could be discarded as low-level waste (LLW) or low actinide content transuranic (TRU) waste, and a concentrated actinide oxide powder that would meet long-term storage standards (DOE-DTD-3013-94) until a final disposition option for all surplus plutonium is chosen.

Other methods are being examined for separating calcium chloride residue salts. These alternatives include vacuum distillation at higher temperatures than sodium chloride-potassium chloride salts, molten salt filtration, recovery of actinides as metal alloys, and a combined aqueous-pyrochemical separation process.

Technology Needs

There are 16 metric tons of salts at Rocky Flats Plant containing ~1 metric ton of plutonium. Most of these salts (11 tons) are composed of a sodium chloride-potassium chloride matrix. The remainder consists of a calcium chloride matrix. These salt residues are the product of past plutonium processing operations. The Defense Nuclear Facilities Safety Board has expressed concern (in Recommendation 94-1) about possibly unstable residues resulting from suspension of weapons-related activities in the DOE complex. These concerns included residue salts stored at Rocky Flats. DOE responded with commitments to mitigate the hazards associated with these residues. Among these were commitments to mitigate the problems associated with 6000 kg of high-hazard pyrochemical salts at Rocky Flats by May 1997, and an additional 4000 kg by December 1997. The high-hazard salts are stored in drums in buildings where workers need routine access. These residues may pose a safety risk if the reactive metals in the residues come into contact with water, creating hydrogen gas that could cause container pressurization.

The full 16-ton inventory is to be made safe by May 2002. In addition to mitigation of hazards, these residues must also be made acceptable for eventual disposal. An additional 2 tons of these salt residues exist at Los Alamos National Laboratory (LANL) and require stabilization by May 2002.

Scientific Background

Distillation separation is based on the large difference in vapor pressures at high temperature between most chloride salts that constitute pyrochemical residues and the actinide oxides. However, the plutonium content in these salts is usually a form of plutonium trichloride. Vapor pressure differences between alkali and alkaline earth chlorides and plutonium trichloride are too small to effect a good separation, therefore $PuCl_3$ must be converted to an oxide through an oxidation process. A process developed at LANL that uses carbonate salts to act as an oxidant has proven effective in converting all plutonium species into plutonium dioxide and can be ultimately combined with a distillation separation process.

The vapor pressure of sodium chloride and potassium chloride at 850°C is about 1 torr. The vapor pressure of plutonium dioxide at this same temperature is 10^{-16} torr. This large difference in physical properties forms the basis for a very efficient physical separation. Simple modeling results indicate that the plutonium concentration in sodium chloride-potassium chloride salts can be reduced to 10^{-10} ppm. The criterion for LLW of 100 nCi/g can be met by salts with a plutonium content of <1 ppm. Therefore, it should be possible to separate sodium chloride-potassium chloride salts from the plutonium content and dispose of the salts as LLW. Calcium chloride salts are also amenable to high-temperature vacuum distillation separation, but because of their much lower vapor pressure, temperatures >1200°C would be required.

Technical Approach

Uncontaminated salts have been used to verify the feasibility of the salt distillation process. These tests used existing equipment and have determined distillation rates as a function of temperature. A target rate of 3 kg per unit per day had been established, and results for sodium chloride-potassium chloride indicated that this was easily achievable. Distillation rates for calcium chloride were found to be too slow at temperatures below 11,000°C. These tests with uncontaminated salts have also been used to provide input for equipment designed expressly for the salt distillation process. This equipment is being fabricated and will be tested to verify expected performance, then transferred to a DOE/EM-60-funded project that will process LANL residues to serve as a pilot demonstration for processing at Rocky Flats.

The high temperatures needed for calcium chloride distillation require extensive modification and redesign of equipment that could be used for sodium chloride-potassium chloride processing. The high temperatures and resulting complications make vacuum distillation of calcium chloride salts a less attractive process than that for the alkali metal chloride salts. Other physical processes, such as filtering solid plutonium dioxide from either the molten salt or aqueous salt solution will also be explored. Chemical conversion of plutonium species into a liquid metal alloy will also allow physical separation of the immiscible phases.

Existing pyrochemical processing equipment at LANL is being used with plutonium-contaminated salts to test the separation achievable by the salt distillation process. A variety of feed sources and pretreatments are being used. These tests also establish the ability to carry out the process in a plutonium glovebox environment.

Accomplishments

Experiments with both uncontaminated and plutonium-contaminated salts have unequivocally established that kilogram quantities of alkali metal chloride salts can be distilled per unit operation per day. This meets an established performance requirement. No problem was encountered with condensation of the salt in a limited area and in a form easily recovered. Excellent mass balance has been achieved with both distilled salt (>99.5%) and distillation heel (>99.9%).

Tests with ~50 kg of salts containing plutonium successfully separated alkali metal chloride salts from the actinide content of the residue. The plutonium concentration of the salts was reduced from the tens of percent level to the parts per million level. Experiments were carried out that established that the plutonium contamination of the distillate salt was the result of the background contamination level of the processing environment and not from an inherent limitation of the distillation process. Even though the salts were in most cases still TRU waste, the plutonium content was less than 100 ppm, and significant benefit could be realized by this as discussed in the benefits section. Salts pretreated by a molten carbonate oxidation process were found to be excellent feed for the distillation separation process. These results led to funding by DOE/EM-60 to design and procure full-scale, production-capable equipment. We expect to begin processing salt residues at LANL in March 1996. The processing campaign will serve as a pilot-scale demonstration for Rocky Flats.

Benefits

Separation of the plutonium from the waste salts will lead to a large reduction in the cost of disposal even if the salts do not meet LLW disposal criteria. Current Waste Isolation Pilot Plant (WIPP) Waste Acceptance Criteria (WAC) would result in a maximum plutonium loading per 55-gallon drum of 23 g. In the best possible circumstance, this would lead to more than 50,000 drums. Efforts are under way to modify the WIPP WAC to allow 200 g of plutonium per drum. This would still result in 8000 drums.

If the plutonium in the salts can be reduced to below 100 ppm, a drum could be filled with salt without impacting even the present 25 g of plutonium limit. In this case, about 200 drums would be generated for WIPP disposal. At a cost of $10K per drum, the cost savings realized could total several tens of millions of dollars. The separated plutonium, consisting of 1 metric ton of plutonium dioxide, could be packaged for long-term storage per DOE-STD-3013-94. Plutonium oxide storage costs would be greatly offset by savings realized from WIPP disposal. Recent estimates of the total costs of processing by distillation the salt inventory at Rocky Flats are $71 million, compared to $103 million for disposal at WIPP with modified WIPP WAC, and $534 million with the current WIPP WAC.

Technology Transfer/Collaborations

After receipt and testing of new full-scale equipment, the technology and equipment will be transferred to supported by DOE/EM-60 personnel to conduct a processing campaign with residue salts at LANL.

Keywords

pyrochemical, salts, plutonium, distillation, separation

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TTP Number: AL16C321

Water-Soluble Chelating Polymers for Removal of Actinides from Wastewater

Presenter: Gordon Jarvinen, Los Alamos National Laboratory

EM Focus Area: facility transitioning, decommissioning, and final disposition; landfill stabilization

Task Description

Polymer filtration is a technology being developed to recover valuable or regulated metal ions selectively from process or wastewaters. Water-soluble chelating polymers are specially designed to bind selectively with metal ions in aqueous solutions. The polymers' molecular weight is large enough so they can be separated and concentrated using available ultrafiltration technology. Water and smaller unbound components of the solution pass freely through the ultrafiltration membrane. The polymers can then be reused by changing the solution conditions to release the metal ions, which are recovered in concentrated form, for recycle or disposal.

Advantages of polymer filtration relative to technology now in use are rapid binding kinetics, high selectivity, low energy and capital costs, and a small equipment footprint. Some potential commercial applications include electroplating rinse waters; photographic processing; cooling water in nuclear power plants; remediating contaminated soils and groundwater, removing mercury contamination; and producing textiles, paint, and dyes.

The purpose of this project is to evaluate this technology to remove plutonium, americium, and other regulated metal ions from various process and waste streams found in nuclear facilities. The work involves preparing the chelating water-soluble polymers; small-scale testing of the chelating polymer systems for the required solubility, ultrafiltration properties, selectivity and binding constants; and an engineering assessment at a larger scale for comparison to competing separation technologies. This project focuses on metal-ion contaminants in waste streams at the Plutonium Facility and the Waste Treatment Facility at both Los Alamos National Laboratory (LANL) and Rocky Flats. Potential applications at other DOE facilities are also apparent.

Technology Needs

Alternative technologies are needed to treat radioactive wastewater to meet regulatory limits, decrease disposal costs, and minimize waste. Currently, most DOE sites handle substantial volumes of dilute aqueous streams that must be treated before they are discharged to the environment.

In particular, this project addresses the need to replace precipitation methods that generate large volumes of radioactive sludge at LANL and other DOE sites and to reduce TRU wastes that will be generated from processing the large volume of plutonium-containing residues at DOE facilities.

Sludge handling and disposal is becoming more expensive as burial requirements increase and approved burial sites become less available. More stringent discharge regulations have been enacted by DOE, the Environmental Protection Agency (EPA), and the states in recent years that require considerably lower metal-ion concentrations in the effluent water from facilities such as the LANL Waste Treatment Facility. Precipitation technology cannot consistently meet current discharge limits for some metals. Even lower discharge limits are anticipated in the future. The longer-term goal of moving to closed-loop, zero-discharge systems for water handling will require new approaches and new combinations of technology.

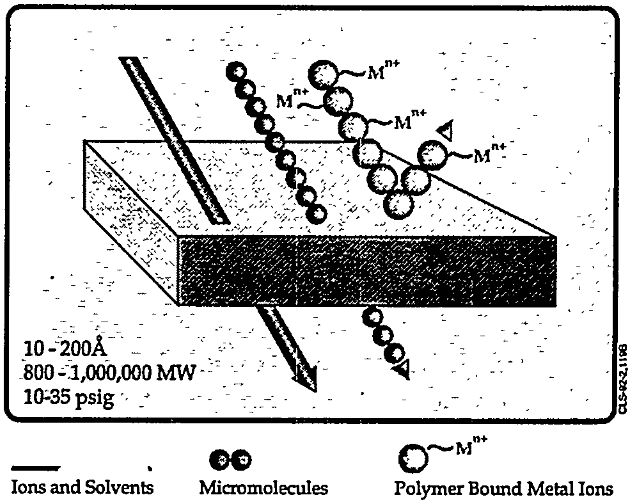
An important subset of the wastewaters of concern are mixed wastes that contain radioisotopes and toxic metals on the Resource Conservation and Recovery Act (RCRA) list. Treating the mixed waste to reduce the amount of toxic metals to levels below regulatory concern could generate a much smaller mixed-waste stream. These can be treated by other technologies that are better established from a regulatory viewpoint. Developing technology to treat mixed wastes is being driven at most DOE sites by schedules established in the various Federal Facility Compliance Agreements between EPA and DOE.

Scientific Background

Removing metal ions from aqueous solution is a major industrial activity covering processes ranging from water softening to "leaching" of metals from ores to detoxification of wastewater and contaminated natural water. The concept of attaching metal-ion-specific ligands to solid polymers is an important approach to solving such problems and has received considerable attention over the past 30 years. Separations involving transition metals have dominated the work in this area. Relatively little work has been done for the actinides and lanthanides, with the exception of a rather large body of work dealing with the use of chelating polymers to recover uranium from seawater. (The term chelate refers to a functional group that contains two or more binding sites for coordination with a metal ion.) Solid chelating polymers are the basis of a number of successful industrial separations including removing calcium to part-per-billion levels from brine and removing radioactive cesium from alkaline waters at nuclear power plants.

Applying *water-soluble* chelating polymers and ultrafiltration to the treatment of wastewater contaminated with low levels of radioactive and RCRA metal ions is a relatively new separations technology being developed at LANL. Bayer and coworkers at the University of Tübingen, Germany demonstrated in the 1980s that it is possible to selectively retain certain radioactive metals on water-soluble polymers, concentrate the metal-loaded polymer through ultrafiltration, and then recover the metals using either acid elution or electrodeposition processes.

The basis for metal-ion separation involves the retention of metal ions bound to the chelating groups of the water-soluble polymer while smaller unbound species and water pass freely through the ultrafiltration membrane (see figure). The *polymer filtration* process allows for the selective concentration of dilute solutions of metal ion contaminants. The reduced volume containing the polymer/metal-ion complex can go directly to disposal or the metal ions can be recovered by a stripping reaction and the polymer can be recycled for further metal-ion recovery. The advantage of this separation technology for dilute metal-ion solutions is its rapid kinetics, which result from the homogeneity of the process. In addition, by careful selection of the chelating functionality, selective metal-ion complexation can be obtained.



Metal ions bound to the chelating water-soluble polymer are retained by the ultrafiltration membrane; water and other small solute species pass freely through

Technical Approach

This project involves preparation of the chelating water-soluble polymers and small-scale testing of the chelating polymer systems for the required solubility, ultrafiltration properties, selectivity and binding constants followed by a large-scale engineering assessment for comparison to competing separation technologies. Reducing the concentration of a target metal ion to extremely low levels will require the water-soluble chelating polymer to have a high binding strength that can accomplish the desired separation. However, in the presence of other cations, the ligand will require a large selectivity for the target metal ion to overcome competition from other cations for the ligand binding sites. In many of the waste streams to be addressed, the target actinide ion is present in very low concentration relative to metals such as sodium, potassium, calcium, and magnesium. Phosphonic acid, hydroxamic acid, and acylpyrazolone groups have a demonstrated affinity for high-valent metal ions, such as the actinides, relative to low-valent metal ions such as magnesium, calcium, or sodium. Therefore, the water-soluble polymers prepared in this project have employed these functional groups.

A systematic series of water-soluble chelating polymers has been prepared in this project. Some of these polymers are based on commercially available polymer backbone structures, and some are prepared from monomer units by polymerization reactions. The polymer backbone has been functionalized with phosphonic acid, acylpyrazolone, and hydroxamic acid groups for the reasons described above. The polymers have been characterized for solubility, stability, and retention during ultrafiltration in the pH range 1 to 9. The polymers with the best characteristics are tested for metal binding properties.

Accomplishments

As described above, a series of water-soluble polymers functionalized with phosphonic acid, acylpyrazolone, and hydroxamic acid chelating groups have been prepared for evaluation. The polymers have been tested for metal ion retention at pH values from 1 to 6 and ionic strengths from 0.1 to 4.0 (sodium nitrate/nitric acid or sodium chloride/hydrochloric acid) with tracer amounts of americium and plutonium. The concentration of the polymer is generally about 1 wt%, and the solution is filtered through an ultrafiltration membrane with the appropriate molecular weight cutoff. To date, the phosphonic acid derivatives have shown the best properties for removing plutonium and americium in the target solutions. Therefore, the demonstration tests in FY 1996 will concentrate on using the phosphonic acid containing polymers.

The phosphonic acid polymers have been used in a series of polymer filtration runs with simulated and actual wastewater representing the average composition of a major wastewater stream treated at the LANL Waste Treatment Facility. The removal of americium was measured after the pH was adjusted to 4, and hydrofluoric acid was added to avoid silicate precipitation. Americium retention was high even though the solution contained a variety of other metal ions and anions in much higher concentrations, which could compete with the polymer binding sites. These include iron(II), copper(II), calcium(II), magnesium(II), zinc(II), nickel(II), fluoride, phosphate, nitrate, and chloride. Adding ferric nitrate showed that iron(III) did not significantly depress the americium binding until the iron level reached about 1500 ppm. The high retention values for americium indicate good selectivity for the target metal ion in the presence of a variety of potentially competing cations and anions commonly present in waste streams.

We have deployed a polymer filtration apparatus for tests on actual waste solutions in the Plutonium Facility at LANL. We tested the polymer filtration process on 7 L of wash solutions with an initial pH of 1.5. The water-soluble chelating polymer was added, and the pH was adjusted with potassium hydroxide to the range of 5 to 6. The final permeate volume was ~6.75 L and the retentate volume was ~0.25 L. The alpha activity due to plutonium and americium was reduced from 75,400 cpm/mL in the original solution to 333 cpm/mL in the permeate (well below the discard limits for the industrial waste line).

We also ran 10 L of nitric acid distillate (~1 N) from an evaporator being tested to recycle nitric acid. About 1 L of 10 N potassium hydroxide solution was added to neutralize the acid and give a final pH of 8 to 8.5. The final permeate volume was ~10.5 L and the retentate volume was ~0.5 L. Permeate rates were in the range of 1 L every 12 to 16 minutes. The alpha activity was reduced from 4288 cpm/mL to 97 cpm/mL. These are very encouraging results that are in agreement with our small-scale batch tests. A demonstration unit will be designed, built, and tested in FY 1996 on wastewater produced in LANL's Plutonium Facility.

Other LANL projects are evaluating the potential of using the polymer filtration technology for other applications. In May 1994, this separation technology was successfully demonstrated by a LANL team on a pilot scale for the recovery and recycle of nickel and zinc from 150 gallons of electroplating bath rinse waters at Boeing Aerospace in Seattle. This demonstration is part of an ongoing collaboration between Boeing and LANL,which is funded by the Office of Industrial Technology within DOE's Office of Energy Efficiency and Renewable Energy.

In September 1994, a workshop describing the polymer filtration technology was held for about 20 industrial firms that responded to a solicitation in the *Commerce Business Daily.* These companies were invited to submit commercialization proposals to LANL. Several companies are developing more detailed business plans for using the technology in different fields.

While application of the polymer filtration technology to electroplating operations is nearest to commercial deployment, we expect the prototype equipment that has been developed for these markets to be readily transferable to operations within the glove box environment at the LANL Plutonium Facility. Four patent applications were filed by LANL in May 1995 that cover a variety of polymer filtration applications including the removal of radioactive metal ions from wastewater streams.

Benefits

This technology can provide a cost-effective replacement for sludge-intensive precipitation treatments and yield effluents that meet increasingly stringent discharge requirements. At LANL, we are working to save millions of dollars in capital and operating costs for renovating the Waste Treatment Facility by using improved extraction technology to reduce greatly the transuranic content of waste streams from the Plutonium Facility.

The polymer filtration technology is one of the advanced extraction technologies under evaluation in this effort. Polymer filtration systems can also be used at Rocky Flats to address Interagency Agreement requirements to develop and evaluate radionuclide treatment technologies, including treatment of environmental surface waters. Applications for these systems at Idaho National Engineering Laboratory, Hanford, and other DOE facilities are also apparent.

We also see potential application for the water-soluble polymers to decontamination and decommissioning work. The polymer solution can be used to wash surfaces and remove contaminating metal ions. The metal ions would then be concentrated and recovered through the ultrafiltration operation and the polymer reused for further cleaning. Water-soluble polymers related to those prepared for this project have already shown promise for removing lead from soils at Superfund sites, and this work is proceeding to the demonstration phase. Other polymers have been developed for removing mercury contamination, controlling acid-mine-drainage, and removing technetium from groundwater. We are currently searching for demonstration sites for these applications.

Technology Transfer/Collaborations

Specific immediate customers for this technology are EM-30's Waste Treatment Facility at LANL and Defense Programs projects at LANL that cannot operate fully without the operations at the Waste Treatment Facility. The effort within EM-60 to stabilize residues and wastes at DOE facilities as a result of the Defense Nuclear Facility Safety Board's Recommendation 94-1 may also require this technology in the near term.

Potential commercial applications beyond electroplating and plutonium processing operations include water cleanup, silver recovery from photographic and jewelry processes, leaching of toxic metals from soils, and decontamination and decommissioning operations. We are pursuing a number of these opportunities with our industrial partners.

Keywords

actinides, plutonium, americium, transuranic waste, TRU, polymer filtration, ultrafiltration, mixed waste, chelating polymers, water-soluble polymers

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TTP Number: AL16C322

Advanced Integrated Solvent Extraction and Ion Exchange Systems

Presenter: Phil Horwitz, Argonne National Laboratory

EM Focus Area: high-level waste tank remediation

Task Description

Advanced integrated solvent extraction (SX) and ion exchange (IX) systems are a series of novel SX and IX processes that extract and recover uranium and transuranics (TRUs) (neptunium, plutonium, americium) and fission products ^{90}Sr, ^{99}Tc, and ^{137}Cs from acidic high-level liquid waste and that sorb and recover ^{90}Sr, ^{99}Tc, and ^{137}Cs from alkaline supernatant high-level liquid waste. Each system is based on the use of new selective liquid extractants or chromatographic materials. The purpose of the integrated SX and IX processes is to minimize the quantity of waste that must be vitrified and buried in a deep geologic repository by producing raffinates (from SX) and effluent streams (from IX) that will meet the specifications of Class A low-level waste.

The first objective of the program involves development and testing of a new technetium selective resin (ABEC-5000) and a new cesium-strontium selective resin (Diphonix-CS) that should have applicability for removing technetium, cesium, and strontium from the highly alkaline supernatant liquid in the single- and double-shell storage tanks at Hanford. Studies will involve the measurement of the influence of major constituents and radiolysis on the uptake and recovery of technetium by the ABEC-5000 resin and on the uptake and recovery of cesium and strontium by the Diphonix-CS resin. After completion of these initial characterization studies, the two resins will be tested in a column mode using simulated alkaline waste. Figure 1 depicts the Advanced Integrated IX Systems in individual columns or in a mixed-bed mode.

The second major task is to develop an advanced acid-side SX process that will remove in one step ^{90}Sr, ^{99}Tc, ^{137}Cs, and TRUs from acidic high-level waste (HLW). Lanthanides would also be extracted together with TRUs. The process is called TOREX (for total radionuclide extraction) and is based on the use of a mixture of strontium-, cesium-, and TRU-(technetium) selective extractants in a novel combined phase modifier-diluent reagent (Figure 2).

The TOREX process is designed to remove the desired radioisotopes at high nitric acid concentration and achieve recoveries at low acid concentrations. Selective stripping of strontium and cesium from TRUs and technetium is possible. The major advantage in performing a TOREX-type process is the significant reduction in the size of the processing facility to pretreat HLW. Studies in FY 1996 will focus on developing and batch testing the TOREX process solvent.

The second part of the advanced integrated SX program is continuation of the development of a front-end combined CSEX-SREX process. Proof-of-principle studies were carried out in FY 1995. FY 1996 studies will involve the hot testing of the process in a continuous countercurrent solvent extraction mode using Argonne National Laboratory (ANL) centrifugal contactors.

Technology Needs

The advanced integrated solvent extraction and ion exchange systems could be applied to the chemical pretreatment of waste retrieved from storage tanks at DOE defense sites (e.g., at Idaho National Engineering Laboratory, Hanford, Savannah River). The objective of these processes is to minimize the amount of waste that must be vitrified by reducing the level of alpha activity and reducing the concentrations of ^{90}Sr, ^{99}Tc, and ^{137}Cs in the dissolved high-level sludge waste and ^{90}Sr, ^{99}Tc, and ^{137}Cs in the alkaline supernatant HLW.

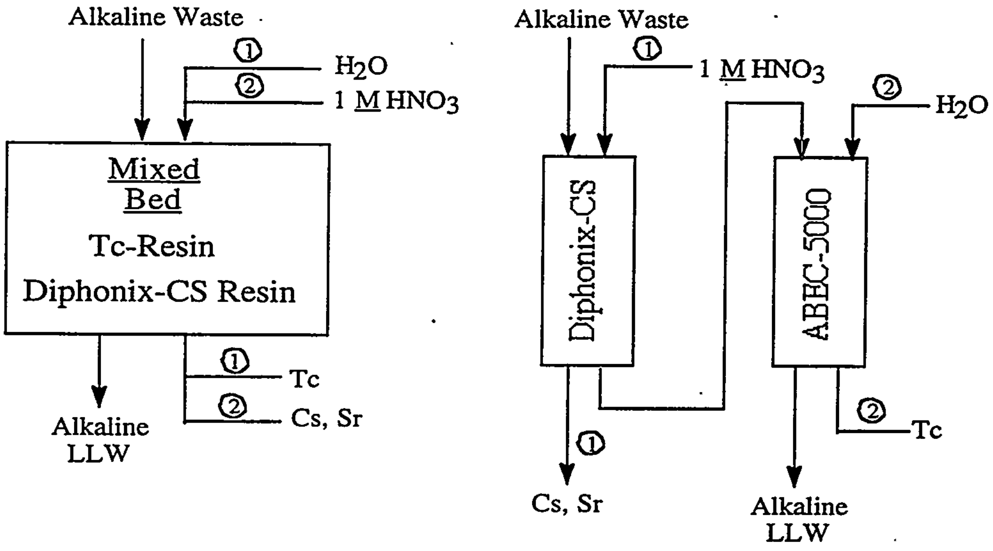

Figure 1. Advanced Integrated IX Systems

Scientific Background

During the last 2 years, members of the Chemical Separations Group, Chemistry Division, ANL, in collaboration with Professor Robin Rogers, Northern Illinois University (NIU), DeKalb, Illinois, and Professor Spiro Alexandratos, University of Tennessee, Knoxville, have made significant progress in developing new resins that may apply to alkaline waste treatment. The NIU/ANL team has developed a new resin that shows high efficiency for the uptake of pertechnetate ions ($D_{Tc} = 10^2$ to 10^3) from high concentrations of salt solutions including sodium hydroxide. Elution of the pertechnetate salt can be achieved using water or dilute nitric acid. Additional studies are needed to adapt and test this new resin for removing ^{99}Tc from the alkaline supernatant solution in the Hanford single- and double-shell storage tanks.

The UT/ANL team has under development a new ion exchange resin belonging to the Diphonix family that has the capability of removing both cesium and strontium from moderate to concentrated sodium hydroxide solutions. The new resin, called Diphonix-CS, can removing both cesium and strontium simultaneously.

Concurrent with the development of new resins for alkaline-side waste treatment, we have made significant advances in the development of an acid-side SX system for cesium and strontium extraction and recovery. The combination of a large ionic radius and low charge makes the selective extraction of cesium and strontium from highly acidic nitrate media difficult. Nevertheless, by exploiting the principles of molecular recognition and solvation effects, we have developed cesium and strontium extractants that can be combined in a plutonium-uranium extraction (PUREX) -like system that can selectively extract cesium and strontium from highly acidic nitrate media. Both cesium and strontium are readily recovered using dilute nitric acid. This combined CSEX-SREX system has been tested in a batch countercurrent mode in FY 1995. Acidic waste simultant from Lockheed Idaho Technology Company (LITCO) was used for the test and results were very favorable. Advantages of a combined CSEX-SREX extraction process at the beginning of a pretreatment sequence include removal of all the major gamma emitters and the need for considerably less shielding in all subsequent processing.

An even larger savings in cost could be achieved if all the major radioisotopes that create problems in waste management, namely, ^{90}Sr, ^{99}Tc, ^{137}Cs, and TRUs, could be isolated in a single process. The TOREX process would involve the use of individual cesium, strontium, and TRU extractants. (The TRU extractant also extracts technetium.) Each extractant would have to be present in a relatively low concentration; for example, <0.20 *M*, to allow sufficient room for the phase modifier and diluent. The former is needed to reduce third-phase formation and the latter to reduce viscosity. We have found that lauryl nitrile can serve as both a phase modifier and a diluent. This observation increases the likelihood that a TOREX process is feasible.

Accomplishments

The Combined CSEX/SREX Process for the simultaneous extraction of cesium and strontium from acidic nitrate media has been successfully batch tested in a countercurrent mode using a dissolved calcine waste simulant from LITCO. The process uses a solvent formulation comprised of 0.05 *M* di-t-butylcyclohexano-18-crown-6, 0.1 *M* Crown 100' (a proprietary cesium selective macrocyclic polyether), 1.2 *M* tri-n-butylphosphate, and 5% (n/n) lauryl nitrile in an isoparaffinic hydrocarbon diluent. The countercurrent test run indicates that >98% of the cesium and strontium initially present in the feed solution can be removed in only four extraction stages. Both cesium and strontium are readily recovered by stripping the process solvent with 0.1 *M* HNO_3.

Considerable progress has been made to date on the synthesis and characterization of both ABEC-5000 and Diphonix-CS resins. The ABEC-5000 resin has been evaluated for technetium uptake as a function of sodium hydroxide concentration and as a function of sodium nitrate, nitrite, carbonate, aluminate, and citrate concentration in 2 and 4 *M* NaOH. The distribution ratios of technetium are in the range of 10^2 to 10^3 and are very insensitive to the above list of anions over a wide range of concentrations. Technetium uptake measurements with simulated 101-SY, neutralized current acid waste, and single-shell tank waste solutions have also been made. The dry weight D_{Tc} is in the 1 x 10^2 to 2 x 10^2 range with all three waste solutions. Elution of technetium from packed bed with H_2O has also been demonstrated.

Benefits

The anticipated benefit of the advanced integrated solvent extraction and ion exchange systems is the minimization of high-level waste that must be vitrified and buried in a deep geologic repository and the recovery of valuable TRUs (e.g., ^{237}Np), uranium, ^{90}Sr, ^{99}Tc, and ^{137}Cs that could have beneficial uses. The advanced integrated solvent extraction and ion

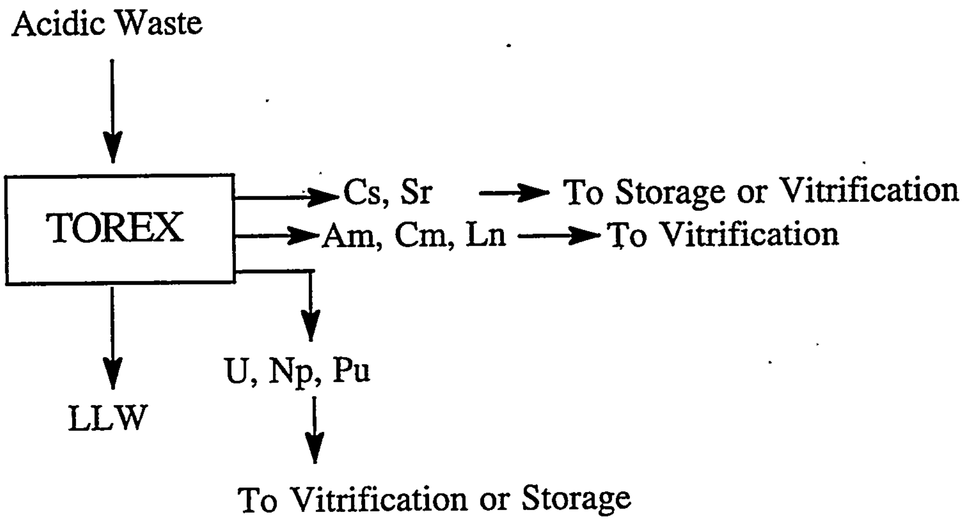

Figure 2. Total Radionuclide Extraction (TOREX) Process Systems

exchange systems should also reduce the cost of chemical pretreatment of waste by reducing the amount of equipment and size of the processing facility.

Keywords

Solvent extraction, ion exchange, high-level waste, TRUs, ^{90}Sr, ^{99}Tc, ^{137}Cs

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TTP Number CH26C321

Thermally Unstable Complexants/ Phosphate Mineralization of Actinides

Presenter: Ken Nash, Argonne National Laboratory

EM Focus Area: contaminant plume containment and remediation

Task Description

In situ immobilization is an approach to isolation of radionuclides from the hydrosphere that is receiving increasing attention. Rather than removing the actinides from contaminated soils, this approach transforms the actinides into intrinsically insoluble mineral phases resistant to leaching by groundwater. The principal advantages of this concept are the low cost and low risk of operator exposure and/or dispersion of the radionuclides to the wider environment. The challenge of this approach is to accomplish the immobilization without causing collateral damage to the environment (the cure shouldn't be worse than the disease) and verification of system performance.

This task involves the measured addition of a reagent designed to generate a precipitant in the groundwater or soil in a manner that is most favorable for the formation of thermodynamically stable insoluble mineral phases. The reagent must be compatible with the groundwater and soil, potentially using groundwater/soil components to aid in the immobilization process. The delivery system should first concentrate the radionuclides, removing them from the groundwater flow by a cation exchange process, then release the precipitating anion, which forms thermodynamically stable mineral phases. The most promising means of delivering the precipitant would be to use a water-soluble, hydrolytically unstable complexant that functions in the initial stages as a cation exchanger to concentrate the metal ions. As it decomposes, the chelating agent releases an inorganic precipitant and crystalline mineral phases are formed.

Technology Needs

The mineralization concept can potentially immobilize radioactive metal ions in the environment. It is a safe, simple, and inexpensive alternative to pump-and-treat methods for groundwater decontamination or the installation of massive barriers to prevent nuclide migration (in situ grouting). Alternatively, it could be applied as a finishing step following the removal of most of the radionuclides from the site. The process could be applied to waste disposal sites (used either before or after burial) like Hanford and Idaho National Engineering Laboratory, areas of accidental environmental contamination (Fernald, Rocky Flats), or even to commercial mill tailings piles.

Scientific Background

Unplanned releases and direct discharges have contaminated soils and waters at many DOE sites. Planned disposal of materials contaminated with radionuclides also accounts for a significant portion of the radionuclides in the subsurface environment. Several mechanisms exist for the dispersal of the contaminants to the wider environment. For those materials possessing appreciable water solubility, serious contamination of the local environment may occur through surface water runoff and percolation through underlying geologic strata. This pathway represents a potential direct route for invasion of the biosphere by radioactive metal ions. Among the long-lived radioactive materials, the transuranic actinides are acknowledged to represent the greatest long-term hazard.

Most of the radionuclides in the buried waste disposal trenches are sorbed on surfaces. These surfaces are usually metallic, organic (paper and plastic), or mineral in nature. The surrounding geologic strata provide additional surface sorption opportunities. The chemical form of the sorbed radionuclides is extremely variable ranging from rather intransigent oxide films to potentially soluble metal nitrate residues. The latter species in particular are susceptible to mobilization when in contact with natural waters. Natural chelating agents like humic and fulvic acids, which are present at low concentration in most groundwater, can facilitate environmental migration of heavy metals even when present in moderately insoluble forms. The potential for migration to the surrounding environment would be greatly decreased if the metal ions were converted to much more insoluble thermodynamically stable forms.

For the actinides, thermodynamic calculations and observation of the natural world suggest that phosphate may be the ideal medium for in situ immobilization. The existence of major deposits of rare-earths, thorium, and uranium in monazite sands in the subtropical environment represented by central Florida is nature's testimony to the stability of this mineral phase. Thermodynamic calculations based on the best available data further supports the low solubility of f element phosphates. Conversion of surface-sorbed actinide ions into thermodynamically stable mineral phases will decrease the tendency of the nuclides to be transported by groundwater and simultaneously improve the predictability of such movement by thermodynamic models.

Technical Approach

The task has as its objectives 1) identification of a hydrolytically unstable organophosphorus complexant and demonstration of its decomposition of under representative groundwater conditions of E_h and pH, 2) demonstration of the formation of crystalline actinide phosphate solids under these conditions, 3) determination of the leachability of actinides from the phosphate solids, and 4) testing with representative geomedia and synthesized analogs. Verification of reduced "solubility" (not thermodynamic solubility products, but actual radionuclide concentrations) of actinide ions in the III, IV, V, and VI oxidation states as a function of pH and phosphate concentration is a primary goal. Ultimately, the concept could be developed to treat various mill-tailings piles in addition to those media contaminated with transuranics.

Accomplishments

As initially conceived, this program was to rely on the class of compounds called Thermally Unstable Complexants (TUCS). These ligands, diphosphonic acid chelating agents designed to spontaneously decompose under suitable conditions, proved too robust for the purpose under environmental conditions. The organophosphate complexing agent phytic acid (Figure 1) (myo-inositol(hexakisphosphoric acid)) was then identified as a potential substitute for the phosphonate chelating agents. Phytic acid has much better characteristics for the design objective than the phosphonate TUCS compounds. It is a natural product, forms insoluble salts with polyvalent cations (Ca^{2+}, for example) thus potentially serving as a cation exchanger, is known to be readily hydrolyzed releasing phosphate, and the organic residue (inositol) does not complex metal ions and hence will not interfere with the mineralization process.

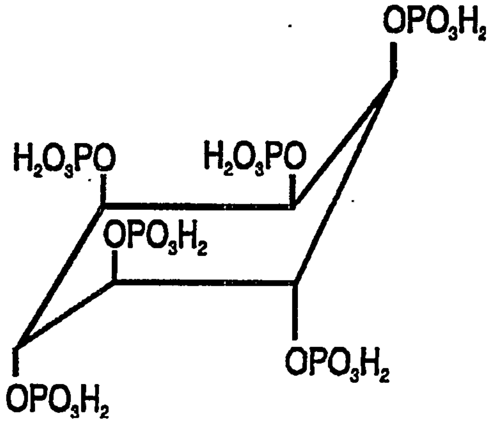

Figure 1. Structure of the organophosphate complexing agent phytic acid.

The rate of production of phosphate from phytate as a function of temperature and pH has been investigated using spectrophotometric techniques and NMR spectroscopy. Independent of the starting pH, all systems tend toward a final pH of 6, buffered by the NaH_2PO_4/Na_2HPO_4 hydrolysis product. NMR spectroscopy indicates inositol as the major immediate organic product. No evidence was found for significant buildup of intermediate inositol(phosphate) species $(I(PO_4H_2)_{6-x})$. Extrapolation of the rate parameters using the Arrhenius relationship at pH 5 and 6 gives the lifetime for phytate 104 ± 22 years at pH 5.1 and 156 ± 42 years at pH 6.0. Literature reports indicate that microbiological effects can shorten this lifetime by orders of magnitude. Other reports have implicated polyvalent metal ions in accelerated phytate hydrolysis. The lifetime of phytic acid in the environment becomes immaterial if it functions in the intermediate term as an effective cation exchange medium.

Crystalline lanthanide ($EuPO_4$ and $EuPO_4 \cdot 1/2\ H_2O$) and uranyl phosphate ($(UO_2)_3(PO_4)_2$) solids have been identified in pH 1-5 phosphate media and further demonstrated to exist as a result of the hydrolysis of lanthanide and uranyl phytates. Results for thorium (as representative of the tetravalent actinides) indicated no evidence for the formation of crystalline thorium phosphates, though the existence of amorphous thorium phosphates cannot be ruled out. Weak $Th(OH)_4/ThO_2$ lines appear in the X-ray powder diffraction pattern indicating that these species may control the solubility of thorium.

The "solubility" of europium, uranyl, and neptunium(V) as a function of pH and phosphate concentration in a synthetic groundwater solution ($I = 0.1\ M$, $[NaHCO_3] = 0.5$ mM) has been determined in a series of experiments using radiotracers. Solid films of metal nitrates, hydroxides, citrates, and TRUEX process solvent solutions were deposited on glass surfaces and contacted with the synthetic groundwater solutions. In both the europium and uranyl systems, the concentration of the radionuclide in the synthetic groundwater was controlled by phosphate even at 0.1 mM total phosphate. Europium concentrations were less than $2 \times 10^{-9}\ M$ even at the lowest phosphate concentration. Uranyl concentrations were below $2 \times 10^{-7}\ M$ in the presence of phosphate with concentrations decreasing at higher pH. Each of these solubility limits is at least 10 times lower than that observed in the absence of phosphate and generally consistent with thermodynamic calculations. NpO_2^+ concentrations were not appreciably affected by phosphate except at $[PO_4]_t > 1.0$ mM and at pH 7-8. Under these conditions, neptunium solubility is controlled at about $10^{-6}\ M$. Ongoing experiments are investigating the effect of coprecipitation on $[NpO_2^+]$ in solution.

Benefits

Because it involves only the application of inexpensive reagents, phosphate mineralization promises to be an economical alternative for in situ immobilization of radionuclides (actinides in particular). The method relies on the inherent (thermodynamic) stability of actinide mineral phases. This has the dual benefit of reduced radionuclide solubility, and predictability based on the application of thermodynamic models for performance verification. In situ immobilization eliminates the need for excavation, thus reducing the risk of operator contamination and airborne dispersion of radionuclides to the surrounding environment.

The principal benefits to be derived from the demonstration of this process are the elimination of the need for pumping of groundwater or excavation of soils to maximize the environmental (geochemical) stability of radionuclides in buried wastes. Immobilization of radionuclides in the subsurface environment can be accomplished by this method at low cost and without the construction of massive barriers to restrict groundwater flow. Because thermodynamically stable actinide phosphates are formed, accurate prediction of the potential for radionuclide migration will be possible via thermodynamics-based geochemical models. The concept also has potential for commercial development as a means of immobilizing radioactive elements in uranium or thorium mill tailings piles, or for the stabilization of nonradioactive heavy metals in mill-tailings piles resulting from surface mining activities to recover strategic metals.

Keywords

mineralization, actinides, phosphate, groundwater, in situ treatment, environment remediation.

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TTP Number: CH26C322

Selective Sorption of Technetium from Groundwater

Presenter: Gilbert Brown, Oak Ridge National Laboratory[1]

EM Focus Area: contaminant plume containment and remediation

Task Description

The purpose of this project is to develop an anion exchange resin that will selectively remove the radionuclide technetium, in the form of the pertechnetate anion (TcO_4^-), from groundwater, leaving behind other interfering anions. A resin bed of this material will be used either as part of a coupled treatment-recirculation system for the in situ remediation of groundwater contaminated with technetium or in a once-through treatment scheme.

The pertechnetate anion is strongly adsorbed on commercially available strong base ion exchange resins, but in view of the low (nanomolar) concentration of technetium involved, enhanced selectivity for the pertechnetate anion over other anions commonly found in groundwater such as chloride, sulfate, and nitrate will be needed. We are preparing and evaluating new anion exchange resins that will be selective for pertechnetate.

Technology Needs

Groundwater at DOE's Paducah and Portsmouth sites is contaminated by radionuclides. Technetium is the principal radioactive metal ion contaminant to be removed, and it is present at a concentration of about 25 ng/L. The principal form of the element technetium in oxygenated groundwater is the TcO_4^- anion, and this species is water soluble and quite mobile in underground aquifers.

A related problem exists at other DOE sites where the processing of uranium or plutonium resulted in the release of technetium to the surrounding groundwater. Commercially available anion exchange resins can remove TcO_4^- ion in the presence of typical anions found in groundwater, but improving selectivity will result in substantial cost savings.

Scientific Background

Strong base anion exchange resins can remove TcO_4^- ion with varying degrees of selectivity from waste streams containing an excess of other competing anions. Schroeder et al.[1] have demonstrated that Reillex™ HPQ was effective in removing pertechnetate from tank waste simulants that have high concentrations of nitrate ion. Del Cul et al.[2] have shown that Dowex™ 1-X8 resin was effective in removing pertechnetate in the presence of typical anions found in groundwater at Paducah.

Other schemes have been proposed for removing technetium from groundwater. One method under examination will reduce the technetium to a lower oxidation state that is insoluble or that precipitates from solution. This method may not be effective if oxygen in the aquifer or from other sources can oxidize the technetium back to the soluble TcO_4^- ion. Use of a resin to sorb the anion will have advantages over reductive schemes if the resin can be made selective. Air stripping is the currently favored technology to remove trichloroethylene and other volatile organic compounds from groundwater, and this process necessarily puts a high concentration of oxygen in the aquifer.

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[1] Managed by Lockheed Martin Energy Research Corp., for the U.S. Department of Energy under contract DE-AC05-96OR22694.

We are developing resins to selectively sorb technetium from groundwater that can be used with a remediation scheme involving recirculation of the water through a decontamination station within the aquifer. These resins will also be effective with once-through treatment schemes such as that being demonstrated at Paducah.

Technical Approach

The pertechnetate anion has a high affinity for strong base anion exchange resins such as those made from quaternary amines. Most commercially available strong base resins are not as selective for TcO_4^- over chloride, sulfate, or nitrate ion as is desirable. These latter anions can be present in the groundwater at a concentration of 10^6 times greater than pertechnetate. We are designing and developing resins that are highly selective for the TcO_4^- anion. After saturation, the resin bed can be taken to the surface and chemically treated to strip or remove the technetium. The cleaned resin can then be returned to the treatment module to process more groundwater. Thus an integral part of this work is the development of effective resin regeneration methods.

The microenvironment of the exchange sites within the resin is expected to play a major role in ionic selectivity, and we began synthesizing a new series of resins in which the properties of the resin were systematically varied. These resins were part of a program to modify the microenvironment of the exchange sites and to thus change the selectivity for pertechnetate ion over the other anions commonly found in groundwater.

This systematic study of the effects of changes in the microenvironment of the exchange site on selectivity of pertechnetate ion sorption provides the scientific basis for understanding which parameters have the most influence on selectivity. In addition, this information allows us to zero in on several classes of resins for further fine tuning of selectivity. The iterative process of resin synthesis, evaluation of technetium selectivity, and further resin synthesis in a close collaboration allowed us to rapidly converge on a resin with superior selectivity for the pertechnetate ion.

Accomplishments

We synthesized and studied a series of resins in which the properties of the resin were systematically varied.[3] We prepared 64 synthetic resins that were tested along with seven commercial resins for sorption of pertechnetate from a groundwater test solution under 24-h batch equilibrium conditions. Our objective in FY 1995 was to prepare resins that would possess higher selectivity for pertechnetate over other anions as compared with existing (commercially available) resins while maintaining good capacity, and we were successful. As shown in Table 1, we have prepared resins that have higher distribution ratios for pertechnetate both on a weight basis (K'_d) and per exchange site ($K'_d(eq)$), the latter being a better indication of selectivity. The best synthetic resin with regard to overall performance has a pertechnetate distribution ratio (K'_d) of 41,700 mL/g, twice that of the best commercially available resin.

We applied our knowledge of the properties of existing anion exchange resins in making both the chemical and physical modifications necessary to improve both the K'_d and the $K'_d(eq)$ for pertechnetate. Some of these new resins may be patentable; therefore, we will not disclose details here about their chemical and physical nature or discuss what chemical and physical properties improve pertechnetate selectivity. Such details will be forthcoming after patent issues are resolved.

The ability to remove pertechnetate from the resins, thereby regenerating the resins, has been demonstrated using a method described by Norm Schroeder and coworkers at Los Alamos National Laboratory.[1] However, we have observed that the microenvironment of the exchange sites of the resin determines the amount of time necessary to elute the technetium. In batch equilibrium tests with one of our best resins, exposure overnight to the stripping solution was required before technetium elution was observed.

Table 1. Sorption results for pertechnetate from groundwater test solution (24-h equilibration times) for selected synthetic and commercial anion exchange resins, with values of K'_d in descending order. Uncertainties are 5%.

Resin	Total Anion Exchange Capacity (meq/g)	K'_d (mL/g)	K'_d(eq) (mL/meq)	Manufacturer
VP02-165	2.13	41,700	19,600	Synthetic
VP02-122	1.76	34,500	19,600	Synthetic
Sybron Ionac® SR-6	1.80	20,700	11,500	Sybron Chemicals
Purolite® A-520E	2.80	11,300	4040	Purolite
Amberlite® IRA-904	2.49	7600	3050	Rohm and Haas
Reillex™ HPQ	3.30	4500	1360	Reilley

Benefits

While commercially available strong base anion exchange resins are effective in removing pertechnetate from groundwater, improvements in selectivity can result in substantial cost savings. The use of exchangeable resin modules is expected to lead to a low maintenance easily cared-for technology for technetium removal.

Technology Transfer/Collaborators

University of Tennessee, Knoxville.

Expected Progress

Further improvements can be made to our best candidate resins to increase both the K'_d, K'_d(eq), and especially the kinetic behavior. In the first few months of FY 1996, we will finalize the resin synthesis and development portion of this project and begin testing the best candidate resins under flow-through column conditions using first more realistic groundwater simulants and then using actual technetium-contaminated groundwater (available from Paducah).

As only equilibrium selectivity has been investigated to date, we plan in FY 1996 to determine selectivity under conditions of solution flow in a column where mass transport issues become important. In addition, we plan to test our best candidate resins under actual flow-through conditions in the ground by pumping non-contaminated groundwater through the resins for a month or more (at Portsmouth) to investigate the stability of the resins to breakdown, fouling, and degradation by the environment (e.g., attack by microorganisms, etc.). Following this test we will include our best resins in a small field demonstration using technetium-contaminated groundwater designed to generate data for scale-up to a larger field demonstration project. We want to include our optimum resin in demonstration projects at both Portsmouth and Paducah in FY 1997.

Finally, we will continue to investigate ways to improve the completeness and kinetics of the regeneration procedure (tin(II)-based stripping procedure) for the resin because the ability to reuse the resin is an integral part of an economically feasible process.

Keywords

anion exchange, groundwater, ion exchange, pertechnetate, plume, resin, selective, technetium

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Solvent Extraction of Radionuclides from Aqueous Tank Waste

Presenters: Peter Bonnesen, Richard Sachleben, and Bruce Moyer, Oak Ridge National Laboratory[1]

EM Focus Area: high-level waste tank remediation

Task Description

The purpose of this task is to develop an efficient solvent-extraction and stripping process to remove the fission products ^{99}Tc, ^{90}Sr, and ^{137}Cs from alkaline tank wastes, such as those stored at Hanford and Oak Ridge. As such, this task expands on FY 1995's successful development of a solvent-extraction and stripping process for technetium separation from alkaline tank-waste solutions. This process now includes the capability of removing both technetium and strontium simultaneously. In this form, the process has been named SRTALK and will be developed further in this program as a prelude to developing a system capable of removing technetium, strontium, and cesium.

Such a system could potentially simplify and improve fission-product removal from tank waste. In addition, it would possess advantages already inherent in our technetium solvent-extraction process: no required feed adjustment, economical water stripping, low consumption of materials, and low waste volume.

Technology Needs

Efficient processes for the removal of technetium, strontium, and cesium from highly radioactive waste are priority needs of the ESP, the Tank Focus Area (TFA) program, and the Tank Waste Remediation System (TWRS) program. How to safely dispose of the large volumes of radioactive wastes stored in underground tanks is one of the largest problems facing DOE. The general goal being pursued is overall cost savings through both reducing the volume of waste that must be committed to a geologic repository and minimizing secondary waste streams.

Several promising technologies as separate unit operations have been under development in DOE programs to remove technetium, strontium, and cesium from alkaline tank supernate. These technologies would presumably be employed in series and would each entail separate process requirements, consumption of materials, effluent streams, stripping (if applicable), and impacts on vitrification.

Although the emerging technologies individually remove their target contaminants effectively, there may be compelling advantages to a single extractant that could remove technetium, strontium, and cesium together and transfer them to water, which can then be simply evaporated to produce a miniscule effluent volume. The overall process would be simpler in that a single technology is involved, and the space requirements could significantly shrink. Chemical consumption and new waste production would be minimal, limited essentially to replacement of extractant. Stripping would be accomplished with water, allowing the high-level effluent to be reduced to a minimal volume in a simple manner and leading to little chemical impact on vitrification processing.

Scientific Background

As depicted in the figure, our technetium extraction process occurs by extraction of an ion pair, where the crown ether binds the cation to form a large, hydrophobic cation. As in anion-exchange processes,

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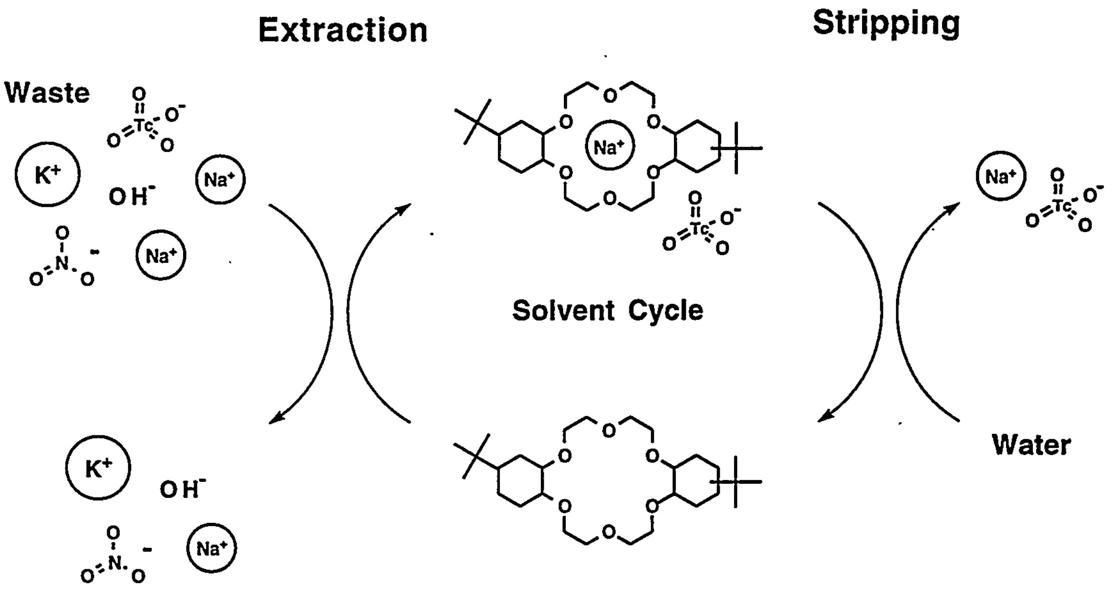
[1] Managed by Lockheed Martin Energy Research Corp., for the U.S. Department of Energy under contract DE-AC05-96OR22694.



the preferred counter-anion generally corresponds to the one having the lowest hydration energy. Pertechnetate anion possesses the lowest hydration energy among the major anions, such as nitrate, in the tank supernate and is thus selected. Typical TcO_4^-/NO_3^- selectivities exceed 10^3.

Of the commercial crown ethers, 4,4',(5')-di-t-butyldicyclohexane-18-crown-6 performs most effectively in extraction from alkaline sodium nitrate solutions. Concentrations ranging from 0.01 to 0.05 *M* in the solvent yield technetium distribution coefficients in the useful range of 1 to 10. Under these conditions, essentially complete stripping occurs in two or three water washes. We have found that TBP in kerosene (Isopar® M preferred) at ratios of 1:1 to 2:1 perform effectively.

Our process depends on the extraction of technetium in the heptavalent state. Ordinarily, the standard reduction potentials favor this state in alkaline solutions exposed to air. Recent results by Norm Schroeder at Los Alamos National Laboratory (LANL) have shown that the Hanford complexant concentrate (CC) contains a significant fraction of technetium in a form not extractable as pertechnetate. Although this result is likely applicable only to the special case of CC waste, where chelating agents can stabilize lower oxidation states, the state of technetium in other Hanford tanks should be investigated.

The chemical literature provides many examples of solvent extraction of alkali and alkaline-earth metal ions by crown ethers. In particular, systems selective for cesium and strontium have been reported, though their applicability for decontamination of alkaline waste has not been demonstrated.

The SREX process developed by Phil Horwitz's group at Argonne National Laboratory (ANL) is an excellent example of application of crown ethers for strontium (and technetium) decontamination of acidic waste solutions using solvent extraction. The crown ether employed in SREX, 4,4',(5')-di-t-butyldicyclohexane-18-crown-6, is the same crown ether we have found to be the most effective for technetium on the alkaline side. The commercial product is a mixture of isomers whose abilities to bind and extract Sr^{2+} ions vary considerably. Aided by molecular-mechanics calculations performed by Ben Hay at Pacific Northwest National Laboratory (PNNL), Horwitz's group has been identifying the most effective isomer, leading to continued improvements in the commercial product marketed by Eichrom Industries.

Technical Approach

Tank wastes at the Hanford Site and elsewhere (e.g., Melton Valley Storage Tanks at Oak Ridge) are typically strongly alkaline and contain technetium, strontium, cesium, and other radioactive contaminants. In proposed treatment processes, these contaminants may be found in the aqueous supernates, or may be solubilized from the sludge during sludge washing or leaching. Because these aqueous streams will contain complicated and variable mixtures of salts, highly efficient separation methods are needed.

Whereas it has been commonly thought that applicable separation methods must also be extremely selective, this work addresses the question of making a practical *group* selection for technetium, strontium, and cesium. Such a disparate trio of elements would ordinarily seem to have little chance of simultaneous extraction, but our tests (see below) together with available literature (see above) reveal that crown ethers may well offer this ability.

Because of its high selectivity and good mass-transfer properties, solvent extraction is a potentially attractive vehicle for combined technetium, strontium, and cesium removal from tank waste. The high ionic strength of the feed promotes good phase separation and minimizes (by "salting out") the solubility of organic solvent components in the aqueous phase. Centrifugal contactors should provide efficient recycle of the solvent, minimizing inventory requirements, solvent entrainment losses, and solvent radiation degradation. Solvent extraction has proven to be effective in many nuclear separations, establishing a good foundation for application to tank waste.

In FY 1996 we plan to develop the process flowsheet for the solvent extraction of technetium from alkaline supernatant and water stripping as needed by potential users. For example, PNNL has proposed to test the process on simulated and actual Hanford supernatant in 2-cm centrifugal contactors. We plan to continue investigating appropriate extractants, diluents, and modifiers for the combined extraction of technetium, strontium, and cesium. Key issues are achieving high extraction and stripping ratios for *all* of these, as some factors that enhance cesium extraction might suppress technetium stripping. This may additionally involve some combined effort with optimizing cesium and strontium extractants.

First, we will define a workable solvent, then we will begin process cycle development and seek ways to optimize the process. Intermediate stages will include demonstration of processes capable of combined technetium and strontium (SRTALK) extraction and combined cesium and technetium extraction from alkaline tank supernate (see figure).

Accomplishments

Technetium Alone. A solvent-extraction and stripping process has been defined for removing technetium from alkaline tank waste. A patent covering this process was issued, and we have refined the process to include an anion-exchange method for removing and concentrating technetium from the stripping water, so that the stripping water can be recycled back into the process.

A highly effective solvent for the process contains 4,4',(5')-di-t-butyldicyclohexane-18-crown-6 dissolved in TBP-modified isoparaffinic kerosene. The solvent has been tested on actual tank waste from ORNL's Melton Valley (MVST); performance was equivalent to that obtained with waste simulants. Extraction and stripping efficiencies of 98% or better are attainable with two-stage extraction and two-stage stripping at unit phase ratio using waste simulants.

Technetium/Strontium. The SRTALK process is under development to simultaneously extract technetium and strontium from alkaline tank-waste supernate. Results using a MVST simulant have shown that combined extraction and stripping efficiencies of

96% and 99% for technetium, respectively, and 62% and >99% for strontium, are attainable with two-stage extraction and two-stage stripping at unit phase ratio. Work toward increasing the extraction efficiency for strontium has produced excellent results from simple alkaline sodium nitrate solutions.

Cesium and Technetium/Cesium. Results to date reveal cesium extraction and stripping efficiencies from actual MVST W-29 waste of 89% and >99%, respectively, following four equal-volume cross-current extraction contacts, and four equal-volume cross-current stripping contacts using only water. Combined technetium and cesium extraction and stripping results from MVST W-29 simulant have shown that combined extraction and stripping efficiencies of respectively 96% and 83% for technetium, and 37% and 93% for cesium, are attainable with two-stage extraction and two-stage stripping at unit phase ratio.

Benefits

The TFA and TWRS will receive the primary benefit from this program. By removing and concentrating fission products directly from tank waste, increased safety and effectiveness in processing tank wastes, and large cost savings will be obtained because of reducing the high-level waste volume that must be committed to a geologic repository.

Compared with a sequence of three fixed-bed technologies, a combined technetium, strontium, and cesium extraction process could simplify processing and reduce space requirements. An effluent of these contaminants in only water allows manyfold concentration by simple evaporation or sorption onto known solid materials.

The proposed technology offers the following major advantages: 1) direct treatability of the waste; 2) safe, economical, and efficient stripping using only water; 3) no additions of chemicals to the extraction or stripping cycle; and 4) use of diluents with high flash point, low toxicity, and low water solubility.

Technology Transfer/Collaborators

Industrial partners will be needed to supply crown ethers and other extractants in large quantities at reasonable cost. Eichrom Industries has a proven record in the production and sale of a key crown ether for solvent extraction of strontium and technetium. Further development of large-scale manufacting procedures is still needed to reduce the cost of these expensive materials. In addition, the assistance of industry will prove valuable in designing and fabricating the appropriate contacting equipment for pilot- and plant-scale use.

Both PNNL and ANL have expressed interest in testing the technetium solvent-extraction process for the TFA. Interaction with Ben Hay at PNNL has provided insight into conformational effects and design of crown ethers.

Keywords

crown ether, technetium, cesium, strontium, fission products, tank waste, alkaline, process, solvent extraction

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TTP Number: OR16C341

Electrically Controlled Cesium Ion Exchange

Presenter: Mike Lilga, Pacific Northwest National Laboratory[1]

EM Focus Area: high-level waste tank remediation

Task Description

Several sites within the DOE complex (Savannah River, Idaho, Oak Ridge, and Hanford) have underground storage tanks containing high-level waste resulting from nuclear engineering activities. To facilitate final disposal of the tank waste, it is advantageous to separate and concentrate the radionuclides for final immobilization in a vitrified glass matrix. This task proposes a new approach for radionuclide separation by combining ion exchange (IX) and electrochemistry to provide a selective and economic separation method.

We are developing a process in which an electroactive IX film is electrochemically deposited onto a high-surface area electrode, and the IX characteristics (ion uptake and elution) are controlled by modulating the potential of the film. The task incorporates both laboratory and bench-scale experiments for process development, and a pilot-scale design is the final milestone.

Although the compositions of DOE tank waste vary significantly among sites, initially we must limit our approach to investigating cesium removal from Hanford tank waste using nickel hexacyanoferrate IX films. Pacific Northwest National Laboratory (PNNL) researchers have performed proof of principle experiments with these films and obtained encouraging results. The films show cesium selectivity in the presence of high sodium concentrations and have a lifetime approximately 10 times that of traditional organic IX materials. The primary advantage to our method is that secondary waste is minimized as compared to traditional IX and electrochemical ion exchange (EIX), which rely on acid elution and caustic sodium loading process steps. These process steps and the need to control interfacial pH are eliminated by using electrochemical redox reactions within the film to control ion binding. This task is a collaboration between PNNL, The Electrosynthesis Company (East Amherst, New York), and the University of Washington.

In FY 1996, we will initially establish subcontracts with the University of Washington and The Electrosynthesis Company and will provide a project management plan to the ESP. One meeting with all participants will be scheduled to ensure cohesive collaboration. The experimental work at PNNL will include optimization of the deposition parameters for the nickel hexacyanoferrate film. This work will be performed in collaboration with the University of Washington and include an experimental matrix for statistical optimization of the following variables: potentiostatic/galvanostatic conditions, waveform of potential/current, deposition time, and reactant composition ($KNO_3/K_3Fe(CN)_6/K_4Fe(CN)_6/KOH$).

The synthesized films will be characterized using traditional electrochemical (voltammetry, electrochemical quartz crystal microbalance, and impedance) and surface science (X-ray diffraction, scanning electron microscopy) techniques. The characterization will address film structure, cesium IX capacity, film stability at high pH, and cesium uptake and elution rates. In addition, the optimal loading and unloading potentials will be determined for high-surface area electrodes. These potentials should not vary significantly between the laboratory-scale and the

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[1] Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

bench-scale designs. The Electrosynthesis Company will assist PNNL in the design of a continuous-flow cell for bench-scale testing. The initial design may incorporate a nickel foam electrode with several reference electrode probes to verify the uniform potential distribution.

Technology Needs

The DOE complex has several underground storage tanks that contain high-level mixed wastes in forms of sludge, salt cake, and alkaline supernatant liquors. Tanks are located at Savannah River, Oak Ridge, Idaho National Engineering Laboratory (INEL), and Hanford. The removal of water-soluble radionuclides such as ^{137}Cs is necessary for the current pretreatment scenarios for several sites, including Hanford. Although the disposal requirements for ^{137}Cs at Hanford have not been set, a reasonable limit for ^{137}Cs in the final glass product lies between 0.1 Ci/m^3 and 4600 Ci/m^3.[1]

Currently, the most accepted option for cesium separation for final disposal is by IX. Both inorganic and organic ion exchangers are under consideration. Unfortunately, in the current state of IX technology a large amount of secondary waste is generated due to the numerous process steps necessary for treating the waste. These steps include acid elution, exchanger water rinse, and sodium loading of the exchanger. In addition, it has been documented that organic exchangers lose approximately 3% of their capacity per cycle. Therefore, typical organic exchangers can be used for only 20 to 30 cycles before they need to be replaced.

Our approach provides an attractive alternative to traditional IX because the process significantly reduces secondary waste generation, the lifetime of the electroactive films is substantially higher than organic IX materials lifetime, and the scale-up procedures for electrochemical systems are well documented. PNNL researchers have shown that an electroactive IX material such as the alkali-metal nickel hexacyanoferrate can be loaded and unloaded with alkali metals up to 100 times with only a 25% loss of film activity (0.3% per cycle). Therefore, the improvement in IX reversibility is expected to be a factor of 10 larger than traditional IX materials. The secondary waste reduction relative to traditional IX is achieved by eliminating several process steps (i.e., acid elution and sodium loading) and using a smaller elution volume. A small elution volume is sufficient because the desorption (or the elution) step is controlled through the applied potential, not by interfacial pH.

Scientific Background

The combination of IX and electrochemistry has been attempted several times with the most successful being EIX technology developed by AEA in the United Kingdom.[2] The work in this task differs significantly from EIX technology, in which the IX properties of a bonded exchanger/electrode are controlled by generating acid (H^+) and base (OH^-), locally by water electrolysis. We will control the uptake and elution of an ionic species in a modified electrode or IX film by modulating the potential of film *directly*, without changing the local interfacial pH. Furthermore, the potentials of film used in this method do *not* exceed that necessary for the electrolysis of water, thereby eliminating the safety issues associated with hydrogen evolution. The film preparation and IX mechanism that will be used for the system are described below.

It is well established that the surface of a conductor or a semiconductor can be modified through the formation of a surface film to control the interfacial charge transfer properties.[3,4] In fact, these surfaces can be tailored for specific charge transfer properties. We will similarly modify electrodes, but with particular emphasis on surface films that offer selective IX properties. Two IX properties of interest are selectivity for cesium and ease of uptake and elution steps controlled through the applied potential. The electrode surface can be modified with either an inorganic IX material or a conducting polymer. The former is desirable for Hanford tank waste applications to avoid film degradation from radiation exposure.

The hexacyanoferrate IX system was selected for several reasons. This system is known to be extremely selective for cesium in the presence of high sodium concentrations and stable at high pH and in radioactive environments.[5-9] Also, over the past 5 years, PNNL has participated extensively in the Hanford Tank Safety program, studying the IX and solubility properties of hexacyanoferrates. This experience provides the necessary background to interpret and understand the IX characteristics of these electroactive films. In addition, hexacyanoferrate complexes have been used in several industrial IX applications to selectively remove ^{137}Cs and ^{134}Cs.[8,10,11] These IX columns are operated in a once-through mode, and columns that have been fully loaded with radioactive cesium are discarded because the hexacyanoferrate exchangers cannot be regenerated. However, our novel approach enables the IX material to be used several times without significant loss of IX capacity. This is an attractive advantage from the standpoint of secondary waste minimization. Although the technical approach is not limited to nickel hexacyanoferrates, our initial efforts are focused primarily on these films.

Technical Approach

Our approach is to deposit nickel hexacyanoferrate films on industrially available substrates such as porous nickel electrodes. Figure 1 shows a simplified schematic of the IX process using this electroactive material. In this system, the oxidation state of the iron (+2 or +3) is easily controlled by relatively small changes in the applied voltage (from 100 to 300 mV). When a cathodic potential is applied to the film, Fe^{+3} is reduced to the Fe^{+2} state, and a cation must be intercalated into the film to maintain charge neutrality (i.e., Cs^+ is uptaken).

$$CsNiFe(CN)_6 + Cs^+ + e^- \longrightarrow Cs_2NiFe(CN)_6 \quad (1)$$
(uptake or cathodic)

Conversely, if an anodic potential is applied to the film, the Fe^{+2} is oxidized to the Fe^{+3} state, and a cation must be released from the film (i.e., Cs^+ is desorbed or eluted).

$$Cs_2NiFe(CN)_6 \longrightarrow CsNiFe(CN)_6 + Cs^+ + e^- \quad (2)$$
(elute or anodic)

Therefore, to uptake cesium, the film is simply reduced; to elute cesium, the film is oxidized. The system includes a counter electrode to complete the circuit.

Accomplishments

We have performed several "proof of principle" experiments with the nickel hexacyanoferrate system to validate the approach. Nickel electrodes, with surface areas up to 100 cm², were coated with a hexacyanoferrate IX film, and the iron oxidation state was modulated through the applied potential. The experiments showed that the iron oxidation state (+2 or +3) can be changed easily without water electrolysis. Figure 2 shows the redox reaction of iron (+2 and +3) in a nickel hexacyanoferrate film for 1515 cycles of sodium uptake and elution. The film is extremely reversible with an approximately 25% capacity loss

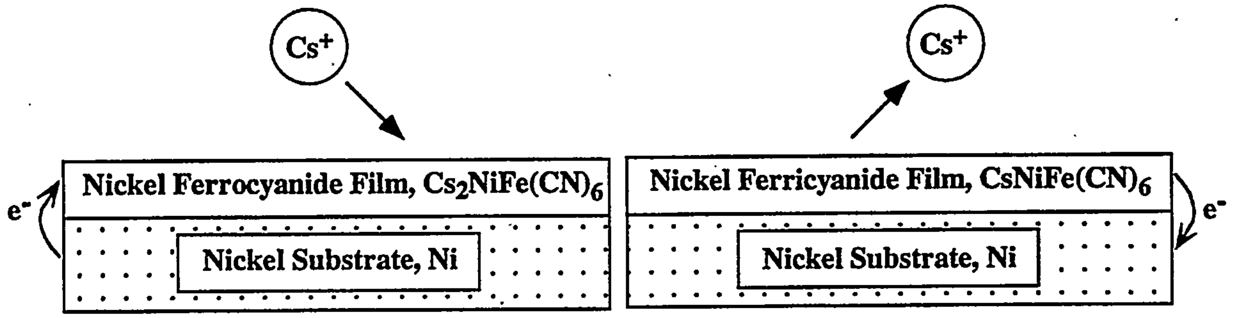

Figure 1. Simplified schematic of a process where the ion exchange characteristics are controlled by modulating the applied potential. The first drawing shows the film driven cathodically, causing an uptake of cesium, and the second shows the film driven anodically, causing a release of cesium.

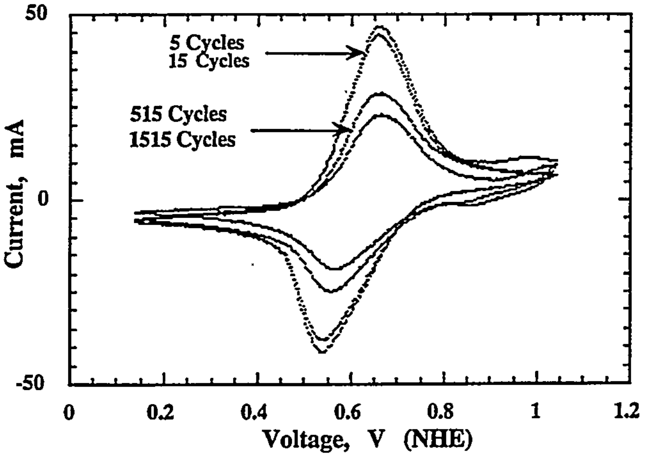

Figure 2. Cyclic voltammograms of a nickel hexacyanoferrate film at 50 mV/s in 0.5 M Na_2SO_4 showing the oxidation and reduction reactions of iron after several cycles.

(i.e., decrease in peak current) after 100 uptake/elution cycles. This stability is substantially higher than the baseline IX technology, which is estimated to be economical for only 20 to 30 cycles. We have also shown qualitatively that the deposited nickel hexacyanoferrate films are selective for cesium.

Figure 3 shows three cyclic voltammograms for a nickel hexacyanoferrate film in solutions of 0.66 mM $CsNO_3$, 0.5 *M* Na_2SO_4, and a mixture of 0.66 mM $CsNO_3$/0.5 *M* Na_2SO_4. The peak current for the pure 0.66 mM $CsNO_3$ solution is significantly lower than that of the pure 0.5 *M* Na_2SO_4 solution. This is partly due to the lower cesium concentration. The peak current in the mixture was also found to be lower than that measured in the pure Na_2SO_4. This strongly suggests that the deposited film preferentially uptakes and elutes cesium even in the presence of a high Na concentration (mole ratio of Na:Cs = 1500).

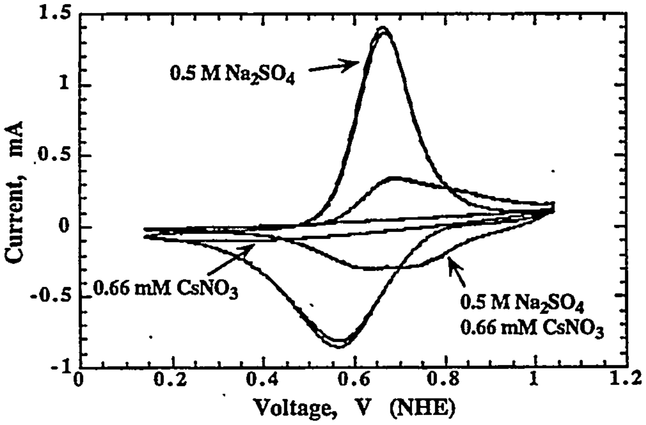

Figure 3. Cyclic voltammograms of a nickel hexacyanoferrate film in 0.5 M Na_2SO_4, 0.66 mM $CsNO_3$, and a mixture of 0.5 M Na_2SO_4/ 0.66 mM $CsNO_3$ showing iron oxidation and reduction reactions.

For the final scale-up demonstration, there are several relevant engineering issues to address. Some of these will be similar to those that have been investigated for traditional IX applications using hexacyanoferrates, such as capacity, stability (physical and chemical) of the hexacyanoferrates, and process flowrates.[10,11] Additional issues to consider include electrochemical cesium uptake and elution rates, film lifetime, and ease of film regeneration. Although this work is targeted on ^{137}Cs, the hexacyanoferrate films can also be used to separate other alkali metals, alkaline earth metals, rare earth metals, and transition metals (e.g., silver).[12-14]

Benefits

The benefits of potentially modulated ion exchange as applied to Hanford tank waste are listed below:

- Minimal secondary waste is generated as compared to using competing technologies such as traditional IX. Several process steps are eliminated, and the elution volume can be controlled.
- PNNL researchers have demonstrated that the IX films can be cycled at least 100 times with only a 25% loss in film activity. This is significantly higher (greater than tenfold) than the traditional IX process.
- The technical approach has enormous potential for multivalent ions, such as strontium, once a suitable electroactive film is identified for those systems.
- The uptake/elution of ^{137}Cs is controlled by the applied potential and not by the interfacial pH. Also, no hydrogen is generated during the uptake or elution process.

- Possible problems, such as uniform potential distribution, can be easily overcome with standard electrochemical engineering practices.
- This approach enables the hexacyanoferrate IX material to be reusable, while in the traditional IX configuration the material cannot be regenerated and must be discarded.

Collaborations

PNNL researchers will collaborate with the University of Washington and The Electrosynthesis Company, Inc. The University of Washington will provide expertise and consultation in the area of thin-film preparation, characterization, and design considerations. The Electrosynthesis Company will aid in the scale-up for a bench-scale unit and pilot-scale design. PNNL will prepare and optimize the IX film, design and manufacture a bench-scale prototype continuous flow-cell to examine simulant and actual tank waste, design a pilot-scale system, and coordinate all research efforts.

Keywords

ion exchange, electrochemistry, redox, thin-film, oxidation, reduction, electroactive, cesium, hexacyanoferrate.

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Sequestering Agents for the Removal of Actinides from Waste Streams

Presenters: Ken Raymond and David White, University of California, Berkeley; Don Whisenhunt, Lawrence Livermore National Laboratory

EM Focus Area: contaminant plume containment and remediation

Task Description

The ultimate goal of this project is to develop new separation technologies to remove radioactive metal ions from contaminated DOE sites. To this end we are studying both the fundamental chemistry and the extractant properties of some chelators that are either found in nature or are closely related to natural materials. The work is a collaboration between Lawrence Berkeley National Laboratory-University of California, Berkeley, and the Glenn T. Seaborg Institute for Transactinium Science at Lawrence Livermore National Laboratory.

Nature has finely tuned chelators (siderophores) to form highly stable complexes with the Lewis acidic metal ion iron(III). Our goal is to develop similar chelators and selective binders for the actinide ions thorium(IV) and plutonium(IV), which show coordination properties similar to iron(III). Differences in charge, preferred coordination number, and pH stability range can be used to make this transition from chelators that are specific for iron(III) to those that are specific for actinide (IV) ions.

In addition we have shown that these naturally occurring chelating groups are versatile ligands for chelating uranium. In particular, we have studied their interactions with uranyl ion $[UO_2]^{2+}$, the almost ubiquitous form of uranium found in aqueous media. With an understanding of this fundamental chemistry it should be possible to develop new agents for sequestering uranium from waste streams, and studies have also shown the ability of such materials to remove uranyl ion from the body in cases of uranium poisoning.

Scientific Background/Technical Approach

In the natural iron(III) sequestering agents, multiple catechols (e.g., *Enterobactin)* or hydroxamic acids (e.g., desferrioxamine *B*) are combined in polydentate ligands to fully bind the metal in a six-coordinate complex. These chelate groups are ideal for sequestering many Lewis acidic metal cations and can readily be incorporated into ligands for actinide (IV) cations. We have therefore focused our efforts on the binding properties of catecholamides, terephthalamides, and hydroxpyridinones (Figure 1).

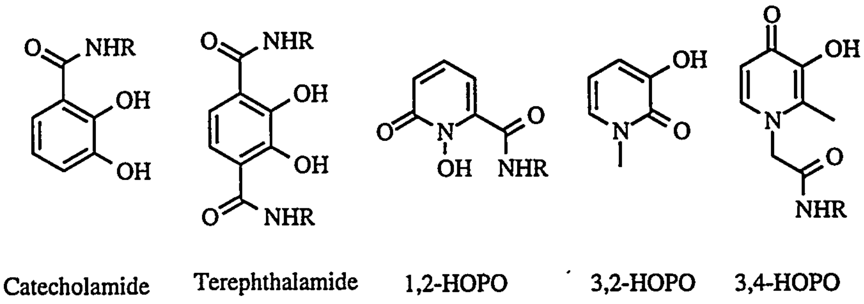
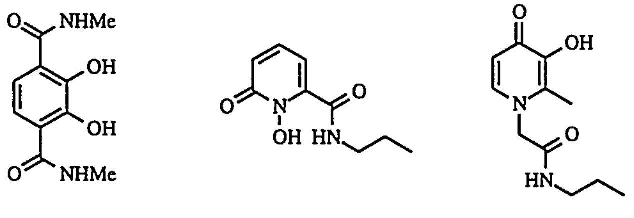


Figure 1. The powerful chelating groups catecholamide, terephthalamide, 1,2-HOPO, 3,2-HOPO and 3,4-HOPO.

Table 1. Thermodynamic constants determined for MTA, N-Pr-1,2-HOPO and N-Pr-3,4-HOPO

	MTA	N-Pr-1,2-HOPO	N-Pr-3,4-HOPO
Protonation Constants	11.1 6.1	4.96(2)	9.47(2) 3.03(4)
Iron(III) Formation Constants (ML)	16.4	9.0(1)	14.6(1)
ML_2	30.9	15.8(2)	26.7(1)
ML_3	41.8	24.1(2)	36.24(4)
Thorium(IV) Formation Constants (ML)	27.9(7)		13.5(2)
ML_2	38.5(5)		25.0(8)
ML_2H	45.0(9)		
$ML_2(OH)_2$		12.1(2)	
ML_3	45.1(1)		35.8(2)
$ML_3(OH)$		24.9(2)	
ML_4	50.5(1)	36.0(3)	41.8(5)

Thermodynamic measurements have been made to ensure that these bidentate groups show selectivity for actinide (IV) ions over iron(III). The thermodynamic binding constants between the ligands shown in Figure 2 and the metals iron(III) and thorium(IV) have been determined and are detailed in Table 1. These measurements show that all three binding groups form 1:4 complexes with thorium(IV).



MTA N-Pr-1,2-HOPO N-Pr-3,4-HOPO

Figure 2. Structures of the bidentate binding groups MTA, N-Pr-1,2-HOPO and N-Pr-3,4-HOPO for which stability constants with Th(IV) and Fe(III) have been determined.

Incorporating these powerful chelating groups into solid/liquid and liquid/liquid extractant systems can produce materials with potential practical application. The liquid/liquid extractants employ the simple bidentate chelating groups modified with a wide variety of lipophilic side chains designed to systematically alter their solubility properties (Figure 3). Initial experiments have been performed to determine the distribution coefficients of the extractants between aqueous and a number of common organic phases used in separations technology. Several materials with low water solubility have been tested for their ability to extract Lewis acid metals from aqueous media under varying conditions of pH and ionic strength. Several of the 1,2-HOPO sequestering agents seem particularly promising, showing quantitative removal of Lewis acid metal ions into organic media.

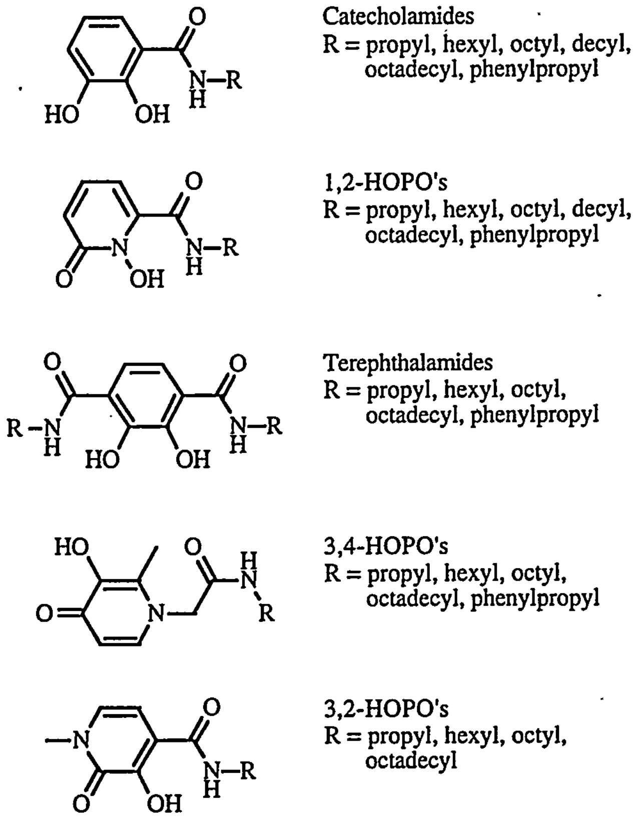


Figure 3. Lipophilic extractants that have been synthesized.

For the solid/liquid extractants these chelating groups have been immobilized on polystyrene resin beads. To aid with extractant properties these beads have been sulfonated to reduce their hydrophobicity. This improves the loading properties of the material with metal cations but the sulfonate groups introduce some degree of nonselective binding (ion exchange). These polystyrene-based materials show excellent kinetics for the uptake of thorium(IV) and have a high loading capacity. They also perform well in the presence of competitive chelators although this reduces loading capacity.

Future studies with these resins and the lipophilic liquid/liquid extractants will use simulated waste streams to determine how well they would perform under these more extreme conditions of pH, ionic strength and solution composition.

The heterocyclic hyroxypyridinones have found a further application in the chemistry of uranium. The simple bidentate form 2:1 complexes with uranyl ion and the isolation and structural characterization of several of theses complexes has been achieved. From a knowledge of these basic binding interactions we should be able to design ligands with increased specificity for $[UO_2]^{2+}$. The ligand N-methyl-3,2-HOPO-4-propylamide (Figure 4) readily forms a 2:1 complex with uranyl ion in which the HOPO ligands bind in the equatorial plane of the $[UO_2]^{2+}$ species as demonstrated by X-ray crystallography (Figure 5).

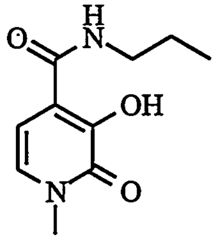


Figure 4. N-methyl-3,2-HOPO-4-propylamide.

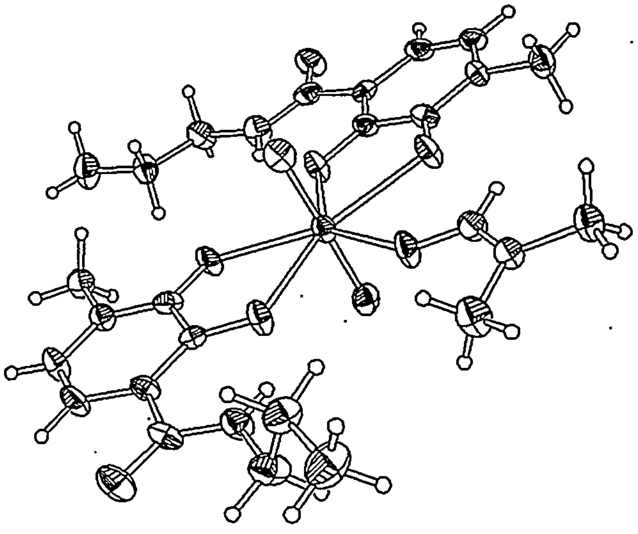


Figure 5. X-ray crystal structure of N-methyl-3,2-HOPO-4-propylamide with uranyl ion as the DMF solvato species.

The ligands are unable to fully satisfy the coordination requirements of the metal and a final coordination site is occupied by solvent. By including an additional neutral donor into a tetradentate ligand a considerable increase in stability should be achieved, and the ligand 5-LIO-Me-3,2-HOPO (Figure 6) has been studied as a possible way to achieve this. Furthermore, increasing the length of the alkyl group on the amide provides a way to increase the lipophilicity of these neutral 2:1 complexes.

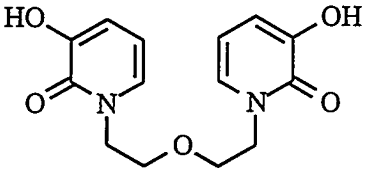


Figure 6. 5-LIO-Me-3,2-HOPO.

Initial animal studies show that bis bidentate hydroxypyridinone ligands show much enhanced ability to remove uranium from mice when compared to more common metal ion seqestering agents such as EDTA and DTPA. Further work to determine the stabilities of these species by solution thermodynamics and to structurally characterize uranyl complexes of bis bidentate ligands, incorporating, 3,2-HOPO, 1,2-HOPO, catecholamides and terephthalamides is now in progress. The possibility of functionalizing these species to form lipophilic or hydrophilic species and immobilizing them on solid supports to form new extractant materials is also under investigation.

Benefits

Development of highly selective and efficient ligands that can complex actinide elements over a wide range of solution composition (pH and ionic strength) could reduce drastically the volume of certain high-level and low-level waste streams and thus reduce the cost of long-term storage in a geologic repository. Even further cost reduction can be realized if the ligands can be manufactured relatively inexpensively, exhibit resistance to both harsh chemical and radiation environments, and show high selectivity in the presence of large quantities of other metal ions.

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Heavy Metals

- ☐ Ligand Modeling and Design
- ☐ Removal and Recovery of Toxic Metal Ions from Aqueous Waste Sites Using Polymer Pendant Ligands

Ligand Modeling and Design

Presenter: Ben Hay, Pacific Northwest National Laboratory[1]

EM Focus Areas: contaminant plume containment and remediation; mixed waste treatment and disposal; high-level waste tank remediation.

Task Description

The purpose of this work is to develop and implement a molecular design basis for selecting organic ligands that would be used in applications for the cost-effective removal of specific radionuclides from nuclear waste streams.

Organic ligands with metal ion specificity are critical components in the development of solvent extraction and ion exchange processes that are highly selective for targeted radionuclides. The traditional approach to developing such ligands involves lengthy programs of organic synthesis and testing, which in the absence of reliable methods for screening compounds before synthesis, results in wasted research effort. Our approach breaks down and simplifies this costly process by using computer-based molecular modeling techniques.

Commercial software for organic molecular modeling is being configured to examine the interactions between organic ligands and metal ions, yielding an inexpensive, commercially or readily available computational tool that can be used to predict the structures and energies of ligand-metal complexes. Users will be able to correlate the large body of existing experimental data on structure, solution binding affinity, and metal ion selectivity to develop structural design criteria. These criteria will provide a basis for selecting ligands that can be implemented in separations technologies by DOE national laboratories and industry. The initial focus will be to select ether-based ligands that can be applied to the recovery and concentration of the alkali and alkaline earth metal ions including cesium, strontium, and radium.

Technology Needs

Efficient separation processes are required for the removal of heat emitters (^{137}Cs and ^{90}Sr), long-lived radionuclides (^{99}Tc), and other metal ions from high- and low-level waste to reduce toxicity and volume at DOE sites. Solvent extraction and ion exchange methods are being developed at a number of sites.

The successful performance of these separation methods largely depends on the properties of the organic ligand (e.g., selectivity, binding affinities, binding kinetics, and solubility). Therefore, much effort is spent on the synthesis, characterization, and testing of many ligands to find those few with the desired properties to meet the separations process needs. Current criteria used to select ligands for a specific application are not highly accurate and result in more failures than successes.

Scientific Background

This technology is based on adapting the most accurate commercial molecular mechanics modeling software, MM3, for application to metal-ligand complexes. Historically, molecular mechanics models have been developed for exclusive application to organic molecules; that is, molecules composed of carbon, hydrogen, nitrogen, phosphorus, oxygen, sulfur, fluorine, chlorine, bromine, and iodine atoms.

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[1] Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

All commercial molecular mechanics software packages come with sets of parameters for organic compounds but most do not contain parameters for treating metal-ligand complexes. This is partly because of the past focus on pure organic systems and partly because of the way molecular mechanics models work; that is, a unique set of parameters is required for each different metal ion and each different type of donor atom. When applying the molecular mechanics technique to metal-ligand complexes, one must focus on a class of metal complexes to limit the number of metal ions and donor atom types and then develop a set of parameters before performing the calculations.

In the early stages of this project, we developed an extended MM3 parameter set that allows accurate molecular mechanics calculations to be performed on metal complexes of the alkali (lithium, sodium, potassium, rubidium, cesium) and alkaline earth (magnesium, calcium, strontium, barium, radium) metal ions with ligands that contain aliphatic ether donor atoms (e.g., ligands such as the SREX reagent, di-t-butyl-dicyclohexano-18-crown-6). This parameter set has been completed and validated. A current objective is to further extend the MM3 parameter set to include metal complexes of the alkali and alkaline earth metal ions with ligands bearing benzo ether donor atoms. This will yield the capability to perform molecular mechanics calculations on a wider range of ligands (e.g., benzocrown ethers, calixarenes, and spherands).

Molecular mechanics calculations provide structures and steric energies for organic ligands and their metal complexes. These results yield a design basis for ligand selection. This design basis includes quantitative structure-activity relationships (QSARs), methods to predict relative complex stability as a function of ligand structure, and criteria for ligand design.

QSARs are obtained by coupling molecular mechanics results with experimental data. These QSARs can be used to predict properties (e.g., thermodynamic stability constants) of ligands for which no experimental data exist. To date, molecular mechanics based QSARs have been obtained for thermodynamic stability constants of sodium, potassium, rubidium, and cesium complexes with aliphatic crown ethers (see Figure. 1), and for solvent extraction distribution coefficients of lithium by alkyl substituted 14-crown-4 ligands and strontium by a series of dicyclohexano derivatives of 18-crown-6.

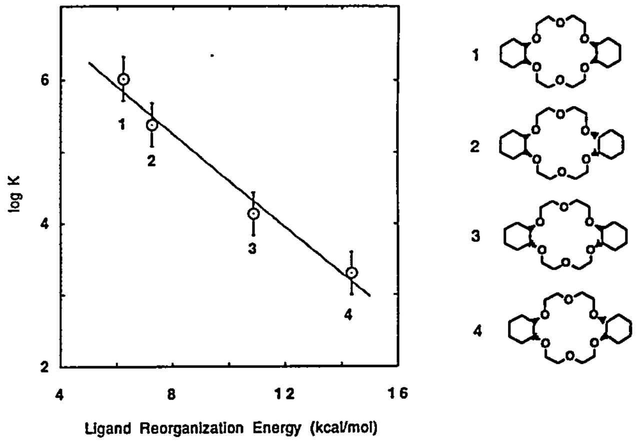

Figure 1. Plot of experimental complex stability (log K in methanol at 25°C) versus calculated ligand reorganization energy for potassium complexation by four diastereomers of dicyclohexano-18-crown-6.

Generating QSARs requires the availability of reference experimental data. In the absence of such data, it is possible to use molecular mechanics calculations to predict the relative metal binding affinities for a series of ligands and, therefore, to identify ligand structures likely to form the most stable metal ion complexes. The calculated increase in ligand steric energy that accompanies metal ion complexation provides a yardstick for the measurement of the ligand's binding site organization, a structural property that correlates with the stability of metal-ligand complexes.

Ligand design criteria, or "rules-of-thumb" that can readily be applied by synthetic chemists, are an important by-product of this work. For example, to clarify a previously unrecognized preference for trigonal planar geometry at ether oxygen donors established that ethylene-bridged, ether oxygen donor atoms form a chelate ring that is structurally organized for large metal ions. Therefore, the presence of ethylene bridges in multidentate ethers will promote selectivity for large metal ions. A study of ethylene-bridge alkylation has yielded a set of simple rules that allows a synthetic chemist to predict how the addition of alkyl groups to crown ethers will alter the complex stability.

Benefits

This new technology, the design criteria coupled with the computer-based molecular model, will provide a way to assess the reactivity of an organic ligand toward a target metal ion on the basis of molecular structure. This capability can be used to screen potential ligands before undertaking the time and expense associated with synthesis and testing.

The costs associated with organic synthesis and performance testing with radioactive materials are expected to rise disproportionately to the average cost of doing business because of increasing regulation regarding the safe handling and disposal of chemical reagents. Therefore, this capability will save significant cost in ligand identification, evaluation, and deployment.

This technology will allow the development of ligands with improved performance including 1) improved selectivity and binding affinity for specific aqueous species, 2) improved performance in solvent extraction systems by optimizing the type and placement of the hydrophobic substituents needed for low aqueous solubility, and 3) improved performance in ion exchange systems by optimizing the type and placement of the tether used for anchoring the ligand to the solid-support. Improved ligand performance will save money by decreasing the amount of ligand required for a process.

Solving problems concerning the stability of metal complexes and selectivity of complex formation is of fundamental importance. This technology can potentially be applied to the wide variety of ligand types and associated metal complexes being addressed by other DOE programs involving environmental cleanup, fate, and transport of environmental contaminants; development of sensors; and nuclear medicine. The private sector may also be able to apply this technology in the chemical industry, medicine and pharmacology, hydrometallurgy, and geochemistry.

Accomplishments

The inexpensive, off-the-shelf molecular model MM3 has been configured to handle aliphatic crown ether ligands and their complexes with the alkali and alkaline earth metal ions. The model has been demonstrated to predict accurately the structure of these ligands and their metal complexes. Correlations between calculated structural data and experimental reactivity (complex stability and solvent extraction distribution coefficients) have been obtained. Design criteria for aliphatic crown ethers have been developed. This model is currently being applied to the design and screening of aliphatic crown ether ligands for the separation of cesium and radium and the optimization of the SREX reagent. The MM3 model is now being extended to treat metal complexes with ligands bearing benzo ether donor atoms such as benzocrown ethers, calixarenes, and spherands.

Collaboration/Technology Transfer

PNNL staff are collaborating with

- Norman Allinger, University of Georgia, author of MM3—adding a methodology for treating high-coordinate metal complexes to the next scheduled release of the software, MM3(96)
- Philip Horwitz and co-workers at Argonne National Laboratory—performing calculations to optimize the performance of the SREX ligand and to design a selective ligand for radium.

- Bruce Moyer and co-workers at Oak Ridge National Laboratory—performing calculations to identify structural factors that control reactivity in benzocrowns and improve the cesium/sodium selectivity that can be obtained with ligand-bearing benzoether groups.
- IBC Advanced Technologies—providing design criteria, MM3 parameters, and a conformer searching algorithm to their in-house theoretician, Robert Hancock.

Keywords

metal complex, ligand, chelate, sequestering agent, design, molecular modeling

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TTP Number: RL36C331

Removal and Recovery of Toxic Metal Ions from Aqueous Waste Sites Using Polymer Pendant Ligands

Presenter: Dick Fish, Lawrence Berkeley National Laboratory

EM Focus Areas: contaminant plume containment and remediation; mixed-waste characterization, treatment, and disposal; facility transitioning, decontamination, and final disposition

Task Description

The purpose of this project is to investigate the use of polymer pendant ligand technology to remove and recover toxic metal ions from DOE aqueous waste sites. Polymer pendant ligands are organic ligands, anchored to crosslinked, modified divinylbenzene-polystyrene beads, that can selectively complex metal ions. The metal ion removal step usually occurs through a complexation or ion exchange phenomena, thus recovery of the metal ions and reuse of the beads is readily accomplished.

The research objectives, which we achieved in FY 1994-96, include synthesizing selective polymer pendant ligands for removal and recovery of the metal ions of interest, determining rates of both removal and recovery of these metal ions, and transferring the technology to our industrial partner, AquaEss, San Jose, California, for application studies and eventual implementation of the polymer pendant ligand technology.

Studies in FY 1994 and FY 1995 were initially focused on acid mine wastewater represented by the Berkeley Pit (~pH = 2.5) in Butte, Montana, with emphasis on Fe^{3+}, Al^{3+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, and Ag^{+}. Because the Fe^{3+} ion was dominant in the Berkeley Pit wastewater, we placed special attention on devising Fe^{3+} ion-selective polymer pendant ligands to remove and recover the other economically important metal ions, such as Cu^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+}, and Al^{3+}. AquaEss has studied the acid wastewater (Berkeley Pit) application with our polymer pendant ligands and has developed a strategy for remediation of this type of wastewater.

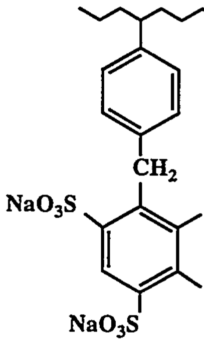
In FY 1996, we are focusing on Resource Conservation and Recovery Act (RCRA) metal ions, including Ag^{+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+}. The application of polymer pendant ligand technology to DOE waste sites with RCRA metal ion contamination (Ag^{+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+}) is opposite to that for acid mine wastewater containing high concentration of Fe^{3+} ions. The polymer pendant ligands developed for these applications selectively remove the above-mentioned RCRA metal ions in the presence of moderate to low concentrations of Fe^{3+} ions. AquaEss is now studying these polymer pendant ligands in column experiments to develop strategies for remediating various DOE aqueous waste sites with RCRA metal ion contamination.

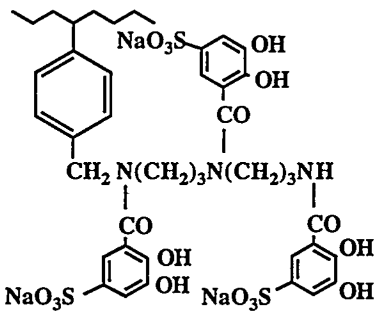
Technology Needs

Removal and recovery of RCRA and radionuclide metal ions from DOE aqueous waste sites will require a considerable amount of technology development. In addition to developing a wide range of technologies for removing and recovering specific metal ions, a generic-based technology can remove a wide range of metal ions from aqueous waste at many sites. In addition, the cost of the polymer pendant ligand technology is modest compared to traditional precipitation techniques.

Accomplishments

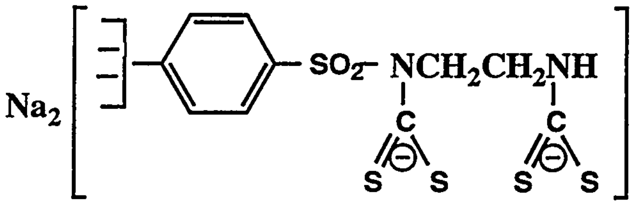
The initial priority for this task during FY 1994 and FY 1995 was to develop selective polymer pendant ligands to remove and recover Fe^{3+} ion (Berkeley Pit acid mine wastewater), and we have accomplished this. The polymer pendant catechol ligand derivatives, sulfonated catechol and sulfonated 3,3-LICAMS, were ideal biomimetic candidates for an Fe^{3+} ion selective polymer pendant ligand, because they are structurally similar to biological ligands that selectively sequester Fe^{3+} (see structures for CATS and 3,3-LICAMS).


PS-CATS


PS-3,3-LICAMS

We have found that PS-3,3-LICAMS and PS-CATS removed Fe^{3+} ions from aqueous acidic waste waters (pH values of 0.5 to 2.5) with high capacities (0.8 to 1 mmol/g beads) and excellent removal kinetic rates (2-4 x 10^{-4} s-1). Recovery of Fe^{3+} from the beads and then re-use of the beads was readily accomplished using a 2N H_2SO_4 solution. In subsequent application studies, AquaEss showed that in column experiments with the above-mentioned polymer pendant ligands a displacement phenomena occurred that can be used to separate Fe^{3+} ions from Al^{3+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+}, and Ni^{2+} ions.

Thus far in FY 1996, we have evaluated a polymer pendant ligand, N-sulfonylethylenebis(dithiocarbamate) (PS-SED, see structure) that appeared to be selective to Ag^{+}, Hg^{2+}, Pb^{2+}, and Cd^{2+} ions in the presence of Fe^{3+} ions. PS-SED, 1.12 mmol/g, anchored on modified, macroporous 6% polystyrene-divinylbenzene beads, is highly selective for the removal of Ag^{+} ions (2.17 mmol/g, 2:1 Ag^{+}/PS-SED complex, rate constant ($t_{1/2}$) = 7 min) from aqueous solution at pH 3.0 in the presence of a variety of competing tri- and divalent metal ions such as Fe^{3+}, Cr^{3+}, Al^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}, Mn^{2+}, and Pb^{2+} (batch experiments).


PS-SED

When Hg^{2+} ions (1.24 mmol/g, 1:1 Hg^{2+}/PS-SED complex, $t_{1/2}$ = 10 min) are added to this mixture of metal ions, including Ag^{+} ions, there is a pronounced selectivity toward Hg^{2+} ions for the PS-SED ligand. In the absence of Ag^{+} and Hg^{2+}, then Pb^{2+} ions (1.06 mmol/g, 1:1 Pb^{2+}/PS-SED complex, $t_{1/2}$ = 6 min) are moderately selective in the presence of other competing metal ions including Cd^{2+} ions; Cu^{2+} ions are the exception (0.93 mmol/g, ~1:1 Cu^{2+} /PS-SED complex, $t_{1/2}$ = 3 min). In the absence of Pb^{2+} ions, Cd^{2+} ions (0.65 mmol/g, ~1:1 Cd^{2+}/PS-SED complex, $t_{1/2}$ = >10 min) also are moderately selective in the presence of other competing metal ions, but again, Cu^{2+} is the exception. Whereas Cu^{2+} has a selectivity over Pb^{2+} and Cd^{2+} in a competitive reaction, Fe^{3+} ion is more selective in competition with Cu^{2+}, while in competition with Fe^{3+} ion, Ag^{+}, Hg^{2+}, Pb^{2+}, and Cd^{2+} are all more selective. The overall selectivity for PS-SED was found to be: $Hg^{2+} \geq Ag^{+} > Cu^{2+} > Pb^{2+} > Cd^{2+} > Fe^{3+} \sim Al^{3+} \sim Cr^{3+} > Ni^{2+} > Zn^{2+} \sim Co^{2+} > Mn^{2+} >> Mg^{2+}$.

AquaEss performed a column experiment with the PS-SED beads with a synthetic wastewater that contained 200 ppm each of Ag^{+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, and Fe^{3+} ions at pH 3. This synthetic wastewater represented a combination of RCRA metal ions that pervade DOE sites including Pacific Northwest National Laboratory, Savannah River Technical Center, Idaho National Engineering Laboratory, Brookhaven National Laboratory, and Oak Ridge National Laboratory. All the Ag^{+}, Hg^{2+}, and Pb^{2+} ions

(200 ppm each) were removed from solution at pH 3 and retained on the column; while Cd^{2+} and Fe^{3+} ions were retained on the column to some extent, both were evident at column breakthrough by the familiar displacement phenomena. Therefore, Fe^{3+} ions form kinetically and thermodynamically less stable complexes with PS-SED in comparison to Ag^{+}, Hg^{2+}, and Pb^{2+}, while Cd^{2+} ions appear to be influenced by the presence of Fe^{3+} and Pb^{2+} ions, and this phenomenon is now being investigated. We will also review progress on a new method to selectively remove and recover metal ion from wastewater with metal ion templated polymers that show selectivity ratios of Cu^{2+}/Fe^{3+} of >50.

Collaboration/Technology Transfer

AquaEss, San Jose, California
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TTP Number: SF16C331

Waste Processing and Treatment

- ☐ Immobilization of Fission Products in Phosphate Ceramic Waste Forms
- ☐ Comprehensive Supernatant Treatment
- ☐ Hot Demonstration of Commercial Nuclide Removal Technology
- ☐ Development and Testing of Inorganic Sorbents for Radionuclide and Heavy Metal Separations
- ☐ Magnetic-Seeding Filtration
- ☐ Salt Splitting with Ceramic Membranes
- ☐ Comparison of Organic and Inorganic Ion Exchange Materials for Removal of Cesium and Strontium from Tank Waste
- ☐ Membrane-Based Separation Technologies for Cesium, Strontium, and Technetium
- ☐ Cesium and Strontium Ion-Specific Exchangers
- ☐ Chemical Derivatization to Enhance Chemical/Oxidative Stability of Resorcinol-Formaldehyde Resin
- ☐ Selective Crystallization of Tank Supernatant Liquid
- ☐ Technical Liaison with the Institute of Physical Chemistry
- ☐ Electrochemical Treatment of Liquid Wastes
- ☐ Advanced Separations at Savannah River Site

Immobilization of Fission Products in Phosphate Ceramic Waste Forms

Presenter: Dileep Singh, Argonne National Laboratory

EM Focus Areas: high-level waste tank remediation; contaminant plume containment and remediation

Task Description

The goal of this project is to develop and demonstrate the feasibility of a novel low-temperature solidification/stabilization (S/S) technology for immobilizing waste streams containing fission products such as cesium, strontium, and technetium in a chemically bonded phosphate ceramic. This technology can immobilize partitioned tank wastes and decontaminate waste streams containing volatile fission products.

Conventional high-temperature immobilization technologies are not feasible for these waste streams because they cause volatilization of contaminants such as technetium and cesium. Therefore, low-temperature processing will be employed to fabricate zirconium-, magnesium-, and titanium- phosphate-based final waste forms for the S/S of waste streams containing fission products.

Contaminants can be chemically fixed in phosphate ceramics because of one or more of the following mechanisms: formation of an insoluble phosphate of the contaminants, elemental substitution in the matrix phosphate, and intercalation reactions within the phosphate matrix. Because the contaminants will be chemically fixed and physically encapsulated in an extremely dense and durable phosphate matrix, the final waste form is expected to have desirable properties.

In this new project, major tasks include 1) demonstrating the S/S of waste streams containing fission products, 2) scaling up the phosphate-bonded immobilization technology for field applications; and 3) transferring the phosphate-bonded immobilization technology to end users. During FY 1996, we will focus on developing appropriate phosphate-bonded ceramic waste forms with optimized process parameters, using specific surrogate fission-product waste streams, and demonstrating their effective stabilization.

Technology Needs

The current volume of high-level waste (HLW) across the DOE complex is several hundred thousand cubic meters. The waste includes solids, sludges, liquids, and salt cakes and comprises radionuclides in three broad categories: actinides, lanthanides, and fission products. Because of the diverse chemical and physical nature of these three components, the HLW cannot be effectively and inexpensively stabilized and disposed of by a single-step process or technology.

The presence of fission products such as ^{137}Cs, ^{90}Sr, and ^{99}Tc in the HLW poses myriad problems. Cesium and strontium are highly volatile and may escape into the offgas system during HLW vitrification, thus generating a secondary waste stream that will require additional S/S. Cesium and strontium radionuclides are also heat generators with half-lives of $\approx$30 years; therefore, they will generate considerable heat for 30 to 50 years if disposed of in a repository in vitrified HLW. In contrast, ^{135}Cs and ^{99}Tc have much longer half-lives ($\approx 10^6$ years) and require an appropriate immobilization system.

Removing fission products from the HLW reduces the overall waste volume and radioactivity levels of the HLW, thus simplifying the waste-handling operations. This and other decontamination processes result in waste streams that are rich in fission products and, if not returned to the bulk HLW stream, require S/S for safe disposal in compliance with federal regulations.

Currently, no robust and reliable low-temperature technologies are available to immobilize the fission-product rich wastes. A low-temperature stabilization and immobilization technology can produce durable final waste forms for long-term storage or disposal of the fission products and/or the "loaded" separating agents used to remove fission products from the HLW streams. To this end, we are developing and demonstrating a low-temperature treatment and stabilization technology based on chemically bonded phosphate ceramics.

Scientific Background

Chemically Bonded Phosphate Ceramics

Novel chemically bonded phosphate ceramics have several advantages that make them ideal candidates for containment of radioactive and hazardous wastes. In general, phosphates have high solid-solution capacities for incorporating radionuclides, as evidenced by several phosphates (e.g., monazites and apatites) that are natural analogs of radioactive and rare-earth elements. The phosphates also have high radiation stability, are refractory, and will not degrade in the presence of internal heating from fission products. Dense and hard chemically bonded phosphate ceramics can be fabricated inexpensively and at low temperatures by acid-base reactions between an inorganic oxide/hydroxide powder and either a phosphoric acid solution or an acid-phosphate solution. The resulting phosphates are extremely insoluble in aqueous media and have excellent long-term durability. Dual stabilization mechanisms, chemical fixation and physical encapsulation, will provide superior contaminant retainment.

Argonne National Laboratory (ANL) has been developing chemically bonded phosphate ceramics to treat low-level mixed-waste streams, particularly those containing volatiles and pyrophorics that cannot be treated by conventional thermal processes. This work was begun under ANL's Laboratory Directed Research and Development (LDRD) funds, followed by further development with support from DOE's Mixed Waste Integrated Program (Office of Technology Development, EM-50).

As part of our previous work, we developed magnesium-phosphate-based final waste forms with several surrogate waste streams, including ash, salts, and cement sludge (all spiked with contaminants such as cerium, lead, cadmium, chromium, and nickel). A variety of performance tests (TCLP and ANS 16.1, leaching tests, 90-day immersion tests, and ASTM compression-strength tests) conducted on the fabricated final waste forms showed excellent results, thus demonstrating the phosphate-bonded technology as a viable method for disposal of radioactive and hazardous wastes.

Stabilization of Fission Products in Phosphate Ceramics

To guarantee safe long-term disposal, the radioactive contaminants must be not only incorporated into a dense and thermodynamically stable crystalline matrix but also chemically bound to it. Several mechanisms can be used to chemically fix the contaminants in a mineral phase, including intercalation reactions and elemental substitution.

Intercalation reactions occur in two-dimensional layered crystalline structures. The guest ions or molecules can be accommodated within the interlayers and are bound. Because a layered host lattice is easily deformable in the third dimension, a wide range of ions and molecules can be incorporated in such a material system by ion-exchange process and chemically bound. These layered materials have high potential for use as absorbents and ion exchangers. Several phosphate ceramics, including zirconium and titanium phosphates, exhibit intercalative ion exchanges; moreover, they are refractory, have high radiation stability, and can tolerate structural changes caused by the decay of radioactive contaminants because of their unique layered crystal structure. These phosphate binders are being investigated for the immobilization of fission products such as cesium and strontium.

Elemental substitution occurs when the contaminant species substitutes for a benign ion in the host mineral with similar chemical characteristics such as valence, ionic radius, etc., and does not disrupt the atomic arrangement of the crystalline phase. The resulting material is a solid solution with stability of the host mineral phase. The literature suggests that titanium minerals may be the ideal hosts for containment of technetium because titanium and technetium have similar ionic radii. Moreover, oxides of titanium and technetium form solid solutions. Thus, in this project, titanium phosphate system will be investigated as a candidate system for the stabilization of technetium containing wastes.

Accomplishments

This is a new task for FY 1996.

Technical Approach

During FY 1996, we will develop durable final waste forms using chemically bonded phosphate ceramics and simulated fission-product-rich waste stream. Three different phosphate systems (zirconium, magnesium, and titanium) will be investigated. We will identify one or more suitable phosphate systems for the waste stream under consideration (based on the requirements of individual waste streams) and then develop the waste forms with optimized properties. The detailed approach for FY 1996 task will be as follows.

Identification, Fabrication, and Characterization of Candidate Phosphate Systems

- Identify the phosphate systems applicable to particular waste streams, based on physical and chemical properties and thermodynamic stability.
- Fabricate dense and strong monolithic ceramics at bench scale, using low-temperature processing routes.
- Perform microstructural and mechanical characterizations and durability studies of monolithic phosphate ceramics.

Development of Optimized Simulated Wastes Forms with Radionuclide Surrogates

- Incorporate surrogate wastes in phosphate matrices with various waste loadings at bench scale. These surrogate wastes will be modeled on the compositions of actual fission-productwaste streams at DOE sites.
- Determine the integrity of simulated waste forms by standard performance tests such as compression strength (ASTM C 39), leaching behavior (ANS 16.1), 90-day water immersion test, mechanical stability after thermal cycling (ASTM B 553), and radiation stability.
- Collaborate with the University of Illinois at Urbana-Champaign on extensive microstructural and mineralogical evaluations on the simulated final waste forms to establish the stabilization mechanisms and the fate of the contaminants in the waste forms.

Benefits

This work will provide a novel low-temperature process for treating and stabilizing fission products generated from D&D processes and cleanup of HLW tanks. This technology will complement high-temperature processes to treat fission-product wastes.

This technology directly addresses waste streams at various DOE sites, primarily at Hanford and Savannah River. In addition, this work will be critical to the ongoing cleanup work at Rocky Flats, Idaho National Engineering Laboratory, Los Alamos National Laboratory, and Oak Ridge National Laboratory.

The technology generates no secondary wastes. Moreover, the approach is relatively low-cost and has only minimal energy requirements, making it extremely attractive for providing a high return on investment.

Technology Transfer/Collaborations

During the initial stages of the project, the University of Illinois at Urbana-Champaign (Advanced Center for Cementitious Materials) will collaborate in the mineralogical evaluations and identification of stabilization mechanisms for the contaminants in phosphate ceramics.

After development of laboratory-scale final waste forms, industrial partners involved in waste solidification will be identified and pilot-scale stabilization will be conducted. Successful S/S by chemically bonded ceramics of actual waste streams containing fission products will have immediate use in cleanup efforts at various DOE sites, especially Hanford and Savannah River. Onsite demonstrations will be sought through concurrence from EM staff. Such an association will be a stimulus for collaboration between industry, universities, ANL, and DOE to ensure successful technology transfer to end users.

Keywords

phosphate ceramics, low-temperature, cesium, strontium, technetium, intercalation, partitioned, fission products, waste forms, solidification, stabilization, zirconium phosphate, magnesium phosphate, titanium phosphate, immobilization, chemical fixation, physical encapsulation

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TTP Number: CH26C344

Comprehensive Supernatant Treatment

Presenter: Zane Egan, Oak Ridge National Laboratory[1]

EM Focus Area: high-level waste tank remediation

Task Description

This task involves testing of sorbent materials for removing cesium, strontium, and technetium from the saline solutions in DOE storage tank supernatant at Oak Ridge and other sites. Staff at Oak Ridge National Laboratory (ORNL) are recovering and treating the liquid (supernatant) portions of Melton Valley Storage Tank (MVST) waste in a hot cell to separate and remove the radionuclides. Batch tests will be used to evaluate and select the most promising materials for supernatant treatment to reduce the amount of waste for final disposal. Small column tests will be made on selected sorbents to verify the batch data and to obtain additional data for process design. Efforts will be made to obtain samples of tank supernatant from Hanford for comparison.

The sorption tests will emphasize evaluation of newly developed sorbents and engineered forms of sorbents such as crystalline silicotitanates and SuperLig® materials. Methods will be evaluated for recovering the radionuclides from the sorbents. This will include evaluating conditions for eluting ion exchange resins, as well as evaluating the stability and storage properties of some of the inorganic sorbents that bind the radionuclides irreversibly.

A final report will summarize the results, along with recommendations for unit operations that could be used to separate and concentrate radionuclides from DOE storage tank supernates at Oak Ridge and other sites. This program will also provide input to the supernatant treatment process demonstration projects at ORNL.

Technology Needs

DOE is faced with remediating millions of gallons of high-level and low-level radioactive waste in underground storage tanks at various sites, including Oak Ridge, Hanford, Savannah River, and Idaho. A large portion of the waste is in the form of liquid solution (supernatant), which contains the soluble radionuclides along with high concentrations of sodium and potassium salts. The radioactivity is derived primarily from cesium, strontium, and technetium. In many cases the radionuclides constitute only a small portion (<1%) of the waste. If these radioactive components could be removed and concentrated, the volume of waste to be disposed of or stored as HLW could be reduced by a factor of 20 to 100.

Technical Approach

Supernatant samples have been retrieved from Melton Valley Storage Tanks W-25 and W-29 and characterized. These supernatants have many similarities to supernatants in tanks at other DOE sites. They are used to test various sorbents, including resorcinol-formaldehyde (R-F) resin; crystalline silicotitanate (CST); sodium cobalt hexacyanoferrate; potassium cobalt hexacyanoferrate; sodium titanate; and ion exchange resins such as Duolite CS-100, Amberlite IRC-718, Reillex™ HPQ and 402, and SuperLig®644, for removing cesium, strontium, and technetium from the highly alkaline, saline solutions. Many of these sorbents have been proposed for waste treatment, but most have not been tested on actual waste solutions.

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[1] Managed by Lockheed Martin Energy Research Corp., for the U.S. Department of Energy under contract DE-AC05-96OR22694.

Initially, batch tests are used to evaluate and select the most promising materials for supernatant treatment. Candidate sorbents for cesium removal include the R-F resin, CST, and hexacyanoferrates. Primary candidates for strontium removal are sodium titanate, silicotitanate, and Amberlite IRC-718. Reillex™ HPQ anion exchange resin has been proposed for pertechnetate ion removal. New engineered forms of some of the inorganic sorbents such as the CSTs and immobilized crown ethers will be tested as they become available. Sodium and potassium are competitors for cesium removal, and nitrate can be a competitor for pertechnetate exchange. The rate of removal is also an important parameter, as well as the loading capacity of each sorbent.

In the batch tests, 5 to 10 mL of supernatant are mixed with 1 to 100 mg of sorbent, and the amount of radionuclide removal is measured. Based on the batch test results, small column tests will be made on selected sorbents to verify the batch data and to obtain additional data for process design. Efforts will be made to obtain samples of tank supernatant from Hanford for comparison.

Most of the sorption studies have focused on radionuclide removal. Additional efforts will be directed toward elution or stripping and on the storage or disposition of loaded sorbents that cannot be eluted.

Accomplishments

Approximately 1 L of supernatant from MVST W-25 was prepared for batch tests by filtering it through 0.45-μm nylon filters to remove the particulates. The specific gravity and the total solids content of the supernatant were 1.232 g/mL and 0.338 g/mL, respectively. The pH was 12.6. About 94% of the activity in the supernatant is contributed by ^{137}Cs. Other radionuclides in the supernatant include ^{134}Cs, ^{60}Co, and ^{90}Sr. The major cations in the supernatant are sodium (3.87 *M*) and potassium (0.36 *M*) and the major anions are nitrate (3.8 *M*) and chloride (0.1 *M*). Smaller amounts of aluminum, chromium, zinc, and calcium are present.

The distribution coefficients and percentage removal of cesium from MVST W-25 supernatant using several ion-exchange materials have been measured. The ion exchangers tested include R-F resin from Boulder Scientific, CST (from Sandia National Laboratories), Duolite CS-100 (Rohm and Haas), granular and powdered potassium cobalt hexacyanoferrate, and composite microspheres containing sodium and potassium cobalt hexacyanoferrates in hydrous titanium oxide and phosphate (prepared at ORNL). In typical experiments, 10 mL of supernatant was mixed with 50 mg of sorbent for periods ranging from 15 minutes to 144 hours. The cesium distribution coefficients were 34 to 44 mL/g for CS-100, 138 to 764 mL/g for the R-F, 451 to 958 mL/g for the CST, and 26,000 to 46,000 mL/g for granular potassium cobalt hexacyanoferrate.

Nine different ion exchangers have been tested to determine the removal of strontium from MVST supernatant. The exchangers tested were Amberlite IRC-718, sodium titanate, CST, R-F, hydrous titanium oxide/polyacrylonitrile (TiO-PAN), sodium titanate/polyacrylonitrile (NaTiO-PAN), titanium monohydrogen phosphate microspheres, Duolite C-467, and Chelex 100. The inorganic ion exchangers outperformed the organic resins in removing the strontium, with the fine powders of NaTiO and CST giving the best results. For the organic resins tested, Duolite C-467 gave the most favorable results overall.

Several sorbents, including Reillex™ HPQ, Reillex™ 402, Amberlite IRA-904, and Amberlite IRA-400 were tested in batch tests for removing pertechnetate from MVST supernatant. All of the anion exchangers removed the pertechnetate anion reasonably well. The hydroxide forms of the exchangers appeared to be superior to the nitrate forms. Overall, the hydroxide form of Reillex™ 402 gave the most promising results.

Benefits

A final report will summarize the results and give recommendations for unit operations that could be used to separate and concentrate radionuclides from

DOE storage tank supernatants at ORNL and other DOE sites. Technologies evaluated in this task are expected to apply to the remediation of tank waste supernatants at most DOE sites, particularly highly alkaline supernatants that contain high concentrations of salts.

Separation and concentration of the soluble radionuclides would result in a much smaller amount of radioactive waste for disposal or long term storage. Removal of the radioactive components would also reduce shielding requirements and make downstream handling much easier for removing nitrates and any other toxic or hazardous components in the salt solution.

Results from this program will directly influence and provide input to demonstration projects currently under way at ORNL. These demonstrations involve removing cesium and other radionuclides from supernatants from the MVSTs.

Keywords

supernatant, tank waste, cesium, strontium, technetium, ion exchange

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TTP Number: OR06C341

Hot Demonstration of Proposed Commercial Nuclide Removal Technology

Presenter: Doug Lee, Oak Ridge National Laboratory[1]

EM Focus Area: high-level waste tank remediation

Task Description

This task covers the development and operation of an experimental test unit located in a Building 4501 hot cell within Building 4501 at Oak Ridge National Laboratory (ORNL). This equipment is designed to test radionuclide removal technologies under continuous operation on actual ORNL Melton Valley Storage Tank (MVST) supernatant, Savannah River high-level waste supernatant, and Hanford supernatant. The latter two may be simulated by adding the appropriate chemicals and/or nuclides to the MVST supernatant.

The technologies tested will be housed in modules that can be attached to the experimental system inside the hot cell and continuously fed the test supernatant until the nuclide of interest exhausts the module capacity. Ultimately, the technologies being developed will be transferred to an end user with the help of the Tank Focus Area (TFA). This task complements the work being done under the ESP task "Comprehensive Supernatant Treatment" by using larger scale, continuous equipment to verify and expand the batch studies done by that task.

The experimental unit will be tested by removing cesium using the ion-exchange materials proposed for the ORNL cesium removal central processing unit (CPU) and tested in batch tests by the Comprehensive Supernatant Treatment task, at a scale that passes up to 20 L of MVST supernatant continuously through the test module until the cesium "breaks through." This may require anywhere from 5 to 10 resin or test volumes (TV) up to more than 1000 TV of supernatant to pass through the module. This work will support the design of the cesium removal CPU demonstration at ORNL.

To test materials provided by the ESP, the experimental unit will be operated at a scale of 1 to 2 L per test. Testing will consist of using the modules or systems supplied by the ESP for cesium removal until the unit has reached its capacity. MVST supernatant, Savannah River high-level waste supernatant, Hanford supernatant, and MVST supernatant modified to simulate Hanford or Savannah River supernatant will pass through the module at a prescribed flow rate, and the effluent from the module will be passed through a gamma detector for analysis on line. The effluent will also be collected in fractions for later analysis as required. The volume of supernatant passed through the test module until 50% breakthrough (or other appropriate end point) and exhaustion of capacity will be determined. The capability for testing actual supernatant treatment technologies can be used for other tests based on requests by the TFA and the ESP.

Once testing of cesium removal has been completed for the desired modules, experiments will begin on the removal of other nuclides of interest, which may include ^{90}Sr, ^{99}Tc, ruthenium, and/or others. These isotopes require different resins for removal than cesium does. After the initial testing of these materials in the Comprehensive Supernatant Treatment task, they will be tested in the continuous flow system. The materials supplied to remove ^{99}Tc may be produced and tested in other ESP programs.

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[1] Managed by Lockheed Martin Energy Research Corp., for the U.S. Department of Energy under contract DE-AC05-96OR22694.

Technology Needs

Radionuclides represent only a small fraction of the components in millions of gallons of storage tank supernatant at various sites, including Oak Ridge, Hanford, Savannah River, and Idaho. Most of the radioactivity is contributed by cesium, strontium, and technetium and high concentrations of sodium and potassium salts. The purpose of this task is to test and select sorbents and commercial removal technologies supplied by ESP for removing and concentrating the radionuclides, thereby reducing the volume of waste to be stored or disposed.

Technical Approach

A 60-L supernatant sample was retrieved from MVST and characterized. This supernatant has many similarities to supernatant in tanks at other DOE sites. These supernatant will be used in testing various sorbents, including resorcinol-formaldehyde (R-F) resin, potassium cobalt hexacyanoferrate, crystalline silicotitanates, SuperLig®644, and other cesium removal materials supplied to the ESP from commercial manufacturers. Many of these sorbents have been proposed for waste treatment, but most have not been tested on actual waste supernatant solutions in a simulation of actual operating conditions. Several additional sorbents for other radionuclides will be tested as they become available in a form that can be used in the cell.

Initial candidate sorbents for cesium removal are the R-F resin and the granular potassium cobalt hexacyanoferrates. Sodium and potassium are competitors for cesium removal. In the continuous column tests of the above materials, 5 to 50 mL of sorbents are placed in a column and the supernatant to be treated is passed continuously through the bed until the resin is at least 50% exhausted.

The results of these tests will be compared to the batch results and small column tests results obtained in the Comprehensive Supernatant Treatment task. The results will be used to supply the TFA's Cesium Removal Demonstration Project with the information to determine design parameters. The rate of removal, resin required, and regeneration requirements are important design parameters, and the loading capacity of each sorbent will help to determine the size of the column required and help define the final volume of solid waste to be disposed.

For testing of the ESP modules, the experimental unit will be operated at a scale of 1 to 2 L per test. A large sample (+20 L) of MVST supernatant will be acquired for the module testing so that all modules can be evaluated using the same feed. The ESP modules or systems will be run until the unit has reached its capacity. Feed supernatant (MVST supernatant and MVST supernatant modified to simulate Hanford or Savannah River supernatant) will pass through the module at a prescribed flow rate, and the effluent from the module will be passed through a gamma detector for analysis on line. The effluent will also be collected in fractions for later analysis as required. The volume of supernatant passed through the test module until 50% breakthrough and exhaustion of capacity will be determined.

In FY 1996 and FY 1997, the tests will be continued using ESP-supplied modules to remove cesium, strontium, technetium, and other nuclides as requested by the ESP. Tests may include demonstrating the removal of technetium from MVST supernatant using materials and methods such as solvent extraction and special ion exchange materials developed by other ESP programs. In addition, MVST supernatant may be supplied to these developers after it has been treated for cesium and/or strontium removal in the earlier tests. This will be followed by cleanup and decontamination of the experimental facilities, and documentation of the results. The final product will be a data base and a final report that summarizes the results and makes recommendations for unit operations that could be used to separate and concentrate radionuclides from DOE storage tank supernatant at Oak Ridge and other DOE sites.

Accomplishments

In FY 1995, experimental equipment for the cesium removal project was installed in hot cell C, and the procedures used during the experiment, and several ion-exchange material tests were completed. The equipment consists of tanks, pumps, tubing and fittings, filters, instrumentation, and connections for testing cesium removal materials in a continuous flow system. System capabilities include remote operation, online monitoring of the column effluent to detect cesium breakthroughs from the material in the module, and the ability to treat ion-exchange resin in the module with any desired eluent or wash solution and monitor the effluent for cesium removal from the module.

The column feed tank receives supernatant from the storage tank through 0.45-µm filters, and the module effluent goes through 0.45-µm filters before passing through the detector. The column can be treated in place to allow repeated cycling of the resin between cesium loading and removal, which is counted before and after elution, and loaded columns can be drained, capped, and stored in the cell for future testing or disposal.

The feed supernatant for the tests was obtained from MVST W-27, in April 1995. Approximately 56 L of the supernatant is in storage in building 4501. Tank W-27 supernatant is at pH 7.2 and has the lowest potassium and ^{137}Cs levels of the available tanks, allowing the supernatant to be more easily handled than that from other tanks. For some absorber tests, this supernatant will be adjusted back to the pH standard in other tanks, pH ~12.5 to 13.0. Analysis of the present sample after pH adjustment to 12.8 and filtration showed ~9.3 E-6 Ci/mL of ^{137}Cs.

The first experiment used R-F resin obtained from Jane Bibler, Savannah River Technology Center. The feed rate during operation was ~1.4 mL/min, and resulted in a feed rate of ~7 CV/h. The original 12.5 cm^3 of resin shrank to 11.5 cm^3 when feed started to flow through the bed and remained at that volume through the run. The fractions were weighed, and samples taken for counting the ^{137}Cs. The column volumes to 50% breakthrough were ~45. During the run, ~0.5 L of feed containing 4.42 mCi of ^{137}Cs was fed to the column.

A second experiment was done with R-F resin in which the feed rate through the bed was reduced to ~2.8-3.0 CV/h. During the first 4 CV of feed through the bed, the bed volume decreased from the original 12.5 to ~10.6 cm^3, which changed the CV per hour rate to ~2.9 to 3.0. After ~25 CV, the bed volume was 10.2 cm^3. The final bed volume after the run was 9.9 cm^3. The 50% breakthrough occurred at ~40 CV, and the shape of the curve was very similar to that in the first R-F run.

Another experiment used CS-100. The feed rate through the column was set at ~0.7 cm^3/min, which is ~2.9 bed volumes per hour, and was constant through the run. Flow was continued until the in cell detector showed that more than 60% breakthrough had been achieved. The run was continued to more than 80% breakthrough. The column volumes to 50% breakthrough were ~12.5. During operation, the column bed height remained constant, and no change in color or appearance was seen.

In addition to the above runs, experiments using SuperLig®644 resin (IBC Corporation) and additional R-F resin with a series of five loading/elution/regeneration cycles, crystalline silicotitanates, and 3M web with SuperLig® were made. Final results have not yet been released.

Benefits

Technologies evaluated in this task are expected to apply to the remediation of tank waste supernatant at most DOE sites, particularly highly alkaline supernatant that contain high concentrations of salts. Separation and concentration of the soluble radionuclides, particularly cesium, would result in a much smaller amount of radioactive waste for disposal or long term storage. Removal of the radioactive components would also reduce shielding requirements and make downstream handling much easier for removing nitrates and any other toxic or hazardous components in the salt solution.

Keywords

supernatant, hot cells, cesium, technetium, strontium, waste characterization

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TTP Number: OR06C342

Development and Testing of Inorganic Sorbents for Radionuclide and Heavy Metal Separations

Presenter: Jack Collins, Oak Ridge National Laboratory[1]

EM Focus Areas: high-level waste tank remediation; contaminant plume containment and remediation

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 Oak Ridge National Laboratory (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 (silver, lead, mercury, nickel, zinc, chromium, and fluoride) from aqueous waste streams. However, in most cases, these sorbents are available commercially 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 by blocking pores and passageways to the exchange sites within the structures and adversely affecting 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 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.

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[1] Managed by Lockheed Martin Energy Research Corp., for the U.S. Department of Energy under contract DE-AC05-96OR22694.

Scientific Background

Inorganic ion exchangers (e.g., 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 molybdophosphate, manganese dioxide, sodium titanate) 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

- removing cesium from acid solutions (Idaho)
- removing strontium, technetium, and cesium from tank supernatants (Hanford, Oak Ridge)
- treating contaminated wastewater (all sites) to remove uranium, technetium, cobalt, lead, zinc, etc.
- 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 europium, cerium, and praseodymium from organic streams (solvent extraction processes, analytical wastes)
- removing fluoride from waste streams
- removing radionuclides (cesium, cobalt, europium, 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 grout. 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 new program involves the preparation of inorganic ion exchangers in the form of microspheres 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 molybdophosphate (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 effectively remove 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 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 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.

Technology Transfer

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.

Keywords

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

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TTP Number: OR16C342

Magnetic-Seeding Filtration

Presenter: David DePaoli, Oak Ridge National Laboratory[1]

EM Focus Areas: contaminant plume containment and remediation; high-level waste tank remediation; mixed-waste characterization, treatment, and disposal

Task Description

This task will investigate the capabilities of magnetic-seeding filtration for the enhanced removal of magnetic and nonmagnetic particulates from liquids. This technology applies to a wide range of liquid wastes, including groundwater, process waters, and tank supernatant. Magnetic-seeding filtration can be used in several aspects of treatment, such as 1) removal of solids, particularly those in the colloidal-size range that are difficult to remove by conventional means; 2) removal of contaminants by precipitation processes; and 3) removal of contaminants by sorption processes.

Technology Needs

This project will focus on two major target problems in liquid waste streams: removal of fine particulates and removal of dissolved contaminants. Particulates pose operational problems for treatment processes such as ion exchange and cause clogging in mixed waste incinerator injector nozzles. In addition, removal of particulates associated with contaminants is necessary to achieve required decontamination factors. DOE facilities at Hanford, Savannah River, and Oak Ridge need methods to remove colloids and fine particulates.

Removal of dissolved contaminants is frequently accomplished by sorption and precipitation processes. Examples of precipitation processes are those being considered to treat liquid low-level waste (LLLW) and newly generated liquid low-level waste (NGLLLW) at ORNL.[1] These baseline processes achieved acceptable decontamination factors for ^{90}Sr, ^{137}Cs, and ^{106}Ru in the laboratory; however, scaleup to a practical process has been hampered by the need to remove colloidal precipitates.

Proof-of-principle experiments have indicated the possibility of applying magnetic-seeding filtration to these processes. Newly devised sorbents (e.g., AMP-PAN, ZrP, etc.) have been developed for contaminant removal. These sorbents are applied by fluidizing them in the form of small particles in solution; thus, an efficient means of particulate removal, such as by magnetic filtration, will enable widespread use.

Although the magnetic-seeding filtration process has been demonstrated in principle, further theoretical and experimental work is necessary to quantitatively determine the effects of several process variables (such as magnetic susceptibility of particles, magnetic field strength, particle size, pH, flow-field conditions, etc.) upon filtration to evaluate the range of applicability to DOE waste streams. The planned laboratory, computational, and pilot testing is expected to result in a viable technology for colloidal particulate removal.

Scientific Background

Magnetic-seeding filtration is based on the interparticle forces that exist in magnetic fields. Particles that have paramagnetic properties (e.g., many iron and cobalt-containing compounds) can be caused to flocculate by applying a magnetic field;[2,3,4,5] in addition, paramagnetic particles and flocs are readily removed

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[1] Managed by Lockheed Martin Energy Research Corp., for the U.S. Department of Energy under contract DE-AC05-96OR22694.

by a simple high-gradient magnetic filtration process that consists of passing the solid/liquid suspension through a bed of ferromagnetic material on which a magnetic field is applied.

In many waste streams, however, none or only part of the particles have paramagnetic properties. Magnetic-seeding filtration, based on a concept that is already used in hydrometallurgical processes for separating weakly magnetic particles, is aimed at complete removal of particulates from suspension. This concept involves seeding a particle suspension with a relatively small quantity of colloidal paramagnetic particles. These particles act as seeds for heterogeneous flocculation. Because of the relatively high magnetic susceptibility of the added particles, the flocs resulting from heterogeneous flocculation have paramagnetic properties and may be readily removed by a high-gradient magnetic filter.

The novel ideas of the proposed work are to 1) employ magnetic seeding to flocculate both paramagnetic and diamagnetic particles, and 2) apply the process to hazardous waste streams. The mechanism of heterogeneous flocculation of particles in the suspension with added seeding particles was theoretically explained by Brownian flocculation and trajectory analysis models.[2,3,5] The basic principle is that superparamagnetic particles move fast in a magnetic field, resulting in a high frequency of collisions with other para- and dia-magnetic particles. Furthermore, flocculation occurs between the resulting flocs. The particle and floc population has been studied using bivariate population balance models, with the particles characterized by size and magnetic susceptibility.

Technical Approach

This task comprises several technical subtasks, including 1) a survey and evaluation of DOE waste streams for the applicability of magnetic-seeding filtration; 2) laboratory studies of magnetic-seeding filtration on precipitation processes, fluidized sorbent processes, and removal of solids from simulated and/or actual DOE waste streams; 3) fundamental modeling aimed at developing predictive tools for the efficiency of high-gradient magnetic-seeding filtration; and 4) pilot-scale demonstration of magnetic-seeding filtration on applicable waste stream(s).

To survey the applicability of magnetic-seeding filtration to DOE waste streams, contact will be made with other researchers of solid/liquid separations as well as EM-30 and EM-40 representatives. The magnetic susceptibility of waste samples and/or their surrogates will be measured, and simple small-volume batch tests of magnetic flocculation, with and without seeding, will be performed to determine the effectiveness of magnetic separation processes on these streams.

The effectiveness of the magnetic-seeding filtration technique will be investigated through experimental and theoretical work. For initial experimental testing of this process, well-characterized particles of materials such as hematite or magnetite will be added to suspensions of known properties such as suspensions of polystyrene microspheres. The suspensions will then be flowed through a magnetic filter. The relevant process variables will include particle properties such as size, concentration, zeta potential, and magnetic susceptibility, as well as magnetic field strength, and input flow rate.

At the filter inlet and exit, samples will be taken at specific time intervals to measure solids concentrations to determine separation efficiency under various operating conditions. This work will be coordinated with computational studies that will further investigate particle interactions in a magnetic field and will study particle collection by a magnetic filter.

A major contribution of the modeling studies will be the introduction of magnetic forces into existing deep-bed-filtration models that are based on trajectory analysis.[6] The result will be a model that can be used to predict magnetic filter performance.

After completing these controlled studies that will define the effects of the governing parameters on particle removal, testing will be aimed at contaminant removal by precipitation and sorption processes.

Laboratory testing will be conducted using materials characteristic of the ORNL NGLLLW precipitation process and with several types of sorbent particles. In addition, solid-liquid separation tests will be conducted with surrogates or samples of waste streams that are identified during a survey of DOE sites. The applicability of the process will be further tested through pilot demonstration of magnetic-seeding filtration with the NGLLLW process and/or other waste streams.

Benefits

This project will benefit all DOE sites by 1) evaluating the capabilities of magnetic-seeding filtration for solid/liquid separations, 2) providing data for the application of magnetic separations to precipitation processes, 3) providing useful information for application of magnetic seeding to processes such as treatment of tank supernatants and mixed waste, and 4) evaluating the applicability of magnetic separations to specific DOE streams through laboratory testing of samples. Furthermore, this project, through mathematical modeling and experimental testing, will result in predictive tools for testing the applicability of magnetic-seeding filtration under various operating conditions.

Technology Transfer/Collaborations

The fundamental modeling work will be performed in collaboration with Georgia Institute of Technology. This interaction serves education and provides a means to transfer ideas and experience.

Keywords

magnetic seeding, magnetic flocculation, magnetic filtration, solid-liquid separation

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Salt Splitting with Ceramic Membranes

Presenter: Dean Kurath, Pacific Northwest National Laboratory[1]

EM Focus Area: high-level waste tank remediation

Task Description

The purpose of this task is to develop ceramic membrane technologies for salt splitting of radioactively contaminated sodium salt solutions. This technology has the potential to reduce the low-level waste (LLW) disposal volume, the pH and sodium hydroxide content for subsequent processing steps, the sodium content of interstitial liquid in high-level waste (HLW) sludges, and provide sodium hydroxide free of aluminum for recycle within processing plants at the DOE complex. Potential deployment sites include Hanford, Savannah River, and Idaho National Engineering Laboratory (INEL). The technical approach consists of electrochemical separation of sodium ions from the salt solution using sodium (Na) Super Ion Conductors (NaSICON). As the name implies, sodium ions are transported rapidly through these ceramic crystals even at room temperatures.

Technology Needs

Many radioactive aqueous wastes in the DOE complex have high concentrations of sodium, which negatively affects waste treatment and disposal operations. Sodium can decrease the durability of waste forms such as glass and contributes to large disposal volumes. Waste treatment processes such as calcination, cesium ion exchange, and sludge washing are made less efficient and more expensive because of the high sodium concentrations. Some disposal strategies[1,2] call for adding more sodium to the wastes as they are prepared for conversion to final waste forms. Separation and recycle of sodium from radioactive wastes can potentially reduce costs by reducing waste disposal volumes, improving the efficiency of waste treatment processes, and avoiding the procurement of additional chemicals.

Scientific Background

The technology being developed involves using an electrochemical salt-splitting process based on inorganic ceramic membranes, as shown in Figure 1. In this process, the waste is added to the anode compartment of the electrochemical cell, and an electrical potential is applied to the cell, subsequently driving sodium ions through the membrane while most other cations (e.g., K^+, Cs^+) are rejected by the membrane. The charge balance in the cell is maintained by the electrolysis of water. The accumulation of potentially flammable gas mixtures can be prevented by providing adequate volumes of a sweep gas or by using oxygen and a gas diffusion electrode. As H^+ is generated in the anode compartment, the pH drops while the production of OH^- in the cathode compartment results in a rise in pH as sodium hydroxide is produced.

The ceramic membranes are from a family of materials known in the electrical battery industry as sodium (Na), super fast ionic conductors (NaSICON). The unique characteristic of NaSICON ceramics is that they possess channels within the crystal structure for fast sodium ion conduction. Silica tetrahedra "rings" and sodium and heavy metal ions form the structure around these channels, which are filled with highly mobile sodium ions. The primary NaSICON compo-

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[1] Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

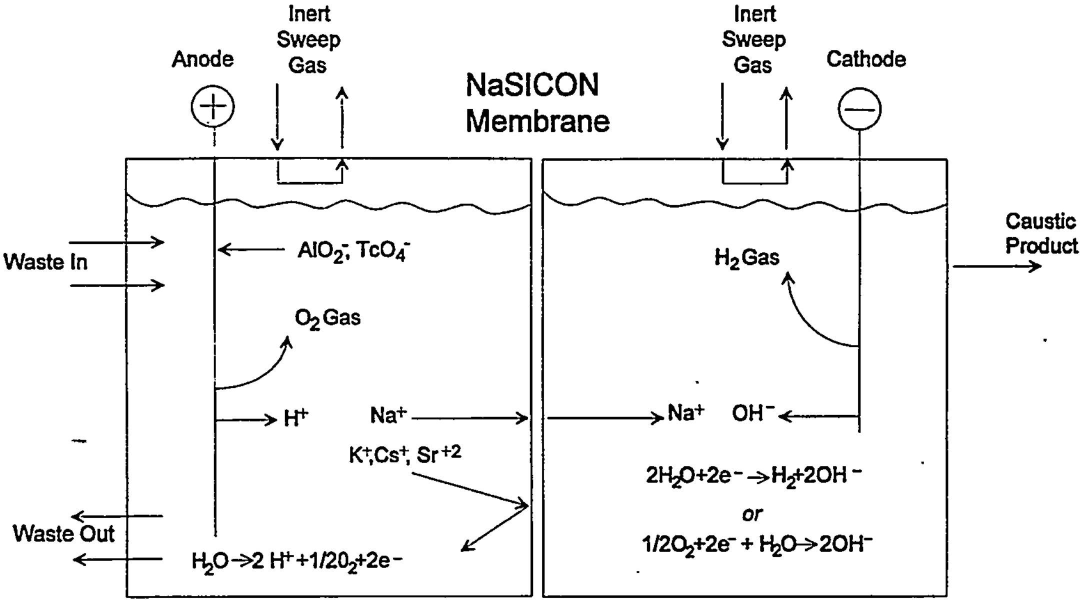

Figure 1. Schematic of an electrochemical process using the NaSICON membrane. Anolyte Composition: Hanford Simulant: 1.5 M $NaNO_3$, 0.2 M $Al(NO_3)_3$, 1 M NaOH. Catholyte Composition: 1 M NaOH. Temperature: 70°C. Applied Potential: 8-10V.

sitions that have been investigated are based on rare earth (RE) ions (i.e., $Na_5RESi_4O_{12}$).

In contrast to conventional organic-based bipolar or ion exchange membranes used in salt splitting, ceramic-based membranes are much more resistant to gamma/beta radiation and are highly selective for sodium ions. This high selectivity is useful for minimizing the transport of fission products (e.g., ^{137}Cs) and nonradioactive components (e.g., K^+), parasitic hydronium conduction, and reducing membrane fouling by multivalent metal ions (e.g., Ca^{+2}, $Fe^{+2,3}$, Al^{+3}). Radiation effects on the organic membranes could lead to rapid failure and high maintenance costs.

Technical Approach

Initial investigations were directed at selecting and modifying membrane compositions compatible with the expected chemical and radioactive environment. FY 1996 work consists of completing a preconceptual design of a ceramic membrane-based salt splitting process for sodium separation and caustic recycle, manufacture and nonradioactive demonstration testing of a unit cell of this design, preparing for radioactive testing, and an applications study. The preconceptual design is primarily to distinguish critical issues for testing and provide a vision for potential users. Work in FY 1997 is expected to include one or more bench-scale demonstrations with actual wastes and nonradioactive testing of the process at the pilot-scale.

Accomplishments

Rare earth-based NaSICON (RE-NaSICON) membranes were fabricated, tested, and evaluated against an initial set of criteria developed on the basis of potential applications. These tests confirmed the high selectivity of RE-NaSICON for sodium ions relative to hydronium, cesium, aluminum, and strontium ions in alkaline waste and slightly acidic solutions. Testing of membrane samples irradiated with a ^{60}Co gamma source indicated an initial decrease in conductivity that recovered after current was passed. Ionic conductivities and current densities achieved in dysprosium-based NaSICON were comparable to those of bipolar or cationic organic membranes. Excellent compatibility with basic or even slightly acidic solutions was observed with dysprosium-based NaSICON; however, mass loss and surface cracks were observed in strong acids. Acid-resistant ceramic compositions are being developed under another DOE program.

Recirculating cell experiments with an advanced RE-NaSICON membrane were conducted at Ceramatec Inc. to demonstrate sodium removal from a Hanford tank waste simulant. The anolyte pH decreased from 12.6 to ~7 as 60 g of sodium ions were transported through the advanced RE-NaSICON membrane (Figure 2). As pH levels decreased to <9, precipitation of aluminum-hydroxide (or salts) occurred. However, the throughput of the cell appeared to fall only slightly.

Benefits

Potential applications have been identified at Hanford, INEL, and Savannah River and include 1) caustic recycle, 2) pH adjustment and reduction of competing cations for enhancement of cesium ion exchange processes, 3) sodium reduction in high-level waste sludges, and 4) sodium removal from acidic wastes to facilitate calcining.

Hanford and Savannah River sites have large inventories of radioactively contaminated wastes that consist primarily of sodium salts. Separation and recycle of the caustic from the tank wastes could reduce the waste disposal volume and avoid the cost of purchasing fresh caustic. Potential uses for the caustic include sludge leaching, regeneration of ion exchange resins, corrosion inhibition in carbon steel storage tanks, and tank waste retrieval.

The efficiency and chemical stability of some cesium ion exchange materials is decreased at high pH levels. For example, the distribution coefficient (K_d) for a powder form of crystalline silicotitanate (TAM-5-11) was reported to increase from about 150 mL/g at pH 14.1 to about 1600 at pH 12 in a Hanford simulant.[3] This difference would result in a tenfold reduction in the required amount of exchanger. This reduction in pH would also permit the use of granular

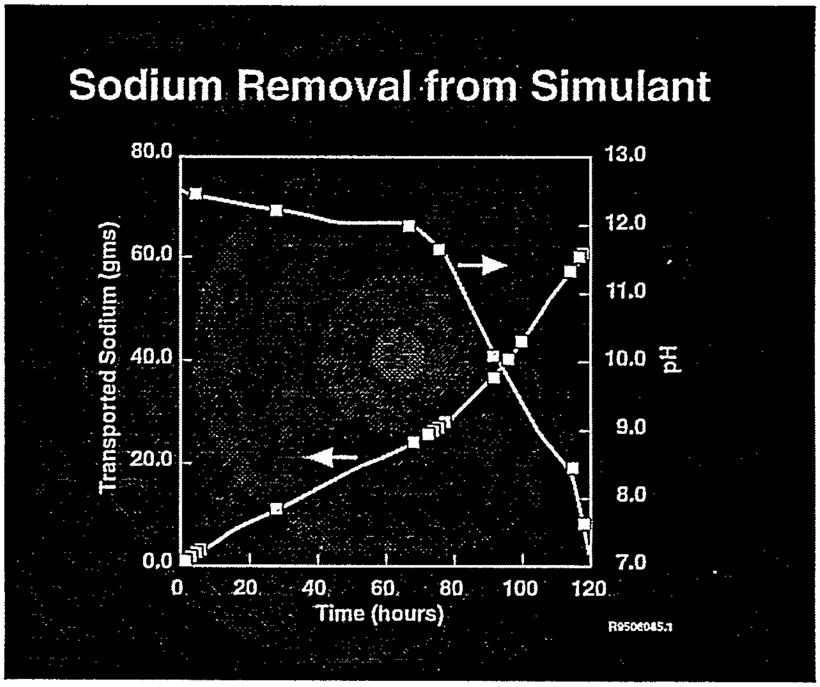

Figure 2. Bench-scale process demonstration with Hanford waste simulant.

potassium cobalt hexacyanoferrate(II). This material has extremely high cesium K_ds^4 but hasn't been considered for application at Hanford because it is unstable in solutions having a pH >13.

Many of the sludges at Hanford and Savannah River will possess interstitial liquid containing sodium concentrations as high as 5 M. Current plans are to remove the sodium by dilution of the interstitial liquid with 0.01 M sodium hydroxide and sodium nitrite with subsequent solid/liquid separation. Electrochemical sodium separation offers the potential for directly removing sodium from the sludge, thereby reducing water usage and radionuclide carryover during solid/liquid separation.

Sodium removal is also considered beneficial for treating 5.7 million gallons of sodium-bearing waste at the Idaho Chemical Processing Plant (ICPP). Calcination at high temperatures is an established process at the ICPP used to convert nonsodium bearing liquid waste into a granular solid. Sodium tends to cause bed agglomeration, anion volatilization, and alpha aluminum formation. Current mitigation strategies include chemical additions or calciner equipment modifications. These strategies slow processing rates and increase waste volume and costs. Removing the sodium before calcining would allow direct calcination of the waste and provide caustic for recycle.

Technology Transfer/Collaborations

Collaborations are under way with Westinghouse Savannah River Company in the design of electrochemical cells for radioactive waste processing and assessment of caustic recycle applications for alkaline supernates and sludge leaching/washing solutions. A sodium-bearing waste simulant will be provided for an initial nonradioactive test at INEL. WHC will participate in design reviews of the preconceptual design, applications studies and process demonstrations on Hanford supernate if applicable.

Ceramatec Inc. (Salt Lake City, Utah) is being aided by Pacific Northwest National Laboratory to adapt nonradioactive electrochemical waste treatment technology to a radioactive environment. Ceramatec Inc. is refining the manufacturing process to produce unit electrochemical cells incorporating the RE-NaSICON membrane. The unit cells are expected to include bench, pilot, and full scale testing. A production run will be completed followed by electrical and mechanical testing to identify and resolve production issues. Initial testing of the unit cells with simulants will be conducted at Ceramatec.

Ceramatec Inc. is funded by DOE's Office of Energy Efficiency and Renewable Energy under a separate program to provide technology that would permit the salt splitting of pulp/paper mill waste into a sodium hydroxide stream and a sulfuric acid product. The primary milestone in this program is development of a NaSICON-type product that is compatible with strong acids. This program is being monitored because some applications require or may benefit from an acidic processing environment.

Anil Virkar and Jan-Fong Jue, University of Utah, participated in this task in FY 1995 and continue membrane development. Materials and Systems Research is funded under the Small Business and Innovative Research program to examine new types of NaSICON membranes.

Keywords

NaSICON, salt splitting, caustic, sodium hydroxide, separation, recycle

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Comparison of Organic and Inorganic Ion Exchange Materials for Removal of Cesium and Strontium from Tank Waste

Presenter: Garrett Brown, Pacific Northwest National Laboratory[1]

EM Focus Area: high-level waste tank remediation

Task Description

This work is part of an ESP task to develop high-capacity, selective, solid extractants for cesium, strontium, and technetium from nuclear wastes. Pacific Northwest National Laboratory (PNNL) staff are investigating novel ion exchangers for use in nuclear waste remediation (groundwater, high-level waste (HLW), and low-level waste (LLW)). Waste components targeted for remediation include cesium, strontium, and technetium.

During FY 1995, experimental work at PNNL focused on batch distribution (K_d) testing in actual and simulated Hanford wastes, chemical and radiolytic stability of exchangers, column ion exchange testing in simulated Neutralized Current Acid Waste (NCAW), various site demonstrations (Idaho National Engineering Laboratory (INEL) and West Valley Nuclear Services (WVNS)) using subcontractor technologies, and technetium and strontium removal from groundwater and LLW. This summary focuses on the actual waste testing and results from the subtask on geologic barriers.

Technology Needs

Numerous selective ion exchangers (e.g., CS-100, resorcinol-formaldehyde (R-F) resin, SuperLig®644, IE-910, IE-911, TIE-96, NaTi, etc.) have been developed to remove trace levels of cesium and strontium from various matrices (e.g., acidic, caustic, high ionic strength, low ionic strength). A pressing need exists to evaluate these and other materials in direct side-by-side comparison experiments using actual Hanford HLW. The information obtained will directly impact decisions about HLW pretreatment and final waste disposition.

Groundwater matrices contain relatively high levels of alkaline earth cations and are qualitatively different than LLW or HLW. For this reason information is needed about strontium removal from groundwater.

Scientific Background

Hanford's 177 underground storage tanks contain a mixture of sludge, salt cake, and alkaline supernatant liquid. The highly caustic supernatant consists of concentrated aqueous solutions of $NaNO_3$/$NaNO_2$ and $NaAl(OH)_4$ salts with smaller quantities of K^+, CO_3^{-2}, SO_4^{-2}, and PO_4^{-3}. The salt cake consists primarily of dried sodium salts. The bulk of the water-soluble radionuclides (e.g., ^{137}Cs) are contained in the interstitial liquid, salt cake, and supernatant solutions. The insoluble sludge fraction consists of metal oxides and hydroxides and contains the bulk of the ^{90}Sr. Although the pretreatment and disposal strategies are still being defined, most strategies contain a solid/liquid separation of the supernatant and dissolved salt cake from the sludges followed by cesium and/or strontium ion exchange.

The matrices of groundwater and LLW systems are generally of lower ionic strength (typically 0.01 M) and different composition (consisting predominantly of calcium and bicarbonate ions) than those for HLW systems. Thus, specific testing is needed to determine the performance of ion exchange materials originally

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[1] Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

developed for HLW applications when in groundwater matrices. Conversely, the development of new ion exchange materials to remove contaminants from groundwater systems may result in materials suitable for LLW and HLW systems. Furthermore, the concentrations of contaminants in groundwater systems are often much lower than in LLW or HLW and require special precautions during testing to ensure that representative behavior is measured.

Technical Approach

This work provides a direct comparison of seven cesium and/or strontium-selective ion exchange materials for the pretreatment of actual and simulated Hanford tank waste. Cesium and strontium decontamination factors (DF), K_d, and lambda ($\lambda = K_d \times \rho_B$) values for each material are compared as a function of exchanger contact duration, solution composition, exchanger/waste phase ratio (150 to 1000), and multiple sequential contacts.

The actual double-shell slurry feed (DSSF) waste used in tests is a volume composite from tanks 101-AW (70%), 106-AP (20%), and 102-AP (10%). The actual waste tests were conducted at 5.0 *M* sodium and 23°C with Na/Cs mole ratios that ranged from 100 to 500,000. Simulant testing was conducted at dilutions ranging from 7 to 0.2 *M* sodium, over a wide range of cesium concentrations (Na/Cs mole ratio from 50 to 500,000). The advantage of batch testing relative to column testing is that a large amount of equilibrium data (i.e., K_d or λ) can be obtained with relatively small amounts of waste at reduced cost per datum.

Simulant testing was conducted to develop procedures for contacting the actual waste and to provide data over a wider range of experimental conditions. During the actual waste testing, three separate contacting methods were used to provide information over a wide range of supernatant:exchanger phase ratios and are discussed below.

Cesium Addition Method

Four separate contacts involving 10 mL of waste and 0.067 g of exchanger were conducted with the actual 70% 101-AW DSSF composite waste. In three of these contacts, different amounts of non-radioactive cesium were added into the actual waste supernatant to provide equilibrium data at four different cesium concentrations. The amounts were chosen so that the equilibrium Na/Cs ratios of the tests bounded the Na/Cs ratio of the actual 70% 101-AW DSSF waste composite.

High DF Method

The supernatant from the previous method (without additional cesium) was contacted with an additional 0.5 g of exchanger to investigate the achievable decontamination factor. The large amount of exchanger was necessary to efficiently remove most of the ^{137}Cs.

High Phase Ratio Method

To adequately investigate the effect that interfering components have on cesium K_d, the supernatant:exchanger phase ratio was increased to match the expected distribution coefficient. The high phase ratio provides a large amount of interfering components relative to the number of exchanger sites and increases the impact of these components on equilibrium behavior.

The approach taken in the geological barriers subtask is to combine an inorganic ion exchanger synthesis effort with an active testing effort that looks at novel ion exchangers from a variety of sources. The synthesis effort makes use of our knowledge of mineral structures and the surface-chemical behavior of analogous naturally occurring ions to design new materials having high selectivity for contaminant ions. The testing effort employs radiotracers (e.g., ^{85}Sr) for measurements of ion exchanger performance at the levels typically found in groundwater systems.

Accomplishments

Seven ion exchange materials were evaluated for cesium, strontium, and metals uptake in side-by-side comparison tests using actual and simulated 101-AW DSSF waste. Actual waste testing required only 270 mL of solution and provides an estimation of the column loading performance of the seven materials. The actual waste results are summarized in Table 1 at the initial feed conditions of 5.0 *M* sodium, 0.48 *M* potassium, 23°C, and a Na/Cs mole ratio of 78,000. The equilibrium data are given as K_d (exchanger mass basis) and λ values (exchanger volume basis) to illustrate the effect of the bed density on the apparent performance. The λ value is useful for sizing ion exchange columns, and the K_d value is pertinent for assessing the impact of converting the loaded materials into a final waste form.

All the materials except NaTi removed cesium (IE-910, IE-911 > SL-644, R-F > TIE-96, CS-100). All materials demonstrated an affinity for strontium with the NaTi providing the greatest removal followed by IE-911, IE-910, and TIE-96. The organic exchangers SL-644, R-F, and CS-100 exhibited relatively low affinities and would not be useful for stronium removal.

In FY 1995 the geologic barriers subask focused on comparative testing of a variety of strontium ion exchange materials, both in groundwater and HLW systems. This testing demonstrated 1) a strong selectivity for strontium of silicotitanate, titanate, zeolitic, and micaceous ion exchangers relative to an organic resin exchanger (R-F), 2) a relatively slow approach to equilibrium (2 weeks for most exchangers) at the temperatures typical of groundwater systems, and 3) the need to incorporate an estimate of surface area into any measurement of the selectivity of an ion

Table 1. Actual waste testing results at feed conditions (5 *M* Na, 0.48 *M* K, and Na/Cs = 78,000)

Exchanger Description	Material Composition	Material Producer	Density[a] g mL^{-1}	Cs K_d mL g^{-1}	Cs λ mL g^{-1}	Sr K_d	Sr λ
IE-911	Silicotitanate	UOP	1.13	710	800	900	1000
IE-910	Silicotitanate	UOP	0.77[b]	910	700	700	540
TIE-96	Zeolite	UOP	0.77	21	16	250	190
NaTi	Sodium titanate	AlliedSignal	0.58[b]	NA[d]	NA	2100	1200
SL-644	Polymeric macrocycle	IBC Advanced Technologies	0.22[c]	500	110	90	20
R-F	Resorcinol-formaldehyde	Boulder Scientific	0.30	220	65	60	18
CS-100	Phenol-formaldehyde	Rohm & Haas	0.24	88	21	13	3

[a] ion exchange material density measured on a dry weight basis in 2 *M* NaOH unless otherwise noted
[b] bulk powder density (dry weight basis)
[c] measured in NCAW waste simulant
[d] not applicable, strontium ion exchange material

exchanger. In FY 1996, we have focused on testing of surfactant-modified inorganic exchangers for removal of pertechnetate from LLW and groundwater. This work has demonstrated very high degrees of removal (K_d as high as 400,000 mL/g) and shown that the adsorption can be nearly perfectly described by the Langmuir isotherm equation.

Benefits

The data collected in these development and testing tasks provide a rational basis for the selection and direct comparison of various ion exchange materials in simulated and actual HLW, LLW, and groundwaters. In addition, prediction of large-scale column loading performance for the seven materials tested is possible using 270 mL of actual waste solution. The method maximizes information while minimizing laboratory and process wastes.

Technology Transfer/Collaborations

The results of our testing activities have helped to guide our industrial partners (3M, AlliedSignal, and UOP) in the development of engineered forms of the ion exchangers. Experimentation with actual waste was completed in collaboration with the subtask "Batch Testing of Crystalline Silicotitanates," which is part of the PNNL Tank Waste Remediation System Pretreatment Technology Development Project.

Keywords

cesium, strontium, technetium, ion exchange, batch K_d, selectivity, actual Hanford high level waste, groundwater, 101-AW DSSF, SuperLig®644, CS-100, R-F, IE-910, IE-911, TIE-96, NaTi, sodium titanate, crystalline silicotitanate, micas, minerals, chemical and radiolytic stability

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TTP Number: RL36C342

Membrane-Based Separation Technologies for Cesium, Strontium, and Technetium

Presenter: Tom Kafka, 3M

EM Focus Areas: high-level waste tank remediation; facility transitioning, decommissioning, and final disposition.

Task Description

This work is one of two parallel projects that are part of an ESP task to develop high-capacity, selective, solid extractants for cesium, strontium, and technetium from nuclear wastes. In this subtask, Pacific Northwest National Laboratory (PNNL) is collaborating with 3M, St. Paul, Minnesota, working in cooperation with IBC Advanced Technologies, American Fork, Utah.

Subtask work began in FY 1992 to develop improved molecular recognition technology agents and implementing their use in the form of flow-through membranes. After selecting novel separation agents, the capacities, distribution coefficients as a function of feed composition, physical properties, and chemical and radiolytic stability of materials with demonstrated potential for application in radiochemical separations were determined.

3M developed a state-of-the-art method, the Empore™ membrane extraction technology, for enmeshing surface-active particles in a net-like matrix of polytetrafluoroethylene (PTFE) fibrils to form a membrane that has good integrity and handling strength and an extremely high particle surface availability. These membranes are formed into cartridges, within which the solution of interest is passed through or by the web, allowing the selective, solid extractant to remove the metal ion of interest. Under severe radiation fields PTFE becomes brittle, thus other materials of web construction have successfully complemented this original concept.

The densely packed membranes can achieve equal or better performance than ion exchange columns at higher flow rates taking advantage of the very high surface area provided by the use of small (10 μm) active particles. Samples were sent to PNNL for confirming tests using a ^{60}Co source. In addition, other membranes have been made with a range of support particles selected to meet DOE's needs.

Technology Needs

This subtask is designed to test the capacity, selectivity, and stability of selected sequestering agents in representative physical, chemical, and radiation environments. Emphasis is on developing and demonstrating extractants with potential applications in nuclear waste management that would result in major cost reductions and environmental benefits. Although contributions from this task should be useful in addressing a variety of problems in the DOE complex, specific applications at Hanford have been targeted.

Accomplishments

In FY 1995, a successful hot cell experiment was conducted at Idaho National Engineering Laboratory (INEL), in which the technology was used to remove cesium and strontium from acid radioactive waste. Also in FY 1995, technology demonstrations were conducted at the West Valley Demonstration Project and at Test Area North (TAN) at INEL in FY 1996 on dilute, moderate pH waste. A modular processing skid including active adsorber cartridges and effective prefilters, was developed as a part of the West Valley demonstration, and a duplicate unit was used at INEL.

At West Valley, the system was used to remove technetium and cesium from process water running at 0.1 gal/min for 8 days, or a volume of almost 1500 gallons. The technetium cartridge was loaded to a 50% breakthrough after processing ~90 gallons, and the cesium cartridge ran for 40 hours (~250 gallons) with no detectable breakthrough. The cesium in the feed was present at 1200 pCi/L, while the detection limit for the cartridge effluent was about two orders of magnitude lower. These results were particularly encouraging because the feed had already been processed through traditional ion exchange columns.

During an 80-h demonstration at TAN, cesium and strontium were removed to below drinking water standards: 1250 gallons were processed at a flow rate of 0.25 gal/min. Strontium was loaded to a 50% breakthrough after ~800 gallons. No detectable cesium breakthrough occurred for the entire demonstration, with a detection limit of 9 pCi/L. Again, this water had already been through the groundwater treatment facility. All other attempts to achieve this at TAN have been unsuccessful.

More technology demonstrations will be made during FY 1996, with the goal of applying the technology on an increasingly large scale in preparation for transfer to EM-30 and/or EM-40 in FY 1997.

Benefits

The cost of waste treatment depends on the ability to efficiently and selectively remove elements that complicate waste disposal. This technology emphasizes removal of the heat-emitting isotopes ^{137}Cs and ^{90}Sr to reduce the amount of waste glass routed to final disposal, thereby reducing the cost.

In addition, several nonradioactive elements in the waste must be incorporated in large amounts of glass to produce a stable waste form; for example, removing chromium from the waste streams would reduce the number of glass canisters required.

This technology can also be adapted to treat other waste streams.

Collaboration/Technology Transfer

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TTP Number: RL36C337

Cesium and Strontium Ion Specific Exchangers

Presenter: Steve Yates, AlliedSignal, Inc.

EM Focus Area: high-level waste tank remediation

Task Description

This work is one of two parallel projects that are part of an ESP task to develop high-capacity, selective, solid extractants for cesium, strontium, and technetium from nuclear wastes. In this subtask, Pacific Northwest National Laboratory (PNNL) is collaborating with AlliedSignal, Inc. (Des Plaines, Illinois) to develop inorganic ion exchangers that are selective for strontium and cesium from alkaline high-level waste and groundwater streams.

In FY 1995, the effort included exchanger screening (subcontracted to Professor Abraham Clearfield at Texas A&M University), exchanger preparation, and exchanger testing. The program thus allows the smooth and rapid transition of materials from laboratory discovery, through process development, scale-up, formation into engineered form materials, and testing by DOE sites where strontium or cesium problems exist.

In FY 1996, our primary goal will be demonstration of our strontium removal technology at DOE sites. We will work with interested sites to evaluate samples onsite, and thereby qualify our materials. The screening focus this year will be the development of cesium-specific exchangers for use in non-alkaline streams, while exchanger preparation and scale-up will focus on preparation of sodium nonatitanate for strontium uptake.

Technology Needs

This work is designed to facilitate the rapid preparation and evaluation of inorganic ion exchangers for testing, evaluation and eventual use by DOE sites. Emphasis is on developing and demonstrating ion exchange materials with potential applications in nuclear waste management that can result in major cost reductions and environmental benefits.

Although contributions from this task would address a variety of problems in the DOE complex, specific applications to high-level waste tanks have been targeted. Groundwater streams are also treatable with the same or related materials. The goal for FY 1996 is to prepare, characterize, and scale-up inorganic ion exchangers tailored for use with specific DOE waste streams, and to work with DOE sites to demonstrate the effectiveness of these exchangers under realistic conditions.

Scientific Background

Our program takes advantage of the inherent high selectivities and radiation stability of inorganic ion exchangers, and of the extensive background of Clearfield's group in preparing and studying these materials. The ion exchangers developed by our team derive their high selectivities from their structure, which sharply limits access to exchange sites to those ions with suitable ionic radii and energies of hydration. Control of this structure is achieved by different methods for each exchanger. Ion exchanger powders are then bound using inorganic binders into engineered form pellets. These pellets must be mechanically strong enough to resist crumbling during packing or pH cycling, but must be porous enough to retain rapid access to interior sites and high capacity.

Accomplishments

FY 1995 has been the first year that our team has been able to distribute our first product widely within DOE for testing. This product, sodium nonatitanate, is a layered inorganic ion exchanger that is highly selective for strontium from alkaline feeds, regenerable, and radiation hardy. Its method of preparation has been refined at lab and pilot-plant scale, and it can be prepared currently at the 10-kg batch scale. Inorganic binding technology has been developed to permit the material to be formed into durable, alkaline-stable pellets for use in ion exchange columns. Our sodium titanate is therefore available for testing in both powder and pellet form.

Sodium Titanate K_ds and Capacity

Distribution constant and capacity measurements were made with our strontium exchangers, as well as column studies. Among the highlights of this work were the demonstration that AlliedSignal strontium exchanger maintains its high selectivity in the presence of complexants such as oxalic or citric acids and EDTA, and that the capacity of this pelletized exchanger for strontium under dynamic column conditions is 2.0 meq/g (from 47.2 ppm strontium, 5 *M* sodium nitrate, 0.1 *M* sodium hydroxide feed). Column studies with sodium titanate after pelletization under column conditions showed that it has good mass transfer kinetics.

DOE Lab Results

Samples of our sodium nonatitanate powder have been tested by investigators at PNNL, Savannah River Technology Center, Los Alamos National Laboratory, and Oak Ridge National Laboratory (ORNL). Many tests are still in progress, but where they are complete, they have shown that sodium nonatitanate is a highly selective agent for removing strontium from aqueous streams, and also has an affinity for americium, uranium, and plutonium. AlliedSignal has also supplied larger samples to 3M for use in preparing Empore™ membranes containing our material. These were recently used successfully to remove strontium from Test Area North injection well water at Idaho National Engineering Laboratory. Engineered form exchangers have only recently become available, and currently are being tested at PNNL and ORNL.

New Cesium Exchangers

In the area of cesium removal for acid wastes, a new phosphate-type ion exchanger was developed based on modification of alkaline titanium phosphates. This ion exchanger can be prepared as a granular material, and shows a K_d for cesium of 25,000 mL/g from 0.1 *M* nitric acid. Capacities are expected to be high. Optimization of this material is in progress, along with testing at various acid concentrations etc., to understand the scope of utility of the material. We plan to scale-up this process as soon as this optimization is complete.

We have also developed a tetraphenylborate (TPB)-mica complex that completely precipitates Cs^+ from high Na^+ solutions. By simply washing the mica-Cs^+ TPB complex, the Cs^+ diffuses into the mica, reforming the sodium tetraphenylborate, which can be recovered and reused. The Cs^+ mica traps the Cs^+ permanently and it may be possible to eliminate the vitrification step. Potassium ion behaves the same way, but Cs^+ is preferred. Efforts to increase the selectivity for Cs^+ over K^+ by alteration of the structure of the boron ligand are in progress.

Benefits

Because the cost of nuclear waste treatment is strongly dependent on the volume of this waste, highly selective ion exchangers, which can remove troublesome radionuclides, can reduce this cost significantly. In particular, removing the heat-emitting isotopes ^{137}Cs and ^{90}Sr will reduce both the amount and activity in low-level waste and the volume of high-level waste forms. This technology also applies to the environmental sector, because materials developed for separating traces of strontium and cesium from voluminous liquid wastes are also well adapted to treat groundwater and other aqueous waste streams.

Technology Transfer

Our principal goal for FY 1996 is to transfer technology in the form of supply of inorganic ion exchangers to potential users or national labs working closely with potential users. Collaborations currently under way with 3M, Savannah River, PNNL, and ORNL will continue, and we expect new opportunities to demonstrate our technology to be identified during the year.

Keywords

cesium, strontium, ion exchange, HLW, groundwater, SRS, titanate, demonstration

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TTP Number: RL36C342

Chemical Derivatization to Enhance Chemical/Oxidative Stability of Resorcinol-Formaldehyde Resin

Presenter: Tim Hubler, Pacific Northwest National Laboratory[1]

EM Focus Area: high-level waste tank remediation

Description

The purpose of this work is to develop modified resorcinol-formaldehyde (R-F) resin with enhanced chemical/oxidative stability in conditions typically encountered in the remediation of radioactive waste tanks. R-F resin is a regenerable organic ion-exchanger developed at Savannah River Technology Center that is being considered for use in the selective removal of radioactive cesium from alkaline waste tank supernates at both the Hanford and Savannah River sites.

Technology Needs

Tank wastes at the Hanford and Savannah River sites contain highly alkaline supernate solutions of concentrated sodium and potassium nitrates in which large amounts of the water-soluble radionuclide, ^{137}Cs, are found. Economically, it is desirable to remove and concentrate the highly radioactive fraction of the tank wastes for vitrification, with the bulk of the waste being disposed of at relatively low cost. This particular tank pretreatment need may be met using the appropriate ion-exchange technology and materials.

Scientific Background

Duolite™ CS-100 is a phenol-formaldehyde (P-F) resin manufactured by Rohm and Haas Company (Philadelphia, PA), that is currently the baseline ion-exchanger for recovering radioactive cesium from alkaline tank waste supernates at Hanford. In 1990, R-F resin was shown to have substantially greater selectivity for cesium ion (versus sodium ion) than CS-100 resin.[1,2] Initial evaluations (measured by determination of distribution coefficients, K_ds) of different batches of the R-F resin showed some variability in the performance of the resin, so there was a need to understand the structure of R-F resin and the important synthetic parameters that may affect the eventual performance of the product.

Structure/function studies for R-F resin were initiated at Pacific Northwest National Laboratory (PNNL) under the Advanced Processing Technology Initiative (APTI) in FY 1994. These studies undertook preparation and characterization of R-F resin synthesized under a variety of conditions to establish the primary structure of the resin and to identify some of the important synthetic parameters critical for obtaining a quality ion-exchange product.

The primary structural unit of R-F resin was found to be a 1,2,3,4-tetrasubstituted resorcinol ring (Figure 1). Both nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopic techniques provided direct evidence for this structure. Solid-state ^{13}C cross polarization-magic angle spinning (CP-MAS) NMR spectra for ^{13}C label-enhanced resin showed the presence of two non-equivalent methylene group carbons as expected for a 1,2,3,4-tetrasubstituted resorcinol ring.

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[1] Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

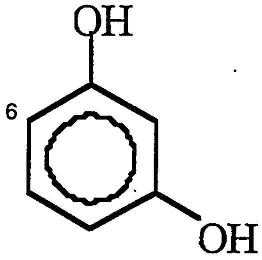

Figure 1. Resorcinol numbering scheme.

FTIR structural analysis for R-F resin showed a primary band at 802 cm^{-1} corresponding to aromatic out-of-plane C-H bending, which is indicative of the 1,2,3,4-tetrasubstituted ring pattern for the resorcinol unit. FTIR analysis also indicated the likely presence of some 1,2,4,5-tetrasubstituted and/or 1,2,4-trisubstituted resorcinol ring units, which comprise 15% or less of the polymer structure, by the presence of an IR band at 865 cm^{-1}. Additionally, elemental analyses obtained for R-F resin in both the H^+ and K^+ forms were consistent with a 1,2,3,4-tetrasubstituted ring structure.

Some of the important synthetic parameters for R-F resin were investigated, including curing temperature and particle size. Optimal curing of the R-F resin occurs between 105°C and 130°C; below this temperature range, insufficient crosslinking of the polymer resin occurs. The result is that the ion-exchange performance of the resin is reduced because the lower crosslinked resin has much lower selectivity for cesium ion. An upper limit of 130°C for curing temperature is suggested because significant organic decomposition of the resin was observed at 135°C during thermogravimetric analysis. Also, analysis of K_ds for R-F resin cured at temperatures above 135°C in an inert helium atmosphere showed reduction of cesium K_ds. The lower K_ds resulted from decomposition of the resin.

Oxidation effects on R-F resins were elucidated by correlating ^{13}C NMR spectra of the resins with their respective batch K_ds. These studies showed that as oxidation of the resin takes place, quinone, ketone, and ether groups become prominent functionalities in the resin, along with a simultaneous drop in the number of phenolic hydroxyl ion-exchange groups.

The optimal particle size for the R-F resin to be used in an ion-exchange process was found to be in the range of 20- to 50-mesh sized particles. Particles larger than 20 mesh gave lower K_ds because ion-exchange is diffusion limited in the larger particles. For particles smaller than 50 mesh, the greater surface area of the resin presented to the solution was more easily oxidized, or otherwise chemically degraded, with a simultaneous loss of ion-exchange sites.

Modified polymers of P-F and R-F resins were prepared to better assess the factors affecting chemical stability. The polymer resins were modified by incorporating fluorophenols and hydroxybenzoic acids into the polymer matrix. The results led to an understanding of the observed structure/performance characteristics of the P-F resins in relation to R-F resin.

It has been determined that both the R-F and P-F polymer resins are structurally similar with crosslinks in the 2- and 4- positions of the ring (Figure 1). R-F resin undergoes facile oxidation to form *p*-quinones (Figure 2) because the resorcinol ring is more activated toward oxidation (i.e., it is more electron rich) and there is a ring site readily available for oxidation that is *para* to a hydroxyl functionality. P-F resin (including CS-100), which has crosslinking similar to R-F resin, appears to be more chemically stable. This chemical stability arises because there is a less electron density present in the phenol aromatic ring and the position *para* to the hydroxyl function is generally alkylated (a methylene crosslinking group).

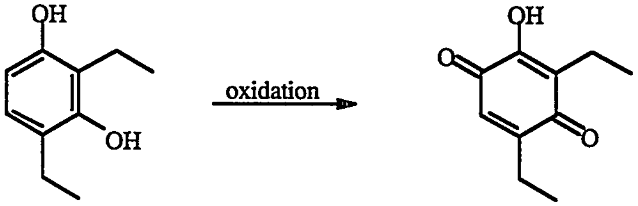

Figure 2. Oxidation of R-F resin gives p-quinones and loss of ion-exchange groups.

Additionally, around 55% of the phenolic ring units are etherified during synthesis as determined by ^{13}C NMR studies (Figure 3), meaning that over half the theoretical ion-exchange capacity of the resin is lost during resin preparation. The K_ds for P-F resin are theoretically 50% that of R-F, but in actuality are closer to 5-10%, largely because of the loss of ion-exchange sites that occurs as ring hydroxyl groups are etherified during preparation.

Technical Approach

Modification of the R-F resin will incorporate information from the earlier studies on structure/function relationships to prepare resins that are chemically more resistant to oxidation but retain high cesium ion selectivity. The technical approach includes design and synthesis of resorcinol derivatives, which are alkylated or otherwise functionalized, such that an aromatic ring carbon *para* to a ring hydroxyl group is more resistant to oxidation.

An alkyl substituent *para* to the phenoxide group should cause formation of peroxo species (which are the likely intermediates in formation of quinones) to be much less kinetically accessible. For a fluorine substituent, thermodynamic bond strength considerations may dominate. The electronegative fluorine group may remove enough electron density from the resorcinol ring such that oxidative susceptibility will be reduced without affecting the ion-exchange characteristics of the hydroxyl groups. A reduction of electron density in the resorcinol ring should decrease the likelihood of reaction with radical species and subsequent oxidation of the ring.

The methyl and the fluoro substituents are both test cases for whether or not substitution at the positions *para* to the hydroxyl groups will slow or stop oxidation of the resorcinol ring to quinones and may provide further useful information about R-F structure/function relationships for design of other ion-specific ion-exchange resins.

Accomplishments

Structure/function studies for R-F resin performed at PNNL under APTI have provided information that can now be used to design and synthesize resins that retain high selectivity for cesium, yet have a much lower susceptibility to chemical oxidation. This research and development work is applicable to phenolic-based condensation resins in general.

Collaboration is under way with researchers in fluorine chemistry at the University of Idaho to prepare the fluorinated materials required to synthesize the new resins; these efforts are also being integrated with an industry partner (Boulder Scientific Company, Mead, Colorado).

Benefits

This work will likely result in organic ion-exchange resins that combine both high selectivity for cesium ion and significantly improved chemical stability under typical conditions encountered during processing of tank wastes. These materials are primarily designed to remove radioactive cesium from alkaline waste tank supernates at the Hanford and Savannah River sites, but will be useful to other DOE sites

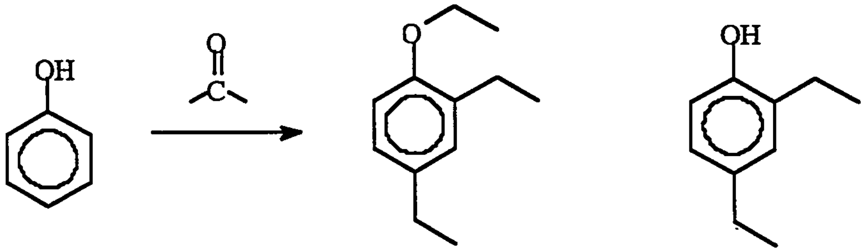

Figure 3. Synthesis of P-F resins gives product with about 55% of the hydroxyl units etherified.

throughout the country for cleanup of radioactive waste streams contaminated with ^{137}Cs. The resin will be more chemically stable, and thus the amount of secondary waste will be reduced.

Organic ion-exchange materials may have a significant impact on environmental remediation efforts at DOE sites because 1) they are regenerable materials, thus reducing processing wastes; 2) they are inexpensive to prepare in usable engineered forms; and 3) organic resins can be synthetically "tailored" for specific applications.

Technology Transfer/Collaborations

Savannah River Technical Center
Boulder Scientific Company
University of Idaho

Keywords

cesium, R-F resin, ion-exchange, phenolic resins, alkaline wastes

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Selective Crystallization of Tank Supernatant Liquid

Presenter: Dan Herting, Westinghouse Hanford Company

EM Focus Area: high-level waste tank remediation

Task Description

The objective of this task is to demonstrate the feasibility of selectively removing sodium nitrate ($NaNO_3$) from Hanford Site tank waste by a large-scale fractional crystallization process. Two-thirds of all the nuclear waste stored in Hanford's underground storage tanks is sodium nitrate (mass basis, excluding water). Fractional crystallization can remove essentially nonradioactive $NaNO_3$ and other sodium salts from the waste, thereby reducing the volume of low-level waste glass by as much as 90%.

Technology Needs

Current baseline waste treatment schemes call for vitrification of all radioactive waste currently stored in underground tanks at the Hanford Site. Pretreatment methods are to be used to separate the waste into high-level and low-level fractions, each of which are then vitrified in separate glass plants. Of the 215,000 metric tons of tank waste, an estimated 145,000 metric tons is sodium nitrate and another 55,000 metric tons is composed of other nonradioactive salts. These salts are the major drivers behind the size and design of the low-level glass plant. Removing the nonradioactive salts from the low-level waste would allow a major reduction in the size of the glass plant, its offgas treatment system, and the vitrified waste storage facility.

Scientific Background

Hanford Site low-level waste is composed of a large volume of nonradioactive inorganic salts mixed with a very small volume of radioactive isotopes. Many waste treatment schemes have been developed that are aimed at removing one or more of the radioisotopes from the waste stream. Fractional crystallization is the conceptually inverse process; that is, the nonradioactive salts are removed from the bulk waste, leaving the radioisotopes behind.

Fractional crystallization works because of the large difference in radii of the sodium ion and cesium ion. The Cs^+ ion is not capable of substituting for a Na^+ ion in the $NaNO_3$ crystal lattice. When $NaNO_3$ crystals form, the ^{137}Cs atoms are excluded from the crystal lattice, so separation of the crystals from the mother liquor results in separation of the $NaNO_3$ from the ^{137}Cs. Separation from the other radionuclides is effected by the same mechanism.

The efficiency of the separation is based on two main factors: the degree to which the solids can be separated from the liquid, and the degree to which the $NaNO_3$ crystals are free of defects (occlusions).

Technical Approach

A process flowsheet was developed in the laboratory using simulated wastes and demonstrated with actual wastes from three Hanford Site waste tanks. The waste is first washed with water or dilute caustic to dissolve the soluble inorganic salts. The liquid phase is then acidified with nitric acid, which converts NaOH, Na_2CO_3, and $NaNO_2$ to $NaNO_3$, allowing recovery of most of the sodium in the waste. The acidified solution is evaporated until $NaNO_3$ crystals begin to form. The slurry is cooled to precipitate more $NaNO_3$, then is filtered or centrifuged to separate the crystals from the mother liquor. The soluble radionuclides stay in the mother liquor, except for the fraction that remains occluded within the $NaNO_3$ crystals or adheres to the surfaces. The crystals are further decontaminated by recrystallizing from water repeatedly until the desired level of decontamination is achieved.

Accomplishments

Initial flowsheet conditions were developed using simulated wastes. The process feasibility was demonstrated when essentially nonradioactive sodium nitrate was recovered from samples of waste from high-level waste tanks 101-SY and 102-AN.

Experiments with simulated waste were done to explore the effects of crystallization parameters on the size and crystal habit of product $NaNO_3$ crystals. Data were obtained to allow prediction of decontamination factor as a function of solid/liquid separation parameters. Experiments with actual waste from tank 101-SY were done to determine the extent of contaminant occlusions in $NaNO_3$ crystals. The occlusion rate determines the theoretical maximum decontamination factor for a single-stage crystallization, and therefore defines the size (number of required stages) of an operating plant.

Fundamental crystallization parameter studies (crystal nucleation rates and growth rates) were conducted under a contract with the University of Arizona under the direction of Dr. Alan Randolph. Randolph, a world-class crystallization expert with expertise in Hanford Site waste chemistry, was instrumental in selecting the design of Hanford's 242-A and 242-S evaporator/crystallizers that have been used here since the mid-1970s to reduce the volume of tank waste.

A detailed process flowsheet and computer model were created using a steady-state process simulator software program. This is the same software being used by the Tank Waste Remediation System (TWRS) program for their waste pretreatment and disposal projections. Therefore, evaluations can be made of the effect of the clean salt process on the low level waste volume and composition resulting from the TWRS baseline flowsheet.

Environmental regulations governing re-use and disposal options for the recovered salts were reviewed under a contract with the consulting firms CH2M Hill and IT Corporation. Current regulations, which could be revised, preclude the free release of the recovered salts for offsite uses or disposal, regardless of the level of decontamination (*de minimis* rule). The regulations encourage re-use and recycling of the salts within the DOE complex, wherever genuine beneficial uses of the salts can be identified. Several such uses were discussed in the consulting firm's final report.

Benefits

Prospective benefits of the selective crystallization of sodium nitrate and other clean low-specific-activity salts are:

- **Waste Reduction.** Up to 90% reduction in the volume of low-level waste glass could be realized.
- **Waste Minimization.** Current baseline tank waste treatment schemes call for the use of more than 30 million pounds of process chemicals in 1 year. By regenerating the process chemicals instead of purchasing them, that additional waste will not be generated.
- **Removal of Nitrate.** This process will significantly reduce the amount of nitrate in the waste stream.
- **Improved Ion Exchange Performance.** The decreased sodium concentration will enhance ion exchange performance because the contaminant-to-sodium ratio will be an order of magnitude higher.

Removal of $NaNO_3$ and other salts from the low-level waste stream, especially those salts that are problematic with respect to glass formulation (fluoride, phosphate, sulfate), can lead to much higher waste loading in the vitrification process. Recent flowsheet modeling predicts that full-scale implementation of the process could reduce the volume of low-level waste glass by as much as 90%.

Combination of the fractional crystallization process with salt-splitting technology, such as the ESP-funded electrochemical destruction process being developed at Westinghouse Savannah River Company, has the potential to convert tank waste into useable products for waste pretreatment. For example, $NaNO_3$ can be converted electrochemically into HNO_3 and NaOH, the latter of which is needed for the Tank Waste Remediation System (TWRS) baseline waste pretreatment (enhanced sludge washing).

Technology Transfer/Collaborations

None in FY 1996.

Keywords

fractional crystallization, sodium, salt, sodium nitrate, low-level waste, vitrification, clean salt process

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TTP Number: RL46C341

Technical Liaison with the Institute of Physical Chemistry (Russian Academy Of Science)

Presenter: Cal Delegard, Westinghouse Hanford Company

EM Focus Area: high-level waste tank remediation

Task Description

DOE has engaged the Institute of Physical Chemistry of the Russian Academy of Science (IPC/RAS) to conduct studies of the fundamental and applied chemistry of the transuranium elements (TRU, primarily neptunium, plutonium, and americium) and technetium in alkaline media. This work is supported by DOE because the radioactive wastes stored in underground tanks at DOE sites (Hanford, Savannah River, and Oak Ridge) contain TRU and technetium, are alkaline, and the chemistries of TRU and technetium are not well developed in this system. Previous studies at the IPC/RAS centered on the fundamental chemistry and on coprecipitation. In FY 1996, the work will focus more on the applied chemistry of TRU and technetium in alkaline media and work will continue on the coprecipitation task.

The technical liaison at Westinghouse Hanford Company (WHC) was established to provide information to the IPC/RAS on the Hanford Site waste system, to define and refine the work scope, to help publish IPC/RAS reports in documents and presentations released to the public, to compare IPC/RAS results with results from other sources, and to test chemical reactions or processes proposed by the IPC/RAS with actual Hanford Site tank waste.

Technology Needs

Knowing the chemistry of TRU and technetium in alkaline media is vital because isolation of the TRU and technetium to a low-volume, high-level waste fraction is a primary goal of Hanford Site tank waste processing (pretreatment). Current knowledge of the chemistry does not predict reliably the TRU and technetium behaviors and distributions (to the solid or solution phases) under existing Hanford Site tank conditions and particularly under possible alkaline waste processing options. Methods must be developed to process tank waste and to separate TRU and technetium from waste and waste process solutions.

Scientific Background

The TRU (neptunium, plutonium, americium) and technetium are elements that have multiple oxidation states available in aqueous solution. In general, the oxidation states (IV) of these elements form oxides or hydrous oxides of low solubility while the higher oxidation states [(V), (VI), or (VII) for the TRU and (VII) for technetium] give oxyanions of appreciable solubility, especially in highly alkaline solution.

In the absence of complexing agents, chemically reducing conditions decrease the solubility of these elements while oxidizing conditions favor their dissolution. The accessibility of the higher oxidation states increases in the order americium < plutonium < neptunium < technetium. The solubilities of these elements in alkaline media (i.e., their distributions to the solid and solution phases) is a function of their solid phase oxidation state and crystallinity, complexation, possible redox reactions, radiolytic reactions (which can produce oxidants and reductants), and coprecipitation reactions (with bulk waste components).

Technical Approach

Laboratory-scale studies at the IPC/RAS initially focused on the solubility, redox reactions, radiolysis effects, and coprecipitation of the TRU and technetium in highly alkaline media. Subsequent studies will continue the investigation of coprecipitation and other methods to remove these radioelements from alkaline waste. The tests and processes performed at the IPC/RAS with simple alkaline systems (simulant wastes) are designed in consultation with the Hanford Site liaison. The processes designed by the IPC/RAS must be verified with genuine wastes available at the Hanford Site. Results from the IPC/RAS and Hanford Site studies will be disseminated in technical publications and presentations.

Accomplishments

In 1994, the IPC/RAS prepared a technical literature review of the chemistry of the TRU and technetium in alkaline media. This review was edited and published by the liaison as a WHC document in May 1995. Eleven tasks to investigate the chemistry of the TRU and technetium were proposed by the IPC/RAS; four were selected by the DOE for FY 1995 support:

- oxidation and reduction reactions and reagents for neptunium, plutonium, americium, and technetium
- solubilities of neptunium, plutonium, americium, and technetium as functions of oxidation states, hydroxide concentration, and presence of other bulk waste components
- reactions and reagents suitable to coprecipitate neptunium and plutonium in the (V) and (VI) oxidation states
- gamma radiolysis reactions of neptunium, plutonium, and technetium.

Draft technical reports on the four tasks received in September 1995 and due in January 1996 are being edited for publication as contractor documents.

The studies showed that the strongly reducing conditions necessary to produce tetravalent TRU and technetium increase in the order americium < plutonium < neptunium < technetium. Thus, only hydrazine was found to reduce technetium(VII) to technetium(IV), whereas hydrazine or dithionite reduce neptunium(V) and plutonium(V) to the (IV) state and americium(V) to the (III) state. Other reductants studied (hydroxylamine, sulfite, ascorbate, hydroquinone, thiourea dioxide) were less effective.

The ICP/RAS studied oxidations of neptunium, plutonium, and technetium solids in the (IV) and (V) oxidation states by atmospheric oxygen. Negligible oxidation of plutonium(IV) was observed; neptunium oxidized to the (V) state and technetium to the (VII) state. Other oxidants studied (though not for all radioelements) were ozone, hypochlorite, hypobromite, nitrate, nitrite, persulfate, permanganate, ferrate(VI), chromate, and ferricyanide.

The solubilities of neptunium(IV) and plutonium(IV) hydrous oxides (in the presence of hydrazine) were 10^{-6} to 10^{-5} M for neptunium and 10^{-7} to $10^{-5.5}$ M for plutonium as NaOH concentration increased from 2 to 14 M. The solubilities of pentavalent neptunium, plutonium, and americium were similar above 6 M NaOH increasing from $10^{-3.7}$ to $10^{-3.5}$ M at 14 M NaOH. Technetium(IV) and (V) solubility measurements are very sensitive to air oxidation; in the presence of hydrazine, solubilities range from $10^{-5.3}$ to $10^{-3.3}$ M. Electrodeposited $TcO_2 \cdot nH_2O$ has a solubility of $10^{-6.2}$ M in 4 M NaOH.

The ICP/RAS studied coprecipitation by the method of arising reagents (MAR) for neptunium and plutonium in the (V) and (VI) oxidation states. The MAR uses precipitating agents that initially are soluble in the alkaline solution. Decomposition of the soluble agent to form the precipitating solid then takes place by reduction or thermal means, and carrier precipitation of the trace radionuclides occurs. Carriers studied included reduced hydroxides or hydrous oxides of chromium, manganese, iron, and cobalt introduced to solution as soluble complexes or oxidized species. Plutonium solution coprecipitation was satisfactory for most reagents (decontamination factor [DF] up to 1000) whereas neptunium removal was unsatisfactory (DF of 5 to 20). Subsequent tests to remove solubilized neptunium by other agents are promising.

Final results of gamma radiolysis studies are not yet reported. Initial results show gamma radiolysis strongly influences redox reactions. The course of the redox reactions can be altered by reagents that are radiolytically active themselves or act as radiolytic scavenging agents.

Benefits

Fundamental knowledge of the chemical behavior of the TRU and technetium in alkaline media is essential to the successful design and operation of the pretreatment processes used to segregate the low- and high-level fractions of Hanford Site tank wastes. Current and future studies to design radionuclide removal processes for the soluble and long-lived neptunium and technetium radioelements are particularly important to pretreatment and are a central part of the IPC/RAS task.

Results to date from the IPC/RAS show the solubilities of the TRU and technetium are strongly dependent on the oxidation state and can be altered successfully by various common chemical oxidants and reductants. Solution decontamination by the MAR for plutonium has been shown to be promising; similar results are possible for neptunium.

Technology Transfer/Collaborations

Institute of Physical Chemistry, Russian Academy of Science, Moscow, Russia

Keywords

americium, neptunium, plutonium, technetium, alkaline, sodium hydroxide, solubility, coprecipitation, radiolysis, oxidation, reduction, redox, TWRS, pretreatment, Hanford Site, tank waste

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Electrochemical Treatment of Liquid Wastes

Presenter: Dave Hobbs, Westinghouse Savannah River Company

EM Focus Areas: mixed-waste characterization, treatment, and disposal; high-level waste tank remediation

Task Description

Electrochemical treatment processes are being evaluated and developed for the destruction of organic compounds and nitrates/nitrites and the removal of other hazardous species from liquid wastes stored throughout the DOE complex. This activity consists of five major tasks: 1) evaluation of different electrochemical reactors for the destruction and removal of hazardous waste components, 2) development and validation of engineering process models, 3) radioactive laboratory-scale tests, 4) demonstration of the technology in an engineering-scale size reactor, and 5) analysis and evaluation of testing data. The development program team is comprised of individuals from federal, academic, and private industry. Work is being carried out in DOE, academic, and private industrial laboratories.

Possible benefits of this technology include 1) improved radionuclide separation as a result of the removal of organic complexants; 2) reducing the concentrations of hazardous and radioactive species in the waste; 3) reducing the size of the offgas handling equipment for vitrifying low-level wastes by reducing the source of NO_x emissions; 4) recovering chemicals of value; and 5) reducing the volume of waste requiring disposal.

Technology Needs

This technology is being developed to destroy and/or remove the following species present in Hanford and Savannah River high-level, low-level, and mixed wastes: nitrates, nitrites, and organic compounds; radionuclides (e.g., ^{99}Tc and ^{106}Ru); and Resource Conservation and Recovery Act (RCRA) metals (e.g., chromium, cadmium, and mercury).

Technology Description

In an electrochemical reaction, charge is transferred at the interface between an electrode and reactive species in a conductive liquid. An electrochemical reactor consists of an anode, a cathode, a conducting electrolyte, and power supply. At the cathode, charge is passed into the reacting species resulting in a reduction in the oxidation state. At the anode, charge is passed from the reactive species into the electrode resulting in an increase in the oxidation state. The change in oxidation state changes the chemical properties and form of the reacting species. The reduced or oxidized species can form a deposit on the electrode or desorb from the electrode surface and dissolve in the electrolyte.

Depending on the characteristics, the modified species may no longer be a hazardous substance or may be easily separated from the liquid phase (e.g., gas or solid). For example, previous work has shown that nitrate and nitrite are reduced to a mixture of molecular nitrogen, ammonia, and nitrous oxide at the cathode of electrochemical cell. These product gases can be easily separated from the waste solution. Testing has also shown that organic compounds (e.g., ethylenediaminetetraacetic acid, citrate, acetate, formate, and oxalate) can be oxidized to carbon dioxide and water at the anode.

Benefits

A significant quantity of waste at Hanford contains complexing agents that prevent the efficient separation of radionuclides. Electrochemical destruction of these organic compounds would enable efficient radiochemical separation processes to be carried out in subsequent processing operations. The destruction of organic compounds in both Hanford and Savannah River waste also reduces risks associated with waste storage and evaporation.

Nitrate and nitrite are two of the major hazardous species present in Hanford and Savannah River HLW. After removing the bulk of radioactivity, the decontaminated salt solution will be disposed of in a cement waste form referred to as Saltstone at the Savannah River site and in a borosilicate glass waste form at Hanford. Destruction of the nitrate and nitrite before disposing of the decontaminated salt solution in Saltstone eliminates the possible groundwater contamination from leaching of nitrate and nitrite from the waste form. Destruction of nitrate and nitrite before vitrification at Hanford would significantly reduce the size of the offgas system by eliminating the formation of NO_x gases in the melter.

In the electrochemical destruction of sodium nitrate and nitrite, sodium hydroxide is the major liquid phase product of the process. If the sodium hydroxide could be recovered and recycled significant reduction in the quantity of waste requiring disposal would be realized. Onsite use of the recovered sodium hydroxide would include neutralization of fresh waste and as a corrosion inhibitor in the waste storage and evaporation facilities. Thus, the quantity of sodium hydroxide that would be available for recovery and recycle would be increased by converting the sodium nitrate and nitrite into sodium hydroxide.

Modern electrochemical reactor designs make it relatively simple to scale the treatment facility to the size of the waste stream by the addition of modular reactor units. Aqueous electrochemical processes operate at low temperature (<90°C) and near atmospheric pressure in contrast to high temperature and pressure processes also being evaluated for the destruction of organic compounds and nitrates. The electrochemical reactions can be shut down instantaneously by shutting off the power to the electrochemical reactor. No additional chemicals are added in the process; therefore, minimal or no secondary wastes are generated.

Electrochemical removal of radionuclides and RCRA metals from the wastes would also be beneficial. For example, removal of ^{99}Tc from the Savannah River decontaminated salt solution would eliminate the possible release of this mobile, long-lived radionuclide from Saltstone. Removal of RCRA metals from a waste stream would allow a mixed waste to be delisted or eliminate the possible leaching of these species from low-level wastes forms into groundwater.

Technology Transfer

Electrochemical processes are used to produce a variety of industrial chemicals and treat waste streams and waters before disposal and release to the environment. Thus, there is a extensive database for the design and scale-up of electrochemical processes. Electrochemical reactors developed by private industry are currently being evaluated in this testing activity.

Alternate reactor designs are also being evaluated. Development of these alternate reactor designs will be carried out in collaboration with private industry through Cooperative Research and Development Agreements or licensing agreements. In addition to the specific waste components that are being evaluated, the technology developed in this program should also be of value in the development of electrochemical treatment processes for nonradioactive, hazardous wastes such as those from the chemical, plating, pulp and paper, and electronics industries.

Accomplishments and FY 1996 Activities

The following items have been accomplished in this technology development effort:

- demonstrated the destruction of nitrate and nitrite in actual Savannah River waste in a laboratory-scale flow reactor
- demonstrated the destruction of organic compounds and nitrates/nitrites in Hanford and Savannah River waste simulants in a full-scale electrochemical reactor
- conducted tests in laboratory-scale flow reactors to determine the effects of key operating parameters on the destruction of organic compounds and nitrates/nitrites in Hanford and Savannah River waste simulants
- developed and validated engineering models for the electrochemical destruction of nitrate, nitrite and organic compounds in a parallel-plate reactor
- conducted evaluations of alternate reactor designs including: porous metal, packed-bed, fluidized-bed, and gas-diffusion electrodes for the destruction of nitrates, nitrites, and RCRA metals.

During FY 1996, the following activities will be carried out: 1) conduct preliminary engineering design and cost evaluations for treating the Hanford complexant waste and the Savannah River decontaminated salt solution waste, 2) demonstrate nitrate/nitrite and organic compound destruction with radioactive Hanford waste, 3) conduct an independent review of nitrate and organic destruction technologies, and 4) complete installation of a pilot-scale testing facility at the Savannah River Technology Center.

Keywords

Hanford, Savannah River, nitrate, nitrite, organics, radionuclides, RCRA metals, alkaline, destruction, removal

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Advanced Separations at Savannah River Site

Presenter: Major Thompson and Dan McCabe, Savannah River Technology Center

EM Focus Areas: high-level waste tank remediation; contaminant plume containment and remediation

Task Description

The Savannah River Site (SRS) has many waste streams that are contaminated with radionuclides and/or hazardous materials that must be treated to remove the radioactivity (cesium, strontium, tritium, actinides) and hazardous components (polychlorinated biphenyls (PCBs), cyanide, metal ions).

This task provides testbeds for ESP-developed materials and technology using actual SRS waste streams. The work combines high-level waste solutions currently stored in underground tanks onsite, groundwater, and other aqueous waste contaminated with tritium and reactor basin water in excess facilities. In addition, ESP separations technology developed for other applications has been demonstrated for sampling of radioactivity from seawater.

High-Level Waste

SRS is constructing facilities to process high-level waste solutions and sludges. The solutions are treated to remove ^{137}Cs, ^{90}Sr, and actinides to levels below Nuclear Regulatory Commission Class A low-level waste. The treated solutions are then grouted for near-surface storage onsite. The separated radionuclides will be transferred for mixing with the sludge and vitrification in the Defense Waste Processing Facility. The current process for cesium is precipitation with tetraphenyl borate (TPB). Strontium, plutonium, and uranium are separated at the same time by absorption on monosodium titanate.

The liquid recycled from the vitrification plant also requires cesium separation. Cesium in the recycle stream occurs because some cesium is volatilized during vitrification of the sludge and is removed by scrubbing and flushing the offgas system. Current plans are to evaporate the solutions in high-level waste evaporators and return the concentrated solutions to the existing process for removal of cesium. Tests of cesium removal from this stream are planned for mid-FY 1996.

Technical Approach. Sodium titanate developed by AlliedSignal, Inc., under ESP funding has been tested for use in the SRS process. Tests were done with several different samples (dry solids and slurries) with simulant and actual waste solutions to determine the strontium decontamination factor (DF) using a procedure previously developed to ensure that purchased material met plant specifications for strontium removal. The highest DF obtained with AlliedSignal material was 101, which although lower than the desired DF of 150, is better than that obtained with current large-scale samples of vendor material. Absorption of uranium and plutonium from the solutions has also been tested to ensure removal without nuclear criticality problems.

Cesium separation tests are under way with the engineered form of crystalline silicotitanate, IONSIV® IE-911 manufactured by UOP Molecular Sieves. The material tested is from experimental batch 38-B, a noncommercial material. Tests involve measurement of the batch K_d for cesium; analytical results are not complete. Tests with actual waste solution will follow the simulant tests.

Reactor Basin Water

SRS has five closed reactors with cooling basins containing about 3 million gallons of cesium-contaminated water in each basin. At least one of the basins is also contaminated with PCBs or other hazardous materials that arose from contaminated water in sumps within the reactor building. Groundwater in the reactor areas may also be contaminated with radionuclides and hazardous metals from agricultural application before building of the plant. The R Reactor basin water contains PCBs, cyanide, cesium, and strontium, making it a Toxic Substances Control Act (TSCA) - regulated waste.

Currently, no integrated systems have been demonstrated that remove radionuclides and Resource Conservation and Recovery Act or TSCA-regulated substances from water and at the same time separate the regulated substances from the radioactivity so that the resulting wastes are not mixed waste.

Technical Approach. Work is in progress to demonstrate an integrated system for water treatment at the R Reactor basin with equipment and materials supplied by 3M. The integrated system processes 0.3 to 2.0 gal/min and uses 3M Empore™ membrane filter cartridges. The system removes PCBs first, then cesium and strontium, and lastly, the cyanide ion. The required permit for the test has been applied for with testing expected to start in January 1996.

Sampling Seawater

Large volumes of seawater must be concentrated to perform accurate environmental measurements. Current practice is to ship 55-gallon drums of seawater to the laboratory for treatment by methods having multiple steps. We are testing membranes and resin for effective removal of cesium, plutonium, and technetium from seawater to simplify separation and analysis of environmental samples.

Technical Approach. Empore™ (3M) membranes were tested for removal of cesium, plutonium and technetium from seawater. Technetium was separated and concentrated from seawater with Teva™ (Eichrom Industries) resin incorporated in an Empore™ membrane. Initial bleedthrough was observed; however, spiking the solution with ^{97}Tc allows recoveries to be calculated to give the desired accuracy. Testing was done with several different concentrations of technetium with no change in the amount of recovery.

Resorcinol-formaldehyde (R-F) resin in an Empore™ membrane removed cesium from seawater, but the recovery was low (<50%). When tested with freshwater, the same membrane demonstrated 99% recovery of cesium. Apparently the selectivity of R-F resin for cesium relative to sodium was insufficient to obtain high recovery of cesium from seawater. The same behavior was observed with R-F resin incorporated in Selentec MagSep™ beads.

Plutonium was adsorbed from seawater with an Empore™ membrane containing sodium titanate. Recovery calculations were complicated by inadvertent contamination; however, the tests demonstrated the feasibility to the point that 3M and ISCO, a manufacturer of environmental sampling equipment, will collaborate to provide equipment for field testing of both freshwater and seawater under another ESP task during FY 1996.

The techniques developed have also resulted in reduced preparation time and cost for analyses of environmental samples of both freshwater and seawater. Implementing automated sampling will reduce costs associated with shipping the samples and disposing of the seawater after analyses.

Catalytic Exchange for Aqueous Detritiation

Several DOE sites have tritium-contaminated groundwater. SRS has some process waste streams, reactor moderator, and water from the Effluent Treatment Facility that contain 10 to 100 times higher levels of tritium contamination than groundwater. Canada recently agreed to allow DOE to use their patented catalyst system to remediate waste streams, but not to treat process-related materials such as reactor moderator. The objective of this portion of the task is to demonstrate bithermal catalytic exchange for detritiation of water using U.S.-manufactured catalysts to ensure availability of a catalyst for remediating DOE waste streams and materials for process streams.

Bithermal catalytic exchange uses a hydrophobic catalyst at two different temperatures and hydrogen gas to detritiate water. The work is being carried out at the University of South Carolina (USC) in Columbia and Savannah River Technology Center (SRTC). USC has constructed a laboratory apparatus to test catalytic exchange of deuterium-protium and very low-level protium-tritium mixtures.

We obtained five catalysts from Hamilton Standard for use in USC's test apparatus. The small-scale laboratory tests will determine experimentally the separation factors, rate parameters, and other parameters necessary to evaluate the performance of catalysts for detritiation of water. SRTC is working on conceptual design of a pilot plant for detritiation of water by catalytic exchange and mathematical modeling of the process. Any tests with process-related streams will be done at SRTC.

Technology Transfer/Collaboration

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Publications, Presentations, and Patents

Publications, Presentations, and Patents

This section lists publications, presentations, and patents for current and past Technical Task Plans (TTPs) funded by the Efficient Separations and Processing Crosscutting Program. They are listed by TTP, along with the Principal Investigator's name and location.

AL16C322 -Water Soluble Polymers for Removal of Pu, Am from Wastewaters, Gordon Jarvinen (Los Alamos National Laboratory)

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