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J. M. Gephart, Editor

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DISCLAIMER

Summary

This document contains summaries of technology development presented at the 1997 Efficient Separations and Processing Crosscutting Program (ESP-CP) Technical Exchange Meeting (TEM), held January 28-30, 1997, in Gaithersburg, Maryland. The ESP-CP is sponsored by the U.S. Department of Energy's Office of Environmental Management (DOE/EM), Office of Science and Technology.

The ESP-CP TEM is held annually to:

- Present current technology development activities funded by the ESP-CP. Developers of ESP-CP-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. Representatives from DOE/EM's Focus Areas also present their technology needs.
- Promote the exchange of technical information among those developing new separations technologies, those responsible for providing new separations technologies to meet DOE/EM needs, and those who need or will potentially make use of such technologies.
- Familiarize the ESP-CP Technical Review Team with the FY 1997 program and solicit reviewers' views on the program as a whole.

This meeting is not a program review of the individual tasks, but instead focuses on the technical aspects and implementation of ESP-CP-sponsored technology or data. This document also contains a list of ESP-CP-sponsored publications, presentations, and patents.

Attendees include program participants, Technical Program Officers and other pertinent staff at DOE operations offices; Technical Program Managers and other pertinent management at participant organizations; staff in DOE/EM's Focus Areas and Site Technology Coordination Groups; potential users within DOE of new separations technologies; DOE, industry, and university laboratory staff with historic or developing affiliations to the ESP-CP or who are active in professional societies emphasizing separations research and development; and members of the scientific and engineering community with expertise in chemical and physical separations research pertinent to DOE/EM needs.

Presenters are asked to address the following areas:

- the need for the technology
- technology description
- benefit of the technology to DOE/EM
- any technology transfer or collaborations with industry and academia
- scientific background
- technical approach
- accomplishments and resolution of technical issues.

The ESP-CP welcomes requests for information, which can be submitted through our home page on the World Wide Web at http://www.pnl.gov/eff_sep/index.html, or by contacting directly those members of the ESP-CP Core Management Team listed on page 1.5 of this document.

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Efficient Separations and Processing Crosscutting Program Overview

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Introduction

The U.S. Department of Energy (DOE) established the Office of Science and Technology (formerly the Office of Technology Development), 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. The Office of Science and Technology (EM-50) is charged with developing and implementing new technologies that are safer, faster, more effective, and less expensive than current methods.

To focus resources and address opportunities, EM-50 has targeted four 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, called 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 radioactive and chemical 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.
- **Mixed Waste Characterization, Treatment, and Disposal.** DOE has site inventories of more than 300,000 m^3 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.
- **Subsurface Contaminants.** Contaminant plumes at DOE sites include an estimated 2 billion gallons (7.58 billion liters) of contaminated groundwater and more than 41 million m^3 of contaminated soils. Limited information exists at many 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 to characterization and data interpretation methods, containment systems, and in situ treatment. Evolving regulations dictate that some landfills must be stabilized to prevent contamination of groundwater and ensure control over contaminants in the waste, leading to the need for containment and 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.

The Efficient Separations and Processing Crosscutting Program

To support the Focus Areas, EM has established Crosscutting Areas that provide technologies in chemical and physical separations and treatment, characterization, and robotics. The Efficient Separations and Processing Crosscutting Program (ESP-CP) 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-CP funds multiyear tasks that address high-priority waste remediation problems involving high-level, low-level, transuranic, hazardous, and mixed (radioactive and hazardous) wastes. The ESP-CP is organized as a crosscutting program under EM-50's Office of Research and Development (EM-53).

The ESP-CP funds only work that, if completed successfully, will meet a need for chemical and/or physical separation identified by EM. Specifically, work supported by the ESP-CP must meet a need identified by at least one Focus Area or at least one DOE site. Preference is given to funding work that provides a technology that benefits two or more Focus Areas, but this is not a minimum requirement.

Work is funded that fills a gap in the availability of some needed technology compared to available or imminently available technologies, or represents a substantial and persuasive reduction in cost or risk or increase in safety or probability of successful implementation compared to available technologies. The typical ESP-CP task directly provides a new technology at a level of R&D sufficiently mature to interest others in demonstrating the technology at a DOE site. The ESP-CP also funds some tasks that indirectly provide a new technology, such as testing using actual waste or narrowly directed modeling activities.

The ESP-CP program includes work that is beyond the proof-of-principle stage but is not ready for demonstration. Therefore, the ESP-CP typically does *not* include further development of technologies that have already been demonstrated by treating actual or equivalent wastes, or further development of commercially available technologies, or development of concepts for which a reasonable probability of successful development is not apparent.

A key goal of the ESP-CP is to apply ESP-CP-sponsored technologies in all Focus Areas regardless of the intended application. The ESP-CP 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-CP tasks begin or continue and review proposals to begin new tasks.

The ESP-CP also fosters future expertise in separations technologies by encouraging university participation. Where possible, the program transfers separations technologies developed by DOE to U.S. industry.

In June 1996, the Oak Ridge Operations Office (ORO) submitted a proposal to EM-50 to serve as the lead implementation center for the ESP-CP in response to EM-50's intention to place that function for the crosscut programs at specific field offices. In August, ORO was designated the field lead for the ESP-CP. As identified in the designation, ORO has responsibility for providing technical expertise, information gathering and dissemination, and linkage to end users. Specific areas in which ORO will be involved will be communications between the ESP-CP and the Focus Areas and the sites; documentation of program activities and decision making; involvement of technology users in the technology development process; and promotion of increased high-quality, private sector involvement in the ESP-CP. The involvement of ORO as field implementation center is being blended with the existing ESP-CP management structure of a DOE-Headquarters Program

Manager supported by three Field Coordinators located at Richland, Oak Ridge, and Savannah River.

Technology Need

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-CP 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-CP R&D efforts focused on treatment of high-level waste (HLW) 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. A number of EM separations and processing development needs were recently identified, and include the following.

RCRA Metals

Technologies are needed to remove Resource Conservation and Recovery Act (RCRA) metals at concentration on the order of 0.1 to 10 ppm from dilute aqueous wastes, including groundwater and process wastes and slightly acidic offgas scrub solutions, with minimal generation of secondary waste. Specific metals of interest include mercury, chromate, chromium(III), lead, cadmium, and copper. Actinides of interest include uranium, plutonium, thorium, and americium.

Technetium

Technologies are needed to remove technetium from highly alkaline sodium nitrate supernatant brines in Hanford HLW storage tanks. This need is complicated by uncertainty about the chemical form of technetium, which is often assumed to be pertechnetate, but for which there is some evidence of complexed, lower valence state forms, and by uncertainty in the ability to retain technetium in molten glass during HLW vitrification.

Fission Product Removal

Technologies are needed to remove fission products such as cesium, strontium, and technetium from dilute aqueous streams, such as groundwater, process wastes, and storage pool water. Sorbents exist for many fission products; ESP-CP activities are limited to new technologies that offer apparent and substantial advantages in selectivity, capacity, efficiency, and simplicity of elution and/or suitability of a loaded sorbent as a waste form. For example, it would be useful to maintain a capacity on the order of 2 to 4 meq/g while increasing selectivities to on the order of 100 for strontium over calcium or magnesium.

Tritium

Cost-effective technologies are needed to remove dilute tritium as HTO from large volumes of water, such as storage pool water, groundwater, or process wastes. At the Savannah River Site, tritium concentrations of 10 million to 200 million pCi/L exist. The K-East Basin at the Hanford Site contains a million gallons at a concentration of 3 million pCi/L. Thus, HTO concentrations corresponding to mole fractions in H_2O of 10^{-14} to 10^{-10} need to be treated. Technologies are also needed to separate mercury and tritium from vacuum pump oil at the Savannah River Site.

TRU

Technologies are needed for leaching transuranic (TRU) elements (including plutonium) from soils and solid wastes (including scrubbing wastes from decontamination and decommissioning [D&D] of concrete surfaces) without generating much secondary waste.

Colloids

Technologies are needed that separate fine solids, including colloidal species, from highly alkaline, high ionic strength brines retrieved from HLW storage tanks at Hanford. The principal challenge is to remove colloids and other fine solids sufficiently to prevent transport of radionuclides as undissolved species into supernatant processing equipment.

Current Program

The ESP-CP 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-CP currently includes 31 multiyear tasks addressing high-priority waste remediation problems. More than half of these tasks include university staff and outside collaboration, including industrial partners. Currently, the ESP-CP 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.

Efforts in these technical areas can be supported where there are conspicuous advantages (cost, timeliness, probability of the technology's success, capability of staff, etc.) relative to existing technologies or current ESP-CP projects.

The ESP-CP is supporting several activities through Program Research and Development Announcement (PRDA) procurements managed by the Federal Energy Research Center (FETC) in Morgantown, West Virginia. Five contracts were awarded in FY 1996 and FY 1997 to address needs identified by the Mixed Waste, Subsurface Contamination, Tanks, and D&D Focus Areas. The ESP-CP is also affiliated with several tasks under EM-50's Industry Programs and supports Small Business Innovative Research (SBIR) activities through the FETC, and seeks to help coordinate these activities with ESP-CP tasks and with separations and processing needs at EM sites.

Funding

Funding for tasks is normally $200K to $500K per year. Table 1 shows the ESP-CP's recent funding profile. These data describe funding disbursed by the ESP-CP and are adjusted to reflect funding cuts imposed during the fiscal years.

Table 1. Funding profile for Efficient Separations and Processing Crosscutting Program, FY 1993-1997

FY 1993	FY 1994	FY 1995	FY 1996	FY 1997
$11.4M	$16.4M	$12.9M	$13.0M	$12.7M

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More information about the ESP-CP is available at our home page at http://www.pnl.gov/eff_sep/index.html.

Removal of Contaminants from Equipment and Debris and Waste Minimization Using TECHXTRACT® Technology

Michael W. Bonem, EET, Inc.

EM Focus Area: decontamination and decommissioning

Technology Need

DOE's decontamination and decommissioning (D&D) program will produce massive volumes of radioactive and/or hazardous wastes. On a mass or volumetric basis, however, the radioactive and toxic constituents in these waste streams comprise a very small percentage. Prime examples of these types of waste are equipment that was used in the production or processing of nuclear materials, structural steel from buildings, and concrete and masonry debris from building demolition. In each case, the gross contamination will have been removed in the initial stages of the D&D process. However, the existence of trace residuals requires that the materials still be treated as low-level radioactive waste (LLRW), hazardous waste, or mixed waste.

This results in three distinct issues for DOE's Environmental Management program. First, large volumes of radioactive waste disposal capacity will be required to handle these waste streams. LLRW landfills are typically very expensive to construct and operate, difficult to permit, and represent an ongoing potential liability.

Second, some of the material in this waste stream is of value to DOE if it is decontaminated to the point of unrestricted release. Certain working equipment can be salvaged and sold for reuse "as is." Most of the remaining metal that is not in the form of salvageable equipment can be sold as scrap. DOE's existing and anticipated scrap metal inventory includes very large quantities of carbon steel and stainless steel and lower volumes of valuable metals such as nickel and aluminum. Even demolition debris can be of value if decontaminated; for example, as fill material.

Third, some of the materials are contaminated with radioactive and hazardous components and are therefore classified as a mixed waste. This greatly limits the options for disposition. Very few landfills or metal melting facilities are permitted to accept mixed wastes. If pretreatment or other disposal options are required, the cost related to the disposition of these materials becomes even greater.

Established waste treatment methods are capable of addressing a subset of these problems, generally in the cases where there is relatively little contamination and where it is mostly surficial. As will be discussed below, the technology development under this Program Research and Development Agreement (PRDA) with the Federal Energy Technology Center-Morgantown[1] expands this capability by removing contaminants that are "fixed," embedded, and electrostatically bonded.

Technology Description

Under this PRDA, EET, Inc., is extending its proprietary TECHXTRACT® chemical decontamination technology into an effective, economical, integrated contaminant removal system. This integrated system will consist of a series of decontamination baths using the TECHXTRACT® chemical formulas, followed by a waste treatment process that will remove the contaminants from the spent chemicals. Sufficient decontamination will result so that materials can be released without restriction after they have been treated, even those materials that have traditionally been considered to be "undecontaminable." The secondary liquid waste will then be treated to separate any hazardous and radioactive contaminants, so that the spent chemicals and wastewater can be discharged through conventional, permitted outlets.

The TECHXTRACT® technology is a unique process that chemically extracts hazardous contaminants from the surface and substrate of concrete, steel, and other solid materials. This technology has been used successfully to remove contaminants as varied as PCBs, radionuclides,

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[1] Activities described here are funded through the U.S. Department of Energy Contract No. DE-AC2196MC33136, which is administered through the Federal Energy Technology Center-Morgantown.

heavy metals, and hazardous organics. The process' advantage over other alternatives is its effectiveness in safe and consistent extraction of subsurface contamination. TECHXTRACT® is a proprietary process developed, owned, and provided by EET, Inc.

The TECHXTRACT® process employs as many as 25 different components in three separate chemical formulations that are used in sequence to extract contaminants. The first two chemicals are surface preparation formulas containing complex blends of acids and other chemical agents to clean dirt, oil, grease, and other interferences from the surface. These blends also solubilize inorganics and organics and prepare the substrate by establishing proper conditions for the extraction step. The third blend uses advanced chemistry in the fields of microemulsification and chemical ion exchange.

The extraction technique uses these blends to interact with contaminants at the molecular level. In essence, the extraction solution penetrates below the surface and binds itself to the contaminants, then pulls horizontally and vertically through the microscopic pores to the surface. Additional components of the formula encapsulate the contaminants to prevent them from recontacting and thereby recontaminating the surface, keeping them in suspension until they can be removed during the rinse step.

The objective of the PRDA is to demonstrate on a full-scale basis an economical system for decontaminating equipment and debris, with further treatment of secondary waste streams to minimize waste volumes. Contaminants will be removed from the contaminated items to levels where they can be released for unrestricted use. The entire system will be designed with maximum flexibility and automation in mind.

Benefit to DOE

The merits of decontamination and waste minimization using the TECHXTRACT® technology should be compared to two standard alternatives: surface decontamination processes, and disposal. The TECHXTRACT® process offers significant advantages over both of these options in the case of "difficult to decontaminate" materials. Surface decontamination can be effective and economical when contaminants have not penetrated into the pores or voids of the materials and when electrostatic bonding has not occurred. Unfortunately, some amount of penetration and bonding often occurs, making simple surface cleaning ineffective. The other common option for contaminated materials (including those for which surface decontamination has failed) is disposal. Disposal may include sorting to identify and segregate clean materials or supercompaction and other volume reduction steps, but it does not include a process to separate or remove the contaminants.

The advantages of any technology that can remove the contaminants from bulk materials are obvious. Significant waste volume reduction, on the order of 99% or more, can be realized if contaminants are removed from equipment, structures, and debris that are otherwise slated for disposal. The economics of a TECHXTRACT® decontamination system, versus disposal, are highly dependent on disposal costs and other project-specific factors. Reported LLRW disposal costs vary widely across the DOE complex. For equipment or scrap metal that is decontaminated, the TECHXTRACT® decontamination economics will reflect a further credit for salvage or scrap value. Economic analysis versus baseline options is a specified portion of this project, but it appears that the TECHXTRACT® system can offer substantial economic advantages for many DOE sites.

Technology Transfer/Collaborations

The core technology for the project is EET's TECHXTRACT® technology. In addition, EET plans to actively incorporate other vendors' capabilities into the overall system. Specifically, existing chemical baths from ultrasonic and materials-handling equipment vendors will be used in the system design. EET is also using "SIMCONs" (simulated waste coupons) developed by Idaho National Engineering Laboratory (INEL) for its surrogates. We also are reviewing other projects funded by DOE for possible waste treatment technologies that can be used in the system. This evaluation is still in its initial stages.

Technical Approach

The scope of the project is to develop an integrated, full-scale system for the decontamination of small equipment and debris and the treatment/waste minimization of the resulting secondary waste. The system will be based on EET's TECHXTRACT® contaminant extraction technology. This technology has already been substantially proven in related applications, but has not been developed to the point of offering an integrated, economical system.

The project begins with limited laboratory testing to optimize the operating parameters for the system. For expediency and cost effectiveness, initial testing will be done using nonradioactive surrogates. Final bench-scale confirmation testing will be done using actual, radioactively contaminated samples. Key design parameters to be evaluated include chemical batch times, temperature, chemical concentrations, recharge rates, and secondary treatment media. Lab testing will be done separately for the decontamination line, waste treatment system, and rubble decontamination.

Once design parameters are established, engineering design will begin on the system. Design will be done for a defined demonstration project. The design phase will include preparation of fabrication cost estimates, operating cost estimates, and operating capabilities of the system.

The system will be constructed during the second, optional phase of the project. The system will be modular so that it can be easily moved between project locations. After construction is complete, a "clean" run will be made to validate the operational readiness of the system and it will be moved to the test site for the demonstration. The full-scale field demonstration will be conducted onsite at a DOE facility. EET recommends a 2-month operational period for the full-scale field demonstration.

Accomplishments

The PRDA was awarded in September 1996, and as such, the project is still in its initial research phase. Because the test phase for the project is relatively short, some preliminary results are available:

- Initial results from surrogate coupon decontamination are very good. Quantitative results from INEL show reductions of up to 98%. Qualitative results from subsequent testing indicate even better performance. These will be verified by quantitative analysis.
- Best results have been obtained using a heated ultrasonic bath, the three-step sequential process, an enhanced version of the TECHXTRACT® chemistry, 20- to 30-minute batch times, and dilution of up to 90%.
- Preliminary waste treatment research has focused on destruction of the chelates that are in the TECHXTRACT® blends. Favorable results have been obtained, but additional testing is needed once the specific radionuclides, decontamination steps, and treatment criteria are defined.
- EET will begin the hot lab testing phase of the project in the near future.
- The preliminary selection of the DOE site for the optional phase is now a major project objective. This selection will enable EET to obtain samples for the hot testing laboratory phase and to tailor the system to the specific site requirements and radionuclides.

EET still anticipates completing the first phase of the project well before the end of FY 1997 and requesting authorization to move into the unit construction and field demonstration phase at that time.

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Innovative Cross-Flow Membrane System for Volume Reduction of Mixed Waste

William Greene, SpinTek Membrane Systems, Inc.

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

Technology Need

DOE has many nuclear weapons-related facilities requiring separation of radioactive materials from a liquid waste or process stream to reduce the quantity of radioactive material for disposal. In addition to minimizing waste, DOE is also interested in concentrating organic materials and in fractionating closely sized particles.

Technology Description

In this task, SpinTek Membrane Systems, Inc., and the Institute of Gas Technology are completing engineering development leading to a full-scale demonstration of the SpinTek ST-II High Shear Rotary Membrane Filtration System (ST-II) under a Program Research and Development Agreement (PRDA) with the Federal Energy Technology Center-Morgantown.[1]

The SpinTek ST-II technology will be scaled-up, and a two-stage ST-II system will be designed, constructed, and operated on both surrogate and actual feed at the Los Alamos National Laboratory (LANL) Liquid Radioactive Waste Treatment Facility (LRWTF). Results from these studies on both surrogate and actual wastewater streams will also be used by LANL personnel to produce a model for determining the applicability and economics of the SpinTek ST-II system to other DOE waste and process streams.

The ST-II is a unique, compact cross-flow membrane system having several advantages in performance and cost compared to currently available systems. These include the following.

- High fluid shear prevents membrane fouling even with very high solids content; hazardous and radioactive components can be concentrated to the consistency of a pasty slurry without fouling.
- Induced turbulence and shear across the membrane increases membrane flux by a factor of ten over existing systems and allows operation on fluids otherwise untreatable.
- Innovative ceramic membrane and mechanical sealing technology eliminates compatibility problems with aggressive DOE waste streams.
- System design allows rapid, simple disassembly for inspection or complete decontamination.
- Produces colloidal- and suspended-solids-free filtrate without the addition of chemicals.

Staff at LANL have performed pilot-scale testing with the SpinTek technology to evaluate its feasibility for enhanced radionuclide removal from wastewater at its 5- to 8-million-gallon-per-year LRWTF. Recent data have shown the system's capabilities to remove radionuclides from the waste stream at concentration factors greater than 2000:1, and performance has exceeded both conventional and all other advanced technologies examined. These efforts provide conclusive data that ST-II can successfully provide long-term, cost-effective, enhanced efficient separations

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[1] Activities described here are funded through the U.S. Department of Energy Contract No. DE-AC2196MC33136, which is administered through the Federal Energy Technology Center-Morgantown.

for radioactively and organically contaminated DOE waste streams to meet both current and evolving discharge requirements.

During Phase 1 of this project, LANL will complete scale-up and verify performance of the scaled-up SpinTek unit with surrogate materials. Phase 2 of this project will involve installation and operation of the full-scale, two-stage SpinTek unit for treating the LRWTF waste stream.

Benefit to DOE/EM

This technology is applicable to many DOE sites. Following successful full-scale demonstration for treatment of LRWTF wastes, the technology will be rapidly deployed on a wide range of waste and process streams throughout the DOE system.

Typical applications for which the SpinTek system is recommended are 1) those requiring fine particle filtration without generating a secondary waste; 2) where it is undesirable to use a thermal dewatering process; 3) where the materials to be removed are colloidal, metal hydroxides; or other suspended solids; 4) fractionation applications where it is desirable to separate components with differing particle sizes; 5) where conventional membrane systems cannot operate without fouling; and 6) in systems constructed with materials such as stainless steel, titanium, Teflon, etc., due to aggressive chemicals in the feed.

Scientific Background

The DOE requirements for wastewater cleanup include selective separation of low-level from high-level radioactive waste, recovery of washing reagents, sludge concentration and processing, and converting waste solutions to recycle streams. Conventional membranes and membrane systems historically have been poor candidates for such challenging separations.

Membranes are classified according to the size of their pores or by their molecular weight cutoff.

1. Microfiltration membranes remove contaminants in the 2- to 0.025-µm range. Although micron-sized particles can be removed by nonmembrane or depth materials such as those found in fibrous media, only a membrane or screen filter having a precisely defined pore size can ensure qualitative retention.
2. Ultrafiltration (UF) membranes separate high-molecular-weight solutes from liquids. The pore sizes are usually given in nominal molecular weight cutoffs (NMWC) rather than micron rejections. UF membrane pore sizes range from 1,000,000 to 10,000 NMWC. Low-molecular-weight species (e.g., salts, sugars, and most surfactants) can permeate the membrane. Suspended solids, colloids, and macromolecules are rejected and concentrated.
3. Nanofiltration (NF) membranes, with pore sizes ranging from 10,000 to 200 NMWC, offer the unique capability of selective separation of low-molecular-weight compounds at low to medium pressures. Organic components such as proteins and sugars are retained as well as a certain percentage of dissolved sodium chloride, while low-molecular-weight dissolved solids are passed through as permeate.

Traditional membrane systems fundamentally consist of dead-end type systems (Figure 1) and cross-flow systems (Figure 2). A cross-flow system must recirculate the process fluid through the membrane modules to permit the "sweeping action" to take place. This requires the use of recirculation pumps, that feed the material to the membrane housing continuously at a much greater rate than the actual flow of permeate effluent being drawn off.

The recirculation pump provides a means of achieving cross flow as well as the driving force for permeation. A valve located on the tank return line adjusts the back pressure, thus controlling the driving force pressure on the membrane

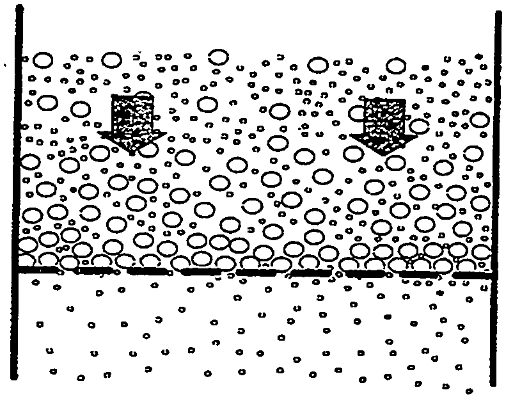

Figure 1. In dead-end filtration systems, particulates rejected by the membrane surface build up and create a layer of particles called a cake. The thickness of the layer soon obstructs the filter media completely, causing the flow to drop off substantially or stop.

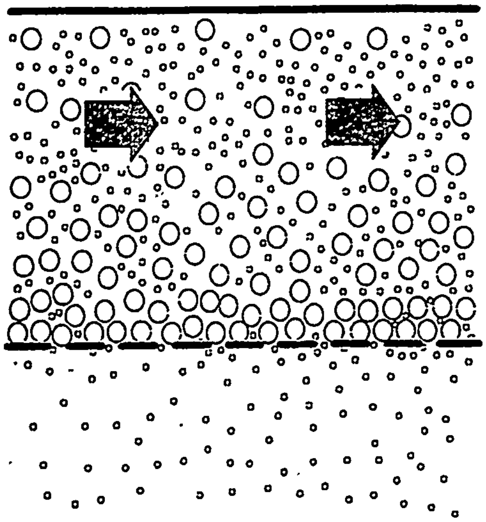

Figure 2. Cross-flow systems allow only part of the feed stream to pass through the membrane. The remaining feed flow is recirculated much more quickly to create a stream of fluid flow parallel to the membrane. The quickly flowing stream creates a fluid shear near the membrane surface that helps minimize particulate layer thickness. Efficiency of this fluid shear increases with the fluid velocity. Unlike dead-end systems, cross-flow systems can be operated continuously with a steady throughput.

surface. Another valve allows the precise control of concentrate to be drawn off, controlling the solute concentration in the recirculating fluid. If the recirculation rate is sufficient to maintain an efficient boundary layer at the membrane surface, a steady-state permeate flow is achieved.

Performance

Cross-flow systems rely on the recirculation flow to maintain the boundary layer at the membrane. Because the pressure losses through the system are due to friction increase with an increase in flow, the driving force pressure becomes dependent on the cross-flow velocity. This severely limits the maximum achievable cross-flow velocity. Typically, cross-flow velocities above 5 m/s are impractical or impossible to reach with conventional equipment.

Concentration Polarization

Concentration polarization is a boundary-layer phenomenon in which solutes retained by the membrane accumulate at the membrane surface. During the membrane separation process, solvent and solutes are transported to the membrane surface. As the solvent and permeable solutes pass through the membrane, the concentration of the retained solutes increases until a critical concentration is reached and steady state is established. At this point, the convective transport rate of these solutes to the membrane surface equals the diffusion transport rate of these solutes out of the boundary layer.

Under the influence of a trans-membrane pressure gradient, water and solute will be forced to flow across this boundary layer to pass through the membrane. However, if the membrane completely retains the solute, the solute concentration adjacent to the membrane will have to increase as a natural consequence of the removal of solvent. This results in the development of a concentration gradient across the boundary layer with the maximum solute concentration located adjacent to the membrane surface. This concentration gradient is referred to as concentration polarization. The concentration polarization boundary layer usually produces two adverse effects: reduction of flux, and a change in particle selectivity.

The boundary-layer resistance to permeation can become much larger than that of the membrane, and thus significantly reduce flux. As the concentration of retained solutes increases at the membrane surface, the pressure required for permeation of the solvent and solutes through this layer increases. As a result, membrane system separation capability is adversely affected.

Fouling

Whereas concentration polarization might be described as a dynamic fouling, other types of membrane fouling can affect membrane performance, sometimes permanently. This kind of fouling may be composed of materials adsorbed directly on the membrane, or may accumulate on the surface where it is difficult to control. In general, fouling is a boundary-layer or sub-boundary-layer phenomenon caused or aggravated by concentration polarization, in which solutes deposit on the membrane surface and reduce membrane flux and selectivity. The deposition mechanisms include chemical reaction, precipitation, electrical attraction, and other interactions. Whereas concentration polarization is a fluid dynamics phenomenon, fouling is a chemical phenomenon between solutes and the membrane. Foulants include organic salts, macromolecules, colloids, and microorganisms. Proper selection of membrane material is the only defense against fouling.

Cleaning

Although it is effective at reducing fouling, cross flow alone is often insufficient to eliminate fouling. If fouling at some level occurs, the only way to reverse its effect is to clean the membrane, typically in situ at an elevated temperature using either acids, caustics, oxidizing agents, enzymatic detergents, or a combination. In many cases, near complete regeneration of performance can be achieved. However, each cleaning causes a certain amount of wear and tear on the membrane. Cleaning frequency can severely limit membrane life. Because concentration polarization affects fouling, a system that limits concentration polarization would tend to limit cleaning frequency, and thus prolong membrane life.

Technical Approach

SpinTek is working closely with LANL to minimize the quantity of low-level radioactive waste from LANL's high-volume LRWTF, which treats all of the wastewater from the LANL site. The wastewater includes that generated by ongoing research and from decontamination and decommissioning operations. LANL has identified a membrane process as the best approach to replace the current chemical precipitation facility to provide a higher quality effluent at their National Pollutant Discharge Elimination System-permitted outfall. However, the aggressive nature of this stream makes available separations technologies unsatisfactory, because of either their inability to achieve the desired degree of concentration, or because of rapid fouling of the membrane surface.

The LRWTF removes radioactive and hazardous material from wastewater and discharges acceptable-quality water into the environment. The concentrate from this process is currently being put into 55-gallon drums and sent to a low-level radioactive landfill, which is reaching its capacity. Additional wastes will be sent eventually to the Waste Isolation Pilot Plant (WIPP), where the storage costs will be much higher, because WIPP is designed to store transuranic wastes. SpinTek's technology offers large cost savings compared to current and other potential treatment technologies.

The current system is shown in Figure 3. In the LRWTF, the wastewater, which contains ^{235}U, ^{239}Pu, and ^{241}Am as the primary radioactive components, enters the facility's settling tanks. Chemicals are added to precipitate the heavy and radioactive metals. The water then enters a clarifier where the overflow is discharged to the environment and the sludge is treated by a rotary drum vacuum filter. The vacuum filter uses a diatomaceous earth pre-coat.

The sludge generated by this system consists mostly of the pre-coat material from the vacuum filters and the chemicals that were added. There is an inefficient separation of the radioactive components from the nonradioactive pre-coat material.

This current system generates 300 55-gallon drums of sludge per year and has a 380:1 waste reduction ratio; that is, for every 380 gallon of wastewater entering the treatment plant, 1 gallon of radioactive waste is generated. SpinTek has achieved a reduction of more than 2000:1 on this waste stream in field pilot tests at LANL.

The current system cannot meet the new proposed discharge standards expected to be imposed by state regulators. Staff at LANL evaluated the ability of the SpinTek pilot unit to improve separating efficiency. Testing was

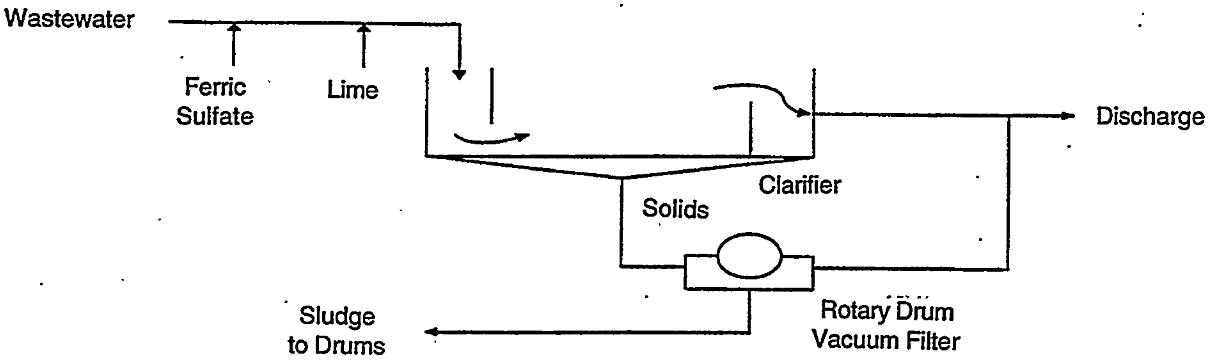

Figure 3. Current Los Alamos TA-21 waste treatment system

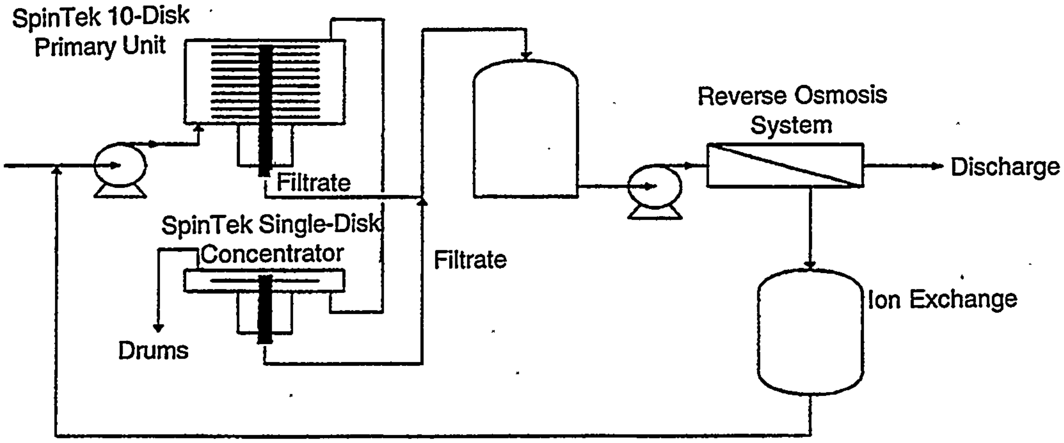

Figure 4. Revised Los Alamos membrane filtration system

conducted with the SpinTek system treating the concentrate directly from the hollow fiber UF system. The combined system produced a concentration factor of 3000:1. The system now being considered is shown in Figure 4.

The SpinTek ST-II (patent pending), shown in Figure 5, has rotating hollow disks covered with either commercially available or specialty flat sheet membranes. The disks are mounted on and connected hydraulically to a common hollow rotating shaft. The entire stack of membrane disks is enclosed within a pressure vessel. The feed fluid enters the vessel, flows between disks and across the membrane surface, where permeate flows through the membrane and exits through the hollow shaft. Concentrate exits the pressure vessel at the opposite end.

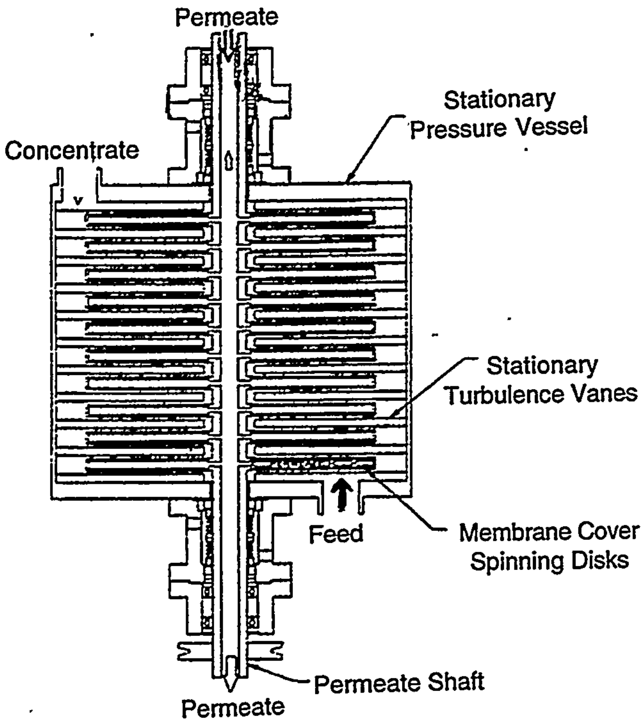

Figure 5. SpinTek II high shear rotary filter

Stationary surfaces oppose the rotating membrane disks, generating large fluid shear rates across the membrane surface. This effectively eliminates the boundary layer that forms in conventional systems yielding very high fluid flux rates through the membranes.

Filtration

The high-shear SpinTek membrane process is similar to that of conventional membrane systems with the exception of the rate at which the process fluid is recirculated. Because the cross-flow velocity is controlled by rotating the membranes, the recirculation flow rate is set based on the amount of permeate removed. Pressure is decoupled from the feed flow rate, allowing more control over the driving force pressure, and independent control of cross-flow velocity. This allows optimization of performance for a broad range of feed characteristics.

A conventional membrane system may have a cross-flow velocity of 8 ft/s while the SpinTek ST-II high shear membrane typically operates at 55 ft/s. This dramatically influences concentration polarization, enhances performance, and allows selectivity to be determined by the membrane instead of by the boundary layer that forms on top of the membrane. The SpinTek ST-II has open channels, uninhibited by mesh-type turbulence promoters, allowing the system to process a wide variety of viscous solutions containing moderate to high solids.

While conventional membrane systems rely on adhesives and plastics for spacers and binders, SpinTek has developed a ceramic-coated metallic membrane disk that uses mechanical sealing methods and can be decontaminated.

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TTP Number ME06C331

Immobilization of Fission Products in Phosphate Ceramic Waste Forms

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

Technology Need

The current volume of high-level waste (HLW) across the DOE complex is several hundred thousand cubic meters. This wastes includes solids, sludges, liquids, and salt cake and comprises radionuclides in three broad categories: actinides, lanthanides, and fission products. Because of the diverse chemical and physical nature of the components in these three categories, 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 ^{99}Tc, ^{137}Cs, and ^{90}Sr in the HLW poses myriad problems. These radionuclides are highly volatile and may escape into the offgas during HLW vitrification, thus generating a secondary waste stream that will require additional stabilization/solidification (S/S). Technetium is readily oxidized to a highly soluble pertechnetate form that is very difficult to immobilize. Technetium and cesium (^{135}Cs) have extremely long half-lives ($\approx 10^6$ years) and require an appropriate durable immobilization system. Moreover, ^{137}Cs and ^{90}Sr are also heat generators with half-lives of $\approx$30 years; therefore, they will be sources of considerable heat loads for 30 to 50 years if disposed of in a repository in vitrified HLW.

The approach under consideration is to remove fission products from HLW and dispose of them separately. Removing fission products from the HLW reduces the overall waste volume and radioactivity levels of HLW, thus simplifying waste-handling operations. In this regard, several separation technologies are being developed as part of the ESP-CP. These separation technologies, along with other decontamination activities, 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 technology is available to immobilize the fission-product wastes. Such a technology could produce durable waste forms for long-term storage and 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. Specifically, the focus of this task is to develop phosphate ceramics to immobilize ^{99}Tc eluted from sorption processes.

Technology Description

Chemically bonded phosphate ceramics (CBPCs) have several advantages that make them ideal candidates for containing 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 have high radiation stability, are refractory, and will not degrade in the presence of internal heating by fission products. Dense and hard CBPCs can be fabricated inexpensively and at low temperature by acid-base reactions between an inorganic oxide/hydroxide powder and either phosphoric acid or an acid-phosphate solution. The resulting phosphates are extremely insoluble in aqueous media and have excellent long-term durability. CBPCs offer the dual stabilization mechanisms of chemical fixation and physical encapsulation, resulting in superior waste forms.

Argonne National Laboratory (ANL) is developing CBPCs to treat low-level mixed wastes, particularly those containing volatiles and pyrophorics that cannot be treated by conventional thermal processes. This work was begun under ANL's Laboratory Directed Research

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[1] Work sponsored by U.S. Department of Energy, Office of Technology Development, as part of the Efficient Separations and Processing Crosscutting Program, under Contract W-31-109-Eng-38.

and Development funds, followed by further development with support from EM-50's Mixed Waste Focus Area.

As part of our previous work, we developed magnesium- and magnesium-potassium-based final waste forms containing several surrogate waste streams, including ash, salts, and cement sludge (all spiked with contaminants such as Ce, Cs, Pb, Ni, Cr, Cd, and Hg). A variety of performance tests (TCLP, ANS 16.1, 90-day water immersion tests, and ASTM compression-strength tests) conducted on the fabricated final waste forms showed excellent results, thus demonstrating that the CBPCs are a viable approach for disposal of radioactive and hazardous wastes.

The goal of this task is develop and demonstrate the feasibility of CBPCs for S/S of wastes containing fission products. The focus of this work is to develop a low-temperature CBPC immobilization system for eluted ^{99}Tc wastes from sorption processes.

Benefit to DOE/EM

This task will provide a novel low-temperature process for treating and stabilizing fission products generated from cleanup of HLW tanks and D&D processes. CBPC technology will complement the various separation technologies used to remove fission products (especially Tc) from HLW tanks by immobilizing the separated volatile radionuclides in a durable final waste form. Also, CBPC can be used to treat mixed wastes to meet land disposal restrictions for waste streams that are incompatible with high-temperature processing, particularly wastes containing volatiles, pyrophorics, and heavy-metal chlorides and fluorides. Therefore, this technology will complement high-temperature treatment processes (e.g., plasma hearth and vitrification) and fill a gap in DOE's strategy to treat wastes that contain volatile contaminants, thus becoming an integral part of a complete system for stabilizing both high- and low-level wastes.

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

Results to date on radionuclide surrogates have shown excellent retainment of contaminants in the CBPCs. The technology generates no secondary wastes; moreover, it is relatively low cost and has only minimal energy requirements, providing an extremely attractive high return on investment.

Technology Transfer/Collaborations

In FY 1997, we are collaborating with Northwestern University to study phase analysis and pore structure of the fabricated waste forms and establish the speciation and valence state of ^{99}Tc in the final waste form. This collaborative work will provide critical insights into leaching behavior of the radionuclide and durability of the final waste form.

Collaborative work is already under way with LANL and Savannah River Site (SRS). The CBPC technology is being targeted for the ^{99}Tc-containing wastes generated by LANL's complexation-elution process, and a treatability study on the eluted wastes containing actual radionuclides is being conducted at LANL. During FY 1996, we used the CBPC process to successfully demonstrate the stabilization of phosphoric acid residue waste generated by the SRS process for destroying ion-exchange resins. We expect this collaboration to continue in FY 1997.

Successful demonstration of CBPC technology on actual wastes during FY 1997 will lead to the development of the technology at the pilot scale. For this work, industrial partners in waste solidification and DOE site(s) for demonstration will be identified. An onsite demonstration will be sought with concurrence from EM staff that will stimulate collaboration between industry, ANL, and DOE to ensure successful technology transfer to end users.

Scientific Background

Based on thermodynamic predictions and evidence from nature, it is clear that only crystalline waste forms will survive under relatively modest temperatures (≈100°C) and in the presence of water. Therefore, to guarantee safe long-term disposal, it is necessary to not only incorporate the contaminants in a dense crystalline matrix but also chemically bind them. Several mechanisms are available to chemically fix contaminants in a mineral phase, including elemental substitution, conversion of the contaminant to an insoluble form, and intercalation reactions.

Elemental substitution occurs when the contaminant species substitutes for a benign ion with similar characteristics such as valence or ionic radius and does not disrupt the atomic arrangement of the crystalline ceramics. The resulting material is a solid solution with similar stability properties.

In general, phosphates are extremely insoluble. If by chemical reactions, contaminants are converted into their phosphate form, they can then be prevented from dissolving in a liquid phase and leaching out. Intercalation reactions occur in two-dimensional layered 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.

Because phosphate ceramics exhibit one or more of the above-mentioned mechanisms, they are being considered for the S/S of fission products. CBPCs are refractory, have high radiation stability, and can tolerate structural changes caused by decay of radioactive contaminants. Moreover, it is expected that in CBPC technology, contaminants will be first chemically fixed and then microencapsulated in a dense phosphate matrix, resulting in a superior waste form.

Technical Approach

During FY 1996, CBPCs were used to stabilize two target wastes: separated Tc wastes from LANL's complexation-elution process and an acid residue waste from oxidation of ion-exchange resins. Radionuclide surrogates were used for this effort. Dense and durable magnesium and magnesium-potassium phosphates were developed. Waste forms were fabricated at room temperature through acid-base reactions. Various standard performance tests for leachability, strength, and durability in aqueous environments were conducted on the forms. Parametric studies were conducted to optimize the waste loadings, radionuclide surrogate, and Resource Conservation and Recovery Act metal content that could be stabilized in the phosphate ceramic. Based on this developmental work in FY 1996, the CBPC technology will be applied to eluted waste with ^{99}Tc in FY 1997. The detailed approach for the FY 1997 task is as follows.

Development of final waste forms with actual radionuclides:

- A treatability study will be conducted on eluted Tc waste from LANL's complexation-elution process. A mixture of ^{95m}Tc/^{99}Tc from solutions of NaOH/ethylenediamine/Sn^{2+} will be incorporated in a phosphate matrix to determine the performance of reduced and complexed Tc. The NaOH/ethylenediamine/Sn^{2+} solution is the material that results from eluting Tc from a Reillex™-HPQ anion exchanger column. In a separate study, Tc will be incorporated directly into the phosphate matrix. These treatability studies will be conducted in collaboration with LANL.
- Fabricated waste forms will be tested for mechanical stability/compression strength (ASTM C 39), water immersion, leaching behavior (ANS 16.1, PCT, and MCC-1), radiation stability, and thermal cycling (ASTM B 553).
- Extensive microstructural and mineralogical evaluations will be carried out to determine the fate of Tc in the phosphate matrix. Specifically, the speciation and valence state of Tc in the waste form will be established through sophisticated analytical techniques.
- Based on the treatability studies, process limits and merits will be defined, and applicability limits will be established. These studies will be aimed at determining acceptability of the stabilized product and the bench-scale technology.

Accomplishments

The project was initiated in March 1996. Using radionuclide surrogates (Re for Tc), we demonstrated successfully during FY 1996 that CBPCs can be used for the S/S of Tc-containing wastes and other low-level mixed wastes. Specifically, two waste streams were targeted: separated Tc wastes from LANL's complexation-elution process, and an acid residue waste from oxidation of ion-exchange resins.

Highlights of FY 1996 results include:

- CBPCs are easily fabricated under ambient conditions. The technology is extremely rugged and can treat waste with a wide range of compositions. Waste loadings can be as high as 40 wt% for LANL's eluted Tc and 55 wt% acid residue waste streams. The presence of NaOH, ethylenediamine, and $SnCl_2$ in the LANL waste does not affect the phosphate solidification process.

- CBPCs are very dense, strong, and insoluble in aqueous environments. Compression strengths of 2500 to 4500 psi were measured for the waste forms. These strengths are similar to those for portland cement without any waste loading.
- CBPCs are extremely effective in the stabilization of Re (surrogate of Tc). A product consistency test conducted on CBPC-LANL eluted waste forms showed the leaching rates of Re to be 3 to 9 x 10^{-4} g/m^2-d. These values are significantly lower than those reported for Tc stabilized in borosilicate glass (0.12 g/m^2-d), but are comparable to those for SYNROC ($\approx 10^{-4}$ g/m^2-d). Similarly, ANS 16.1 tests on the waste forms indicated a leachability index (LI) for Re of >12. For comparison, LI for Tc in cement waste forms is 7 to 9. In addition, TCLP on CBPC-acid residue waste shows excellent stabilization of RCRA metals such as Cr and Ni in the phosphate matrix.
- CBPC waste forms show excellent long-term durability. Ninety-day water immersion tests show <0.5% change in sample weight, indicating no apparent dissolution of the matrix material.
- Microstructural and mineralogical characterization show the presence of both crystalline and amorphous phases in the waste forms. There is uniform distribution of the contaminants in the matrix, and no agglomeration. Contaminants are believed to be microencapsulated in the dense phosphate matrix.

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TTP Number CH26C322

Inorganic Ion Exchangers for Nuclear Waste Remediation

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

Technology Need

The objective of this work is to provide a broad spectrum of inorganic ion exchangers that can be used for a range of applications and separations involving remediation of groundwater and tank wastes. We intend to scale-up the most promising exchangers, through partnership with AlliedSignal Inc., to provide samples for testing at various DOE sites.

While much of the focus is on exchangers for removal of Cs^+ and Sr^{2+} from highly alkaline tank wastes, especially at Hanford, we have also synthesized exchangers for acid wastes, alkaline wastes, groundwater, and mercury, cobalt, and chromium removal. These exchangers are now available for use at DOE sites.

Technology Description

Many of the ion exchangers described here are new, and others are improved versions of previously known exchangers. They are generally one of three types: 1) layered compounds, 2) framework or tunnel compounds, and 3) amorphous exchangers. In some cases, they are composite exchangers in which a gel exchanger is used to bind a fine powder into a bead for column use. Most of these exchangers can be regenerated and used again. Some exchangers fix the radioactive species permanently. In the tables that follow, some of the more interesting exchangers are listed according to function.

Groundwater

Figure 1 shows the results of 12 equilibrations for two of the exchangers listed in Table 1. M151 is the Na-Mica, and SZ-72 is a sodium zirconium trisilicate, a member of a new family of ion exchangers in which other members include titanium, cerium, lead, and tin. P266H and P266Ca are tin phosphates in H^+ and Ca^{2+} forms, respectively.

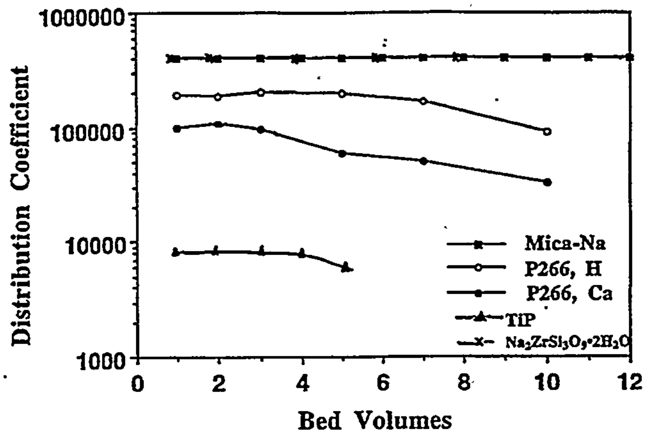

Figure 1. Cesium uptake from groundwater simulant

Figure 1 shows that both M151 and SZ72 completely removed Cs^+ from the groundwater simulant for all 12 cycles. This represents an uptake of ~0.45 meq/g of Cs^+. This is about half the capacity of the mica and only 20% of the capacity of SZ-72. Sodium mica is best used as a barrier-type exchanger because it traps the Cs^+ permanently; therefore, it can be added to soil to confine Cs^+ in place. The SZ72 can be regenerated and used for many cycles. Both exchangers are prepared hydrothermally, but the mica may be the least expensive exchanger of those listed in Table 1.

Other excellent candidates for groundwater are members of the pharmacosiderite group. In preliminary tests at 3M, the titanium silicate member TiSi-Ph (Table 1) showed efficient uptake of Sr^{2+} from a groundwater simulant. Our own trials with a simulant of 100 ppm Ca, 1 ppm Fe^{3+}, 8 ppm Mg^{2+}, 1 ppm K^+, and 15 ppm Na^+ spiked with 1.1×10^5 cpm $^{89}Sr^{2+}$ (~5 ppm) gave a K_d (V:m = 200) of 58,400 mL/g.

Table 1. K_d values in groundwater of composition in ppm, ^{100}Ca, ^{10}Mg, ^{15}Na, ^{5}Cs, ^{5}Sr; V:M = 1000

Exchanger	Type	pH	K_d(mL/g) Cs^+	 Sr^{2+}
Mica-Na	Layered	6.3	>400,000	<5
TS-156	Layered	7.3	350,000	10,650
TSC-87	Framework	7.1	19,700	78,200
TSC-104	Framework	7.3	270,000	111,600
SZ-72	Framework	6.6	400,000	4300
NbS-5	Framework	6.4	400,000	136,000
TiP-M	Amorphous	3.7	15,500	1020
TiP-M	Amorphous	6.3	30,000	4500
δ-SnP-NH_4^+	Layered	4.6	200,000	1400
TiSi-Ph	Framework	7.2	9700	58,500

Toxic Metals

Screening tests were run on new and altered forms of some of our exchangers to see if they are selective for toxic metals in groundwater or contaminated sites. These tests consisted of measuring K_d values of 0.001 *M* metal nitrate solutions at V:m = 200. Results are presented in Table 2.

To determine that the K_d values are not all due to precipitation of insoluble oxides arising from the basic properties of the exchanger upon hydrolysis, the K_d values were rerun in the presence of 1 *M* $NaNO_3$. These values are listed in Table 2. It is apparent from the reduction in K_d values that pH plays a role but so does the increase in Na^+ content. To further test one of the exchangers, the K_d values were obtained in acid solutions for P209 for Pb^{2+}. The results are listed here.

Conc. HNO_3(M)	**0.01**	**0.03**	**0.1**	**0.3**	**1.0**
Kd (mL/g)	142,000	78,700	30,750	17,200	1620

At up to 1 *M* HNO_3, this exchanger is selective for Pb^{2+}. P209 is a single member of a family of tunnel-type exchangers of which we have prepared several members. We

Table 2. K_d values of various inorganic ion exchangers toward toxic metals

Sorbent	Cr^{3+}	Cu^{2+}	K_d (mL/g) Co^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}
P209 NH_4TiOPO_4	~100,000	>100,000	750	~20,000	100,000	100,000
SZ133 $Na_2Zr_5Si_2$	~100,000	3500	28,900	8900	~70,000	500
SZ47 Na_4ZrSi	1000	24,5000	>100,000	4200	330	80
SZ143	1050	10,700	18,600	7500	6100	2500
SZ148 $Na_2ZrSi_3O_{10}$	>100,000	20,000	17,600	6900	17,400	240
			In 1 *M* $NaNO_3$			
P209	100,000	8300	170	290	46,400	1900
SZ133	25,100	1960	4	57	4900	170
SZ47	19,200	6000	3360	2600	32,100	170
SZ143	25,800	6000	260	2060	29,700	530
SZ148	33,500	5280	110	500	27,500	115

believe that these materials will be effective in many problems dealing with toxic metals in the environment. The key is the tunnel size, which can be altered by degrees.

Tank Wastes

We have prepared ammonium molybdophosphate (AMP) as prills, 0.5- to 1-mm-diameter ready for column use. K_d values of ~5000 mL/g have been obtained for Cs^+ in 2 *M* HNO_3.

Sodium zirconium silicate (SZ-72) exhibits a high selectivity for Cs^+ in groundwater (Table 1, Figure 1) and in 1 *M* $NaNO_3$, but then the selectivity decreases as the amount of sodium ion and base increase. In 5 *M* $NaNO_3$ + 1 *M* NaOH, $K_d(Cs^+)$ is 280 mL/g. Efforts to improve the selectivity focus on changing the size of the cavities in a systematic fashion to optimize the Cs^+ selectivity.

A final group of exchangers described here is that of pillared clays. These are most effective in alkaline solution. Pillared clays are prepared by swelling smectite clays and then inserting an inorganic polymer having a high charge between the layers. By firing to 500°C, the pillars are permanently fixed, creating three-dimensional porous materials. Alumina, silica, and zirconia were used as pillars. These exchangers were effective for Sr^{2+} uptake from the double-shell slurry feed (DSSF) -7, as shown in Table 3.

A second group of layered materials, sodium titanates, were pillared by silica polymers. K_d values for Sr^{2+} in DSSF-7 tank waste ranged from 4000 to 12,300 mL/g. Of interest is the fact that these silica-pillared titanates showed no uptake of strontium in the tank waste solution CC, which contains complexing agents (EDTA, sodium gluconate, etc.), but did take up Cs^+ from CC (K_d = 375 mL/g). While a K_d of this magnitude is not outstanding, the question is whether this can be improved by further study. This exchanger could then be used wherever complexing agents are present.

Technology Transfer/Collaborations

Previous reports indicated that a sodium titanate of composition $Na_4Ti_9O_{20}$ is highly selective for Sr^{2+} in alkaline solution. This compound is being tested for use in tank wastes at Pacific Northwest National Laboratory and Savannah River Site. Several tests have been carried out with this exchanger for Sr^{2+} removal from groundwater. Because of the low alkalinity, the sodium titanate is less effective in groundwater. However, preliminary data for pharmacosiderite of composition $Na_3HTi_4O_4(SiO_4)_3 \cdot 4H_2O$ show it to be highly selective for Sr^{2+} in groundwater containing high Ca^{2+} and to have a high capacity ~4 meq/g. In addition, our sodium mica and sodium zirconium silicate (SZ-72) are very effective for removing Cs^+ from both groundwater and waste solutions with salt contents in the 1 to 2 *M* range. Both the mica and SZ-72 are in process of being sealed up and will be supplied to end users wishing to examine these materials.

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Table 3. K_d values for Sr^{2+} on several pillared clays in DSSF-7 waste solution

Exchanger	Pillar	K_d (mL/g)	S. A. (m^2/g)	Interlayer Spacing (Å)
Saponite TYT-1-61-31H	$[Cr(OH)_x]_n$	4290	78	24.2
Saponite TYT-1-050-13N	ZrO_2	13,560	278	25.4
Phlogopite TYT-1-084-52C	ZrO_2	4534	114	14.9
Saponite TYT-1-053-13P	ZrO_2	6767	252	21.5

Waste Separation and Pretreatment Using Crystalline Silicotitanate Ion Exchangers

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

Technology Needs

Within the DOE complex, hundreds of tanks are used for processing and storing radioactive waste by-products generated by weapons material production facilities. These tanks contain tens of millions of gallons of highly radioactive supernatant liquid containing molar concentrations of sodium (Na^+) in a highly alkaline solution (pH >14), along with solid salt cake (primarily $NaNO_3$ and $NaNO_2$), and sludge that is a complex mixture of insoluble metal oxides and hydroxides. Most of the highly soluble cesium (Cs) salts and small amounts of strontium (Sr) salts are present in the liquid supernate. Some of the wastes, primarily at the Idaho National Engineering Laboratory (INEL), are in acidic solutions or in calcine that is proposed for acidic dissolution and reprocessing. Removing Cs and Sr from these wastes will be an important processing step in preparing the wastes for long-term safe storage, because these elements are partially present as strong gamma- and beta-emitting isotopes. In addition to the radiation hazard, the decay energy from these isotopes is a major contributor to the heat generation in the radwastes.

Technology Description

A new class of inorganic ion exchangers called crystalline silicotitanates (CSTs) has been developed jointly by Sandia National Laboratories and Texas A&M University to selectively remove Cs and other radionuclides from a wide spectrum of radioactive defense wastes. The CST exhibits high selectivity and affinity for Cs and Sr under a wide range of conditions. Tests show it can remove part-per-million concentrations of Cs^+ from highly alkaline, high-sodium simulated radioactive waste solutions modeled after those at Hanford, Oak Ridge, and Savannah River. The materials exhibit ion exchange properties based on ionic size selectivity. Specifically, crystalline lattice spacing is controlled to be highly selective for Cs ions even in waste streams containing very high (5 to 10 *M*) concentrations of sodium. The CST technology is being demonstrated with actual waste at several DOE facilities.

The use of inorganic ion exchangers offers many advantages over regenerable organic ion exchangers. The inorganics are more resistant to chemical, thermal, and radiation degradation. Their high selectivities result in more efficient operations offering the possibility of a simple single-pass operation. In contrast, regenerable organic ion exchangers require additional processing equipment to handle the regeneration liquids and the eluant with the dissolved Cs.

This task has three primary activities in FY 1997:

1. Continue the testing program to address problems that may arise during testing of CSTs for various applications. Focus on studies relating to pretreatment of the commercial product.

   IONSIV® IE-911 could have a varying proton concentration from lot to lot, thus requiring pretreatment by the user to avoid lowering the solution pH during use and to avoid potential precipitation of aluminum hydroxides and other compounds. We will develop specific procedures for converting the hydrogen form to a sodium form.

2. Further develop the mathematical model to enable prediction of column performance under various experimental conditions and to facilitate its use by others.
3. Develop new inorganic materials to meet specific DOE challenges for the separation of radionuclides from radwastes; for example, Sr separation from acidic solutions, and separation of Tc, actinides and other anionic radionuclides and Pb and Cd from solutions.

Benefit to DOE/EM

The technology developed and demonstrated under this task will be extended to further meet DOE needs by identifying new materials for advanced, efficient radioactive or Resource Conservation and Recovery Act (RCRA) separations technology.

Technology Transfer/Collaboration

Texas A&M University (CST co-inventor)
UOP (CRADA partner)
Pacific Northwest National Laboratory
Oak Ridge National Laboratory
Los Alamos National Laboratory
Idaho National Engineering Laboratory
Westinghouse Savannah River Company
West Valley Nuclear Services

Accomplishments

A stable, Cs-selective CST powder called TAM-5 was developed by carefully controlling the crystal structure (Figure 1). TAM-5 is highly selective for removing Cs from solutions throughout the pH spectrum (Figure 2), and selective for Sr in alkaline and neutral solutions (distribution coefficients [K_d] >10,000 mL/g).

The CST structure was determined, and positions of individual atoms are known using x-ray and neutron diffraction. The structural information has permitted identification of the ion exchange sites and insights into the strong effect of pH on Cs ion exchange.

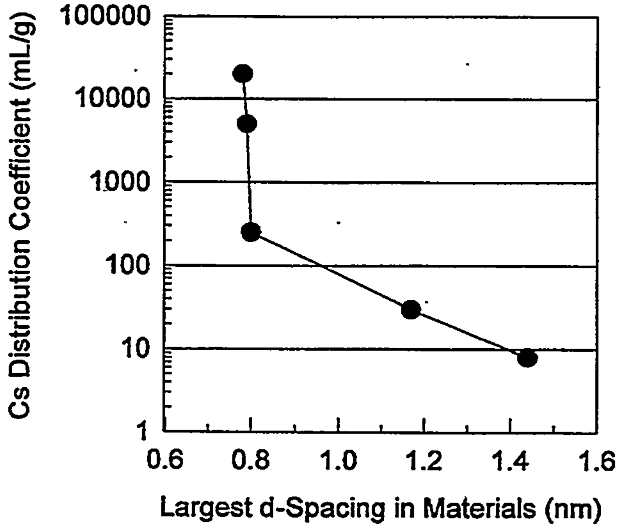

Figure 1. Cesium distribution coefficient (K_d) in 3 M $NaNO_3$, 100 ppm Cs solutions as a function of the largest lattice spacing (d-spacing)

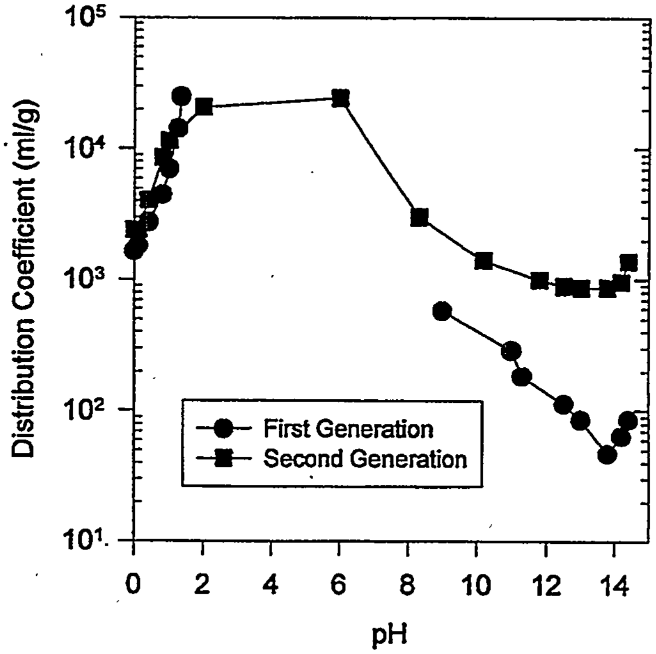

Figure 2. Cesium distribution coefficients as a function of equilibrium pH

This material has been engineered into a granular form suitable for column ion exchange operations and is now commercially available from UOP as IONSIV® IE-911. Characterization and testing of IE-911 has continued at Sandia and other DOE facilities. As a result of these efforts, the material is being recognized as the preferred choice for a number of important DOE applications. In 1996, IE-911 was chosen for the 25,000-gal Cesium Removal Demonstration (CsRD) with actual Melton Valley Storage Tank (MVST) waste at Oak Ridge National Laboratory. This product has outperformed its competitor by a factor of almost 50 in actual waste column testing carried out at Hanford. An independent study conducted by Los Alamos National Laboratory concluded that the use of IE-911 for Hanford cleanup would result in more than $300 million in savings over the baseline process. It was these positive results that resulted in the TAM-5 CST, in the form of IONSIV® IE-910 and IE-911, being awarded a 1996 R&D 100 Award as one of the 100 most technologically significant products of the year.

Ion exchange column tests using simulated wastes indicate 50% Cs breakthrough points over 500 column volumes (CV) for double-shell slurry feed (DSSF) -type wastes. An example of results with actual waste is the work at Hanford with supernatant from tank 241-AW-101, which showed a

50% Cs breakthrough of 670 CV, compared to 13.5 CV 50% breakthrough for the resorcinol-formaldehyde resin.

In evaluations of the chemical and thermal stability of CST, we determined that the dry heating of Cs-loaded CST to several hundred degrees (up to 400°C for several days) should not cause any loss in the ability of the material to retain Cs. Temperatures should be maintained at less than 60°C when the CST is exposed to chemically aggressive solutions (e.g., concentrated acids, DSSF) for long periods (months). At ambient temperature, the CST powder is highly stable in alkaline solutions with no loss in performance or structural integrity over at least 2 months. In concentrated acid solutions (up to 6 *M* HNO_3) at ambient temperature, the powder is stable for at least 5 days with no significant loss in performance. However, several percent of Ti is leached after 5 days in concentrated nitric acid.

Data obtained on the laboratory-produced CST powder showed that the powder in various solutions and various states of treatment had no structural breakdown or decrease in performance when exposed to 10^9 Rads.

Equilibrium and column models were developed to predict the material performance under various practical situations. The column model is a one-dimensional mathematical model that incorporates axial dispersion and mass transfer resistances caused by film (interparticle) and pore (intraparticle) diffusion.

In the equilibrium model, based on data from ion exchange and structural studies, the solid phase is represented as Na_3X instead of the usual form of NaX. By using this solid-phase representation, the solid phase can be considered as an ideal solid, and developing a solid-phase activity coefficient model, and estimating model parameters for the interaction between different ion exchange sites are avoided. A set of model ion exchange reactions are proposed for ion exchange between H^+, Na^+, K^+, Rb^+, and Cs^+. The equilibrium constants for those reactions are estimated from experiments in simple ion exchange systems. Bromley's model for activity coefficients of electrolytic solutions was used to account for liquid-phase nonideality. The model has been used to interpret the differences observed in the 50% breakthrough observed for the MVST versus the Hanford tank supernatants.

Commercialization Status

The CST ion exchange material is now commercially available from UOP (contact Dennis J. Fennelly (609) 727-9400).

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Development and Testing of Spheroidal Inorganic Sorbents

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EM Focus Area: mixed waste characterization, treatment, and disposal; high-level waste tank remediation; subsurface contaminants; decontamination and decommissioning

Technology Need

Inorganic ion exchange materials have high selectivities and efficiencies for separating and removing fission products, actinides, and other elements from aqueous waste streams. However, in most cases, these sorbents are available commercially only as fine powders or as unstable granular particles that are not readily adaptable to continuous processes. Some of these powders are also made into pellets by using binding materials. However, the binders tend to lessen the number of exchange sites 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.

Using inorganic ion exchangers as microspheres improves the flow dynamics for column operations and expands their practical applications. Another disadvantage of many of the inorganic ion exchangers 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 cause variances in the crystal morphology and compositions of the products. These same materials, made by the internal gelation process, are more reproducible. Furthermore, in some cases, the densities and porosities of an ion exchanger made as microspheres can be tailored by varying the chemical and physical process parameters; this allows some control over the selectivity and loading behavior of the exchanger.

Technology Description

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

The initial task of this program involves the development of sodium titanate (NaTi) sorbents as microspheres by the HMTA internal gelation process. In previous studies at Oak Ridge National Laboratory, Pacific Northwest National Laboratory, Sandia National Laboratories, and Savannah River Technical Center, NaTi was found to be the best sorbent material for removing the strontium from alkaline supernatants of high ionic strength. Two types of composite materials are in the process of being developed and optimized. Initial preparations of several composite microspheres of hydrous titanium oxide (HTiO) and titanium monohydrogen phosphate (TiHP) homogeneously embedded with very fine particles of NaTi have been completed. Both sorbents are being optimized by determining empirically the amount of NaTi powder that can be embedded to obtain maximum strontium loading. These composite microspheres were chosen for development because both matrix materials (HTiO and TiHP), as well as the NaTi, are good sorbents for removing strontium from alkaline supernatants.

Following the development of the spheroidal composite sorbents, attempts will also be made to make pure sodium titanate microspheres. Two chemical conversion methods will be tried; both require the use of HTiO gel spheres made

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

by the HMTA internal gelation process. One method involves the hydrothermal conversion of HTiO gel spheres with NaOH. The other method uses an alkoxide conversion process for converting HTiO gel spheres to pure NaTi.

As part of the optimization process, the prepared sorbents are being tested in batch experiments for the removal of strontium from both simulated and actual supernatant waste solutions. For comparison, commercial NaTi sorbents and other strontium-selective sorbents are also being tested. Based on the batch studies, the most promising microspheroidal materials will be selected for further evaluation using column chromatography studies. Bench-scale studies will be used to determine the radionuclide and metal removal efficiency, maximum loading, etc., in a continuous process. BET surface measurements will be made on the best microspherical sorbents.

Benefits to DOE/EM

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 spinoff of these highly developed fuel technologies. The major benefit of this program is to further develop the technology for use in making inorganic ion exchangers more usable for large-scale column use. These materials could have several advantages in treating a variety of waste streams.

Numerous inorganic ion exchangers are (or have the potential to be) used in treating supernatant 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 Sr, Tc, and Cs from tank supernatants (Hanford, Oak Ridge, Savannah River)
- treating contaminated wastewater to remove U, Tc, Co, Pb, Zn, etc. (all sites)
- removing radioisotopes from groundwater (all sites)
- removing actinides and fission products from waste sludge leachate (Idaho, Hanford, Oak Ridge, Savannah River)
- removing heavy metals from acid mine drainage runoff (mine tailings, non-DOE sites)
- removing radionuclides such as Eu, Ce, and Pr from organic streams (solvent extraction processes, analytical wastes)
- removing fluoride from waste streams
- removing radionuclides, Cs, Co, Eu, etc., from liquid wastes generated in hot cell operations, to convert them to a more transportable, storable waste.

In addition to these applications, these inorganic sorbents also have high potential as in situ barrier materials to prevent the migration of metals and radionuclides from burial grounds, leaking tanks, and other sources of contamination.

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

Technology Transfer/Collaborations

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. Two companies have expressed interest in licensing and expanding the use of the technology. A patent application entitled *Method for Preparing Hydrous Titanium Oxide Spherules and Other Gel Forms Thereof* was filed with the United States Patent and Trademark Office on November 1, 1996.

Scientific Background

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

complexation/decomplexation

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

hydrolysis

$$Ti^{4+} + xH_2O \rightarrow Ti(OH)_4 \bullet yH_2O\downarrow + 4H^+ \text{ and} \qquad (2)$$

$$TiO^{2+} + xH_2O \rightarrow TiO(OH)_2 \bullet yH_2O\downarrow + 2H^+,$$

HMTA protonation

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

HMTA decomposition

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

The major constituents of a broth for making microspheres of hydrous metal oxide are HMTA, urea, and the metal salt. Urea serves as a complexing agent for the metal (reaction 1) and at certain concentrations allows stable broths to be prepared at 0°C that remain clear and free of gelation or precipitation for reasonable periods of time. As the temperature of the broth droplets rises in the hot organic medium, decomplexation occurs (reaction 1), allowing hydrolysis of the titanium to occur (reaction 2). HMTA, a weak organic base, drives the hydrolysis reaction to completion. At first the HMTA molecules are singularly protonated (reaction 3). Once most of the HMTA molecules (≥95%) are protonated, they begin to decompose (reaction 4) into ammonia molecules, which make the system even more basic. Each protonated HMTA molecule can effectively remove three additional hydrogen ions. The reaction products are ammonium chloride and formaldehyde. In addition to being a complexing agent, urea also functions as a catalytic agent in the decomposition of protonated HMTA molecules.

One of the more interesting features of the chemistry of the process is the conversion of the reaction products back to HMTA in the basic wash step. When the microspheres are washed with NH_4OH to remove the reaction products (NH_4^+ and CH_2O), the reaction products react to reform HMTA,[6] which is washed from the microspheres along with unreacted urea. This feature makes it possible, by chemical adjustments, to convert evaporator concentrates of the wash solutions back to process-usable HMTA/urea solutions. This feature aids in making the HMTA internal gelation process even more economically attractive.

Technical Approach

The HMTA internal gelation process used in this task is similar to the process used in developing light-water and breeder reactor microspheroidal fuels at ORNL and other laboratories worldwide.[7,8] A schematic of the lab-scale apparatus for making the microspheres is shown in Figure 1. The procedure for making HTiO microspheres by this process involves first mixing formulated amounts of HMTA, urea, and titanium at temperatures near 0°C to form a broth. Broth formulations that remain clear and free of gel for reasonable periods of time (≥1 h) at that temperature are used.

To make the HTiO/NaTi microspheres, a predetermined amount of NaTi is also mixed into the broth. It is added as slurry of very fine hydrated NaTi particles. To keep the NaTi particles suspended, the broth is continuously mixed in the chilled broth tank while it is injected as droplets through a flat-tipped, stainless steel hypodermic needle into a flowing stream of heated organic medium. From there, the droplets are transported into the gel-forming apparatus. The size of the droplets is controlled by using a two-fluid nozzle concept and varying the gauge of the needle and the flow rate of the hot organic medium and the broth. Broth formulations with gel times of 8 to 12 s are used. About 35 s are required for the droplets to pass through the sphere-forming column and the serpentine residence tube to a collection basket (a cylindrical stainless steel wire-mesh basket). Once collected, the microspheres in the basket are lowered into the reservoir of hot organic medium and are aged for 10 to 30 min. The reaction impurities are removed from the microspheres by washing them several times with dilute NH_4OH and then with deionized water.

This project involves the development, preparation, characterization, and testing of NaTi sorbents made as microspheres by the HMTA internal gelation process. The goal is to develop spheroidal NaTi sorbents that are equal to or better than the commercially available engineered forms of NaTi in removing strontium from waste streams.

Composite microspheres of HTiO and TiHP that are homogeneously embedded with very fine particles of NaTi are in the process of being developed and optimized. Optimization involves empirically determining the amount of sodium titanate that can be embedded to obtain maximum strontium loading. The HTiO and TiHP matrix materials were chosen because they are also good sorbents for removing strontium from alkaline supernatants of high ionic strength.

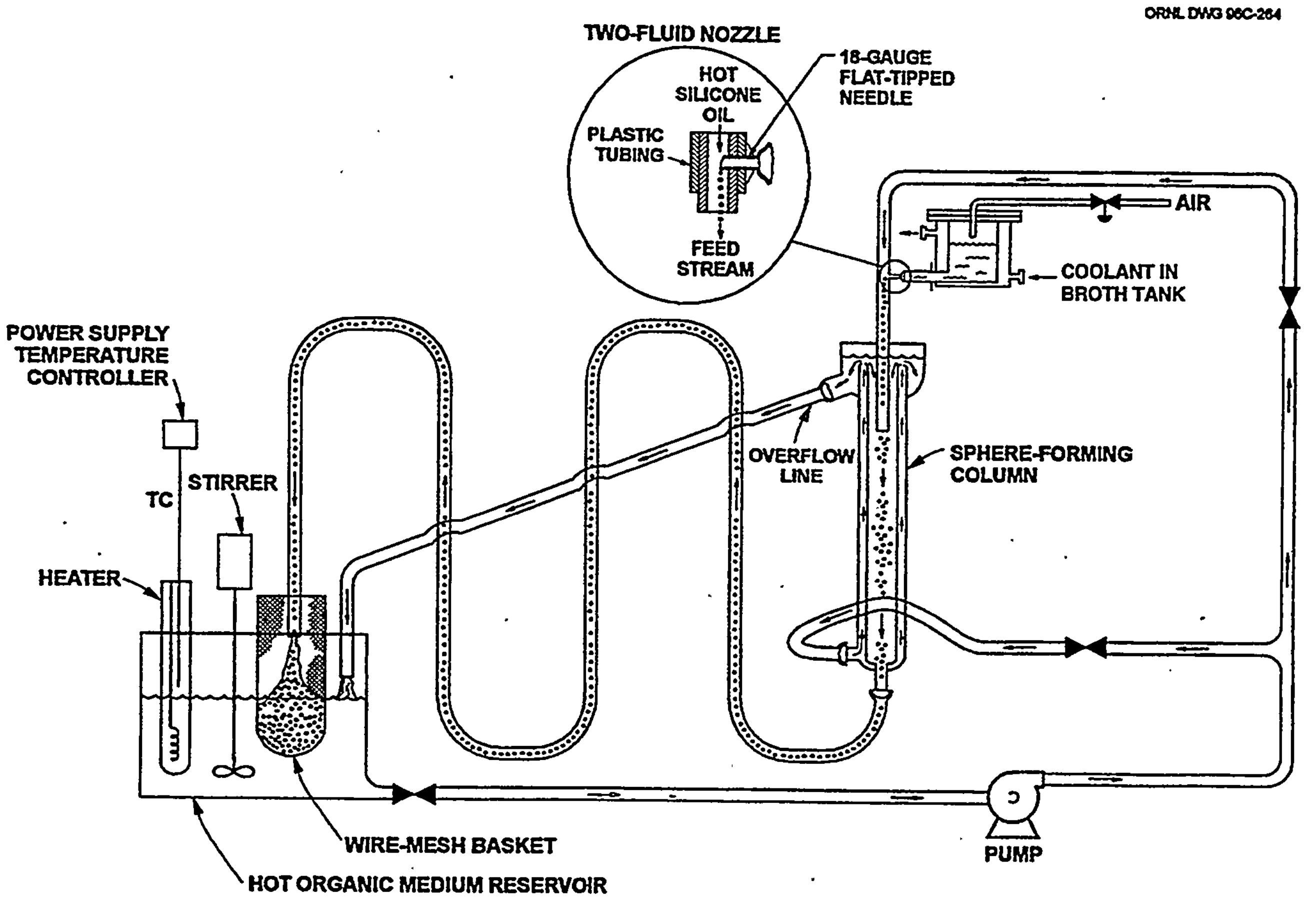

Figure 1. Schematic of HMTA internal gelation process experimental apparatus

Parallel to the development of the spheroidal composite sorbents, attempts will be made to make pure NaTi microspheres by chemical conversion of HTiO microspheres. Two methods will be employed. One method involves the hydrothermal conversion of HTiO microspheres with NaOH, and the other uses an alkoxide conversion of the HTiO microspheres. As proof of principle, a batch of NaTi microspheres was successfully prepared by an alkoxide conversion method. Analyses showed that ~70% of the HTiO was converted to NaTi.

The broth formulations and process conditions, which are essential for making HTiO microspheres by the HMTA internal gelation method were determined in earlier work at ORNL by this research team. Being able to make HTiO as microspheres is the key to making all of the sorbents. Furthermore, the chemical procedure for converting HTiO microspheres to either the amorphous semicrystalline and crystalline spheroidal forms of TiHP, also good sorbents for removing strontium, have been determined. In many cases, the crystalline form determines the type of ions that are sorbed.

The prepared sorbents are being tested in batch experiments to determine their effectiveness in removing strontium from both simulated and actual MVST supernatants. The most promising materials, based on the batch tests, will be selected for column chromatography studies.

Accomplishments

As an initial exploratory step to determine the optimum amount of NaTi that can be embedded in HTiO microspheres, several batches of the composite microspheres were made. Weight percentages of NaTi of 9.2%, 13.2%, 16.8%, 20.2%, and 23.3% in HTiO were prepared. The size of the composite microspheres ranged from 28 to 48 mesh. The NaTi was obtained as a slurry of hydrated NaTi particles from Boulder Scientific Company (Mead, CO). An additional batch of the microspheres containing 13.2% NaTi was prepared in which the HTiO matrix material was converted to the TiHP. Samples of the composite microspheres are being characterized that 1) were not dried, 2) were air dried to a constant weight, and 3) were air dried to a constant weight and then dried at 110°C for 24 h.

The average crush strength for each composite microsphere composition was determined dynamometrically. This is the force in grams needed to crush the microsphere. For these measurements, 10 microspheres were randomly chosen from each composition. The average crush strength of the microspheres before they were dried was 58 ± 3 g. In general, the crush strength of air-dried microspheres was much higher, an average of 2500 g for the NaTi/HTiO microspheres, and 275 g for the NaTi/TiHP microspheres. For comparison, the average crush strength for the commercially available granular NaTi was 425 g, and for the IONSIV® IE-911 was 105 g.

To determine the effectiveness of the composite microspheres for strontium removal, batch tests were conducted using simulated MVNaTi W-29 supernatant of the following composition: 3.9 M $NaNO_3$, 1.0 M NaOH, 0.14 M Na_2CO_3, 0.1 M NaCl, 0.25 M KNO_3, 1.0 x 10^{-4} M $CaCO_3$, and 1.1 x 10^{-5} M Sr (1 ppm). The strontium was added as strontium nitrate, which was traced with the gamma-emitter, ^{85}Sr ($t_{1/2}$ = 64.8 d). Batch tests were conducted by mixing masses of exchanger equivalent to about 0.025 g of air-dried exchanger with ~5 mL volumes of supernatant simulant for 1-h and 24-h periods. To establish a baseline for comparison for the optimization process, batch tests were also conducted with pure HTiO and TiHP microspheres; NaTi obtained from Boulder Scientific Company as a powder slurry; granular NaTi obtained from AlliedSignal Inc.; and granular crystalline silicotitanate (IONSIV® IE-911) obtained from UOP.

Strontium was effectively removed from the simulated MVNaTi W-29 supernatant by all of the composite microsphere samples. For mixing times of 1 h, the composite samples with 13.2% composite microspheres/HTiO that were not dried seemed to work best, removing 98.9% of the strontium with an average distribution ratio (D) of 18,200 mL/g. For tests with mixing times of 24 h, the values were much higher; most of the D values were greater than 100,000 mL/g with ≥99.8% of the strontium removed. Samples of the 13.2% NaTi/TiHP microspheres gave Ds of 150,000 mL/g and removed 99.9% of the strontium. These values were similar to those obtained for the NaTi slurry.

Of the NaTi/HTiO composite microspheres that were air dried, the one with 13.2% NaTi worked best in the 1-h tests, removing about 95.9% of the strontium. The average D was 4800 mL/g, which was similar to the value obtained for the commercial, granular NaTi. The pure TiHP and HTiO microspheres removed 92.2% and 93.2% of the strontium with Ds of 2400 and 2800 mL/g. For the 24-h tests, the strontium D for the composite microspheres ranged from 4500 to 7800 mL/g, resulting in the removal of 95.5% to 97.3% of the strontium. The samples containing 16.8% NaTi had the highest D. The granular NaTi removed 98.3% of the strontium with a D of 12,600 mL/g. Samples of the IONSIV® IE-911 removed 93.4% (D = 2900 mL/g) of the strontium in 1-h tests and 92.2% (D = 2400 mL/g) in the 24-h tests.

Interesting results were obtained with samples of composite microspheres heated for ~24 h at 110°C. More strontium was removed by these microspheres than by the air-dried microspheres. The distribution ratios ranged from 12,200 to 17,300 mL/g, corresponding to 98.3% to 98.8% strontium removal.

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

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

Technology Need

Numerous selective ion exchangers have been developed to remove trace levels of cesium and strontium from various matrices (e.g., acidic, caustic, high ionic strength, low ionic strength, etc.). There is a pressing need to evaluate these and other materials in direct side-by-side comparison experiments using actual Hanford Site tank wastes. Material evaluations using simulated wastes provide valuable input into the expected performance but cannot always be used to accurately predict the actual waste processing performance. The information obtained by this task will directly impact high-level waste (HLW) pretreatment, remediation, and final waste disposition. Groundwater matrices contain relatively high levels of alkaline earth cations at neutral to moderately basic conditions and are vastly different than most low-level waste (LLW) or HLW at Hanford. For this reason, there is a great need for information concerning the removal of various radionuclides (e.g., strontium) under these conditions.

Technology Description

This work is part of an ESP-CP task to develop and evaluate high-capacity, selective, solid extractants for the uptake of cesium, strontium, and technetium (Cs, Sr, and Tc) from nuclear wastes. Pacific Northwest National Laboratory (PNNL) staff, in collaboration with researchers from industry, academia, and national laboratories are investigating these and other novel and commercial ion exchangers for use in nuclear waste remediation of groundwater, HLW, and LLW.

Since FY 1995, experimental work at PNNL has focused on small-scale batch distribution (K_d) testing of numerous solid sorbents with actual and simulated Hanford wastes, chemical and radiolytic stability of various organic ion exchanger resins, bench-scale column ion exchange testing in actual and simulated Complexant Concentrate (CC) and Neutralized Current Acid Waste (NCAW), and Tc and Sr removal from groundwater and LLW. In addition, PNNL has continued to support various site demonstrations at the Idaho National Engineering Laboratory, Savannah River Site, West Valley Nuclear Services, Hanford N-Springs, and Hanford N-Basin using technologies developed by our industrial partners. This summary will focus on batch distribution results from the actual waste tests.

Benefit to DOE/EM

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 groundwater. In addition, prediction of large-scale column loading performance for the materials tested is possible using smaller volumes of actual waste solution. The method maximizes information while minimizing experimental expense, time, and laboratory and process wastes.

Technology Transfer/Collaborations

The results of the testing activities described here have helped to guide our industrial partners (3M, AlliedSignal Inc., IBC Advanced Technologies, Texas A&M University [TAMU], and UOP) in the development of engineered forms of novel ion exchangers.

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 scenarios contain a solid/liquid separation of the supernatant and dissolved salt cake from the sludges followed by Cs, Sr, Tc, and/or transuranic element 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 developed for HLW applications when in groundwater matrices. Conversely, the development of new ion exchange materials for removing contaminants from groundwater systems may result in some materials suitable for LLW and HLW systems. Furthermore, the levels 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

The approach taken in the Develop and Test Sorbents and Geological Barriers Subtasks is to combine an inorganic ion exchanger synthesis effort with active testing that looks at novel ion exchangers from a variety of sources. The synthesis effort uses 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. Testing employs radiotracers (e.g., ^{137}Cs and ^{85}Sr) to measure ion exchanger performance at the levels typically found in tank waste and groundwater systems.

We evaluated several inorganic and organic ion exchange materials for removing Sr and Cs from actual and simulated 100 Area N-Basin water using the equilibrium batch contact method. In the current experiment, 100 mL of N-Basin water was contacted with 0.010 g of each exchange material in duplicate. The total volume of actual N-Basin water consumed was 5 L. Six additional batches were prepared with each batch containing 5 L of simulated N-Basin water with a variable Cs concentration ranging from 1.00E-04 to 2.57E-10 *M* Cs. The extremely high liquid:solid phase ratio (~100,000) was necessary due to the low ionic strength matrix, the low Cs concentration, and the high removal efficiencies of the ion exchange materials tested.

Based on several analytical samples, an approximate composition of the actual N-Basin water is shown in Table 1. The Cs concentration of the actual basin water was determined by Gamma Energy Analysis to be 1.74E-06 Ci L^{-1} ^{137}Cs. The same sample contained less than 2.26E-09 mol L^{-1} of nonradioactive Cs as determined by Graphite Furnace Atomic Absorbance Spectrometry. Assuming that approximately 30% of the total Cs in the basin water is radioactive, a reasonable estimate of the total Cs concentration is 4.87E-10 *M* Cs. Therefore, the range of Cs chosen in the simulant batch contact experiment will effectively bracket the expected actual water composition.

The batch distribution coefficient ($K_d = [Cs]_{solid} \div [Cs]_{liquid}$) is an equilibrium measure of the overall ability of the solid phase ion exchange material to remove an ion from solution under the particular experimental conditions that exist during the contact. In most batch K_d tests, a known quantity of ion exchange material is placed in contact with a known volume of solution containing the particular ions of interest (in this case Cs and Sr). The material is allowed to contact the solution for sufficient time to achieve equilibrium at a constant temperature, after which the solid ion exchange material and liquid supernate are separated and analyzed. The equation for the determination of the K_d can be simplified by determining the concentration of the analyte before and after contact and calculating the quantity of analyte on the ion exchanger by difference (Equation 1).

$$K_d \doteq \frac{(C_i - C_f)}{C_f} * \frac{V}{M*F} \tag{1}$$

C_i is the initial amount or activity of the ion of interest in the feed solution before contact, C_f is the amount or activity after contact, V is the solution volume, M is the exchanger mass and F is the mass of dry ion exchanger divided by the mass of wet ion exchanger (F-factor). K_d (mL/g^{-1}) represents the theoretical volume of solution that can be processed per mass of exchanger under equilibrium conditions. Lambda, the theoretical number of bed volumes of solution that can be processed per volume of exchanger, is obtained by multiplying K_d by the exchanger bed density, ρ_b (g/mL^{-1}) as shown in Equation 2.

Table 1. Chemical composition of Hanford 100-N basin water

Species	Concentration (mol/L)
Al^{+3}	2.892E-05
B^{+3}	2.627E-03
Ba^{+2}	2.270E-05
Ca^{+2}	8.333E-04
Cs^{+}	Variable
K^{+}	6.400E-05
Mg^{+2}	2.900E-05
Na^{+}	1.619E-03
Sr^{+2}	4.450E-06
CO_3^{-2}	1.080E-03
Cl^{-}	1.213E-03
F^{-}	6.320E-06
NO_3^{-}	8.900E-06
SO_4^{-2}	1.395E-04

$$\lambda = K_d * \rho_b \qquad (2)$$

Lambda, termed the column K_d, is useful for estimating the 0.5 C/C_0 point in column loading experiments.

Accomplishments

Twenty-five organic and inorganic ion exchange materials (Table 2) were evaluated for Cs and Sr uptake in side-by-side comparison tests using actual and simulated 100 Area N-Basin water. Actual waste testing required 5 L of solution (100 mL per duplicate, 25 exchangers, and two blanks). The experimental results provide an estimation of the batch distribution performance (and by inference, column loading performance) of the 25 ion exchange materials over a wide range of Cs concentrations.

A milled potassium cobalt hexacyanoferrate (CoHex) produced by 3M demonstrated the highest Cs K_ds (2.8E+07 mL g^{-1}). The engineered form of the same material gave somewhat lower results (1.6E+06 mL g^{-1}). Some of the micas produced by TAMU and AlliedSignal produced similar Cs K_d values (1.0E+05 to 6.0E+06 mL g^{-1}). The powdered IONSIV® IE-910 and engineered IONSIV® IE-911 crystalline silicotitanates produced by UOP demonstrated Cs K_d values of 7.5E+05 and 5.0E+04, respectively.

Sr K_d values were generally lower than those obtained for Cs. The powdered IE-910 and engineered IE-911 produced values of 3.4E+05 and 5.3E+04 mL g^{-1}, respectively. Two pharmacosiderites produced by TAMU gave results up to 5.0E+04 mL g^{-1}. A sample of Amberlite® IRC-76 produced by Rohm & Haas gave results near 2.0E+04 mL g^{-1}. Some zeolytic materials (e.g., IE-96, TIE-96, and clinoptilolite) demonstrated K_ds near 8.0E+03 mL g^{-1}. All of the other materials gave Sr K_d results less than 6.0E+03 mL g^{-1}.

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Table 2. Experimental ion exchange materials evaluated using N-Basin water

3M #2999-14 unmilled CoHex
3M #2999-14 milled CoHex
TAMU #TSP-137
TAMU #E-B Pharm-1 5/1/95
TAMU #E-B Pharm-2 5/1/95
TAMU #Phlogopite 90% Na^+ 5/5/95
TAMU #Biotite 60% Na^+
AlliedSignal #8212-32A Zr-Biotite
AlliedSignal #8212-15D PA-Biotite
AlliedSignal #8212-15E IBA-Biotite
AlliedSignal #8212-5-3 EDA-Biotite
UOP IONSIV® IE-96 #939691090035-C
UOP IONSIV® TIE-96 #975791000012-A
UOP IONSIV® IE-910 #993794040002 9/94
UOP IONSIV® IE-911 #07398-38B 6/95
UOP IONSIV® IE-911 #8671-08 6/95
UOP IONSIV® IE-911 #999096810002
IBC SuperLig®644 #10-SM-171
Rohm & Haas Duolite™ C-467
Rohm & Haas Duolite™ CS-100
Rohm & Haas Amberlite® IRC-76
Rohm & Haas Amberlite® IRC-718
BSC R-F #BSC 187-210
Amberlite CG-120 Type 2
Clinoptilolite zeolite

2. Tuesday Presentations—Second Half-Day

☐ Fission Product Separations Testing

☐ Selective Sorption of Technetium from Groundwater

☐ Electrically Switched Ion Exchange

☐ Sequestering Agents for the Removal of Actinides from Waste Streams

☐ Evaluation and Testing of Sequestering Agents for the Removal of Actinides from Waste Streams

☐ Water-Soluble Chelating Polymers for Removal of Actinides from Wastewater

☐ Selective Removal/Recovery of RCRA Metals from Waste and Process Solutions Using Polymer Filtration™ Technology

☐ Decontamination of Soils and Materials Containing Medium-Fired PuO_2 Using Inhibited Fluorides with Polymer Filtration Technology

Fission Product Separations Testing

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EM Focus Area: subsurface contaminants

Technology Need

Most DOE sites manage very large volumes of dilute liquid waste that must be treated before discharge 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, ^{137}Cs, ^{3}H, and ^{99}Tc, with trace quantities of heavy metals and organics.

Current treatment processes for these wastes are either inefficient or generate large amounts of solid secondary waste that must be disposed of as radioactive waste. The handling and disposal of these secondary wastes are very expensive; therefore, new processes are needed that will improve sorbent capacity and minimize the volume of secondary waste produced.

Task Description

The initial goal of this task is to adequately understand the treatment needs of the end user in treating contaminated wastewater. These needs are then incorporated into the evaluation of new treatment technologies for wastewater treatment. Pertinent information is then supplied to the end user so that they can select a preferred process to meet their waste treatment needs.

New sorbent materials, ion-exchange materials, or other processes of interest to DOE's Office of Environmental Restoration (EM-40) will be evaluated initially for the removal of ^{90}Sr and ^{137}Cs from groundwater and process wastewater. 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.

Experimental data for the most promising sorbents will then be fit to an equilibrium model so that nuclide sorption can be predicted for variable wastewater composition. 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 to validate the equilibrium sorption model and to obtain the defining column operating parameters for scaling up the technology.

Benefits to DOE/EM

This task will evaluate ESP-CP separation technologies for removing ^{90}Sr and ^{137}Cs from process wastewater and contaminated groundwater. Successful tests of these processes may lead to full-scale demonstrations as part of the Subsurface Contaminants Focus Area. These technologies may eventually be deployed by the Tank Waste Remediation System or similar waste remediation operations at Savannah River, Oak Ridge, and Idaho sites that may generate large volumes of secondary, slightly contaminated process water, groundwater, or surface water.

Technology Transfer/Collaborations

New sorbent materials have been obtained through collaboration with 3M, AlliedSignal Inc., Boulder Scientific Company, Pacific Northwest National Laboratory, and UOP. Formulations of wastewater and groundwater simulants, representing water on the Oak Ridge Reservation, have been forwarded to developers of both new sorbent materials and new treatment methodologies to aid in the development of wastewater applications. Sorption results using chabazite zeolite have been forwarded to Parsons Engineering Science, Inc., Oak Ridge National Laboratory

(ORNL) Process Waste Treatment Plant staff, and Westinghouse Electric Corporation for guidance in the treatment of contaminated wastewater.

Developers of the new sorbents and local end users are apprised of task results through informal discussions as laboratory data become available.

Scientific Background

A number of sorbents, ion exchangers, and advanced extractants are currently being developed for removing Sr and Cs 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 molecular recognition materials developed by IBC Advanced Technologies, Inc., and immobilized using 3M technology; resorcinol-formaldehyde (R-F) resin developed at Savannah River Technology Center; engineered crystalline silicotitanates (CSTs) developed at Sandia National Laboratories; and sodium nonatitanate, pillared clays, and micas developed by Texas A&M University and AlliedSignal, Inc.

Technical Approach

A survey of customers at ORNL is being performed to define the critical parameters required by the user to implement a given treatment technology within the local geographic area. This survey will be supported with end user input from other DOE sites. Parameters included in the user appraisal are the types, quantities, and locations of wastewater. The extent of current treatment efforts, as well as the drawbacks that the user experiences in operating these processes, are being ascertained. Possible drivers that might influence the decision of the user to select a given wastewater treatment or to alter a current process are also being determined. These drivers might include environmental regulatory requirements, limitations in secondary waste generation, operational costs, mandated time frames for waste decontamination, and compatibility with current treatment flowsheets.

Concurrent with the user survey, laboratory testing of the new sorbents is also under way. Testing is performed using a standard wastewater simulant containing all major wastewater cations. Sorption results are then compared with those obtained using the baseline sorbent, natural chabazite zeolite. Further experimental data are acquired if sorption results of a new material compares favorably with standard zeolite. Additional batch testing includes observing sorption in binary and ternary combinations of nuclides with the major cations. The sorption data will then be fit to a multicomponent equilibrium model that was successfully developed for a five-cation component system exchanging on chabazite zeolite. The model uses liquid- and solid-phase activity coefficients to predict equilibrium for a multicomponent system. An accurate model of nuclide sorption will be developed on the new material to estimate sorbent efficiency under variable waste stream composition. The model will be validated under dynamic flow conditions in a small column test and will also be used to treat actual wastewater samples.

Accomplishments

Testing of the new materials began by first preparing a standard wastewater simulant that simulated process wastewater and groundwater encountered at DOE sites. Batch sorption studies using prepared zeolite in the wastewater simulant were completed. Radionuclide sorption on the zeolite was fit to an empirical sorption model so that ^{90}Sr and ^{137}Cs sorption on zeolite columns can be predicted. Zeolite sorption efficiency was determined in the presence of the major cations present in wastewater (e.g., Na, Ca, K, and Mg) to determine the impact that variations in water compositions might have. The chabazite zeolite was also used to decontaminate batch samples of actual process wastewater and groundwater. The sorption characteristics of a small zeolite column were observed using the wastewater simulant; 50% breakthrough for Sr and Cs occurred at 13,000 bed volumes (BV) and 50,000 BV, respectively.

After the sorption characteristics of baseline zeolite sorbent had been determined, testing of emerging sorption materials was initiated. R-F resin was the first new material available for testing. Although the resin was initially developed for Cs removal in highly alkaline waste streams, the material has demonstrated promise in removing both Cs and Sr from the wastewater simulant. The Cs sorption capacity (or quantity of radionuclide retained per gram of sorbent) on the resin was similar to that found using zeolite treatment. However, the Sr sorption capacity from the multicomponent simulant was approximately ten times less than that observed for the zeolite. The R-F resin demonstrated little selectivity for Sr over Mg and Ca sorption. Because the sorption ratio of each alkaline earth metal is approximately equivalent on the resin, Sr sorption can be estimated as a function of total alkaline earth metal content in the wastewater. Both Cs and Sr sorption on the resin are significantly more affected by the presence of interfering cations, as compared to that observed with the zeolite. The 50% breakthrough points in a comparable column test were 525 and 3800 BV for Sr and Cs, respectively.

Samples of crystalline sodium nonatitanate ($Na_4Ti_9O_{20} \bullet xH_2O$) powder and pellets were received from AlliedSignal. Results using the multicomponent simulant indicate that, in addition to strontium, other alkaline earth metals also sorb on nonatitanate. Alkaline earth metal sorption on nonatitanate is time dependent. Both Sr and Ca sorption ratios increase with time to a peak value, whereas the Mg sorption ratio remains constant with time. Beyond the peak sorption time, Sr desorbs from the nonatitanate. Relative sorption ratios for Sr in process wastewater are 17,000, 1200, and 2000 L/kg on zeolite, R-F resin, and nonatitanate powder, respectively. (The value stated for the nonatitanate reflects the maximum value for strontium observed at the peak sorption time.) As the result of a Ca concentration approximately 2.5 times greater than that of process water, the Sr sorption ratios decrease to 10,000, 600, and 1000 in groundwater, respectively, on each of the stated sorbents.

Engineered CST was recently received from UOP. Preliminary experimental efforts include measuring the average particle size, surface water content, total sodium content, ion exchange capacity, and equilibration mixing time. Once the initial physical and chemical characteristics of the sorbent are defined, the remainder of FY 1997 will be involved with the collection of binary sorption data so that cation selectivity can be estimated and results can be incorporated into the equilibrium sorption model.

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Selective Sorption of Technetium from Groundwater

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EM Focus Area: subsurface contaminants

Technology Need

Groundwater used for processing uranium or plutonium at DOE sites is frequently contaminated with the radionuclide ^{99}Tc. DOE's Paducah and Portsmouth sites are typical of the contamination problem. Solutions contaminated with radionuclides were poured into lagoons and burial pits, which created a plume that has seeped into the sandy aquifers below the vadose zone. Technetium is the principal radioactive metal-ion contaminant in Paducah site groundwater, and it is present at a concentration of about 25 ng/L. At Portsmouth, Tc is present in the groundwater at a concentration that varies greatly with distance from the source, and concentrations of >400 ng/L have been reported.

Under the oxidizing conditions of near-surface groundwater, the principal form of the element Tc is expected to be TcO_4^-, the pertechnetate anion.[1] Pertechnetate salts are highly water-soluble and quite mobile in underground aquifers and, when coupled with the long half-life of ^{99}Tc (213,000 years), the resulting probable transport into the biosphere makes the presence of this radioisotope in groundwater a great concern. A related problem exists at other DOE sites where the processing of uranium or plutonium resulted in the release of Tc to the surrounding groundwater. Commercially available anion-exchange resins can remove the TcO_4^- ion in the presence of typical anions found in groundwater, but improving the selectivity will result in substantial cost savings in terms of the quantity of resin needed and the scale of the equipment required to treat huge flow rates.

Technology Description

The pertechnetate anion is strongly sorbed on commercially-available strong-base anion-exchange resins, but in view of the low (typically nanomolar) concentrations of Tc involved, enhanced selectivity for the pertechnetate anion over other anions commonly found in groundwater such as chloride, sulfate, and nitrate will be needed. We have prepared and evaluated new anion-exchange resins that were designed to be highly selective for pertechnetate. The technology involves building those features that are known to enhance the selectivity of pertechnetate over other anions into the exchange sites of the resin (hydrophobicity), while at the same time maintaining favorable exchange kinetics.

A resin bed of this material will be used either as part of a coupled treatment-recirculation system for in situ remediation of groundwater contaminated with technetium or in a once-through treatment scheme.

Benefits to DOE/EM

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

Technology Transfer/Collaborators

Collaborators: Department of Chemistry, University of Tennessee, Knoxville; Oak Ridge National Laboratory (ORNL) Environmental Sciences Division.

Technology Transfer: Eichrom Industries, Inc., Darien, Illinois.

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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. Ashley et al.[2] at Los Alamos National Laboratory have demonstrated that Reillex™-HPQ resin is effective in removing pertechnetate from tank waste simulants that have high concentrations of nitrate ion. At ORNL, Dowex™ 1-X8 resin has been shown to be effective in removing pertechnetate in the presence of typical anions found in groundwater at Paducah.

Other schemes have been proposed for removing Tc from groundwater. One method under examination will reduce the Tc 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 Tc 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.

We are developing resins to selectively sorb Tc 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 do not have as high a selectivity for TcO_4^- over chloride, sulfate, or nitrate ion as is desirable or attainable. These latter anions can be present in the groundwater at concentrations 10^6 times that of pertechnetate.

On theoretical grounds, the microenvironment of the exchange sites within the resin is expected to play a major role in ionic selectivity, and the synthesis of a new series of resins in which the properties of the resin were systematically varied was undertaken. These resins were part of a program to modify the microenvironment of the exchange sites and to thus enhance the selectivity for pertechnetate ion over the other anions commonly found in groundwater.

During the past 2 years, we have prepared and evaluated over 80 laboratory resins. These were tested along with seven commercial resins for sorption of pertechnetate from a "groundwater test solution" consisting of pertechnetate at a concentration of 6.0 μM in a matrix of sodium chloride, sodium nitrate, and sodium sulfate (each at 60 mM), as previously described.[3,4] The affinity of a resin for pertechnetate was determined by measuring the batch distribution coefficient (K'_d) for TcO_4^- sorption on the resin following a given equilibration period (e.g., 1-, 4-, 24-, and 168-h time periods). The batch equilibrium testing method for measuring pertechnetate uptake provided a useful means for comparing the affinity of a resin for pertechnetate as a function of time. Early results were instrumental in alerting us to the key structural and chemical properties of the resin that enhanced both the overall pertechnetate selectivity and the rate of pertechnetate uptake.

We have 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) (the K'_d per exchange site) for pertechnetate. The iterative process of resin synthesis, evaluation of Tc selectivity, and further resin synthesis in a close collaboration allowed us to rapidly converge on a novel class of resins with superior selectivity for the pertechnetate ion. These resins were studied more thoroughly under flow-through column conditions using our groundwater test solution, with the objective of determining selectivity under conditions of solution flow in a column where mass-transport limitations become important. The best resin from this study was then tested using actual Paducah groundwater, followed by a field test, in which pertechnetate-contaminated groundwater from monitoring well #106 in the pits and trenches area of ORNL at the DOE Oak Ridge Reservation was pumped through a column containing the resin for a month.

We are currently evaluating different methods of preparing the best resins to determine the most economical synthetic procedures that can be used for preparing bulk quantities of the best resins, while maintaining optimum pertechnetate sorptive performance.

Accomplishments

Best Candidate Resins Identified

A new class of anion exchange resins with improved selectivity and sorptive capacity for the pertechnetate anion as compared to commercially available resins has been prepared and evaluated, both in batch-equilibrium and flow-through column testing conditions using a groundwater test solution. When evaluated in column flow-through experiments, the best laboratory resin, code-named VP02-217, can process more than 30 times the volume of groundwater test solution before reaching the same level of breakthrough as the commercial resin Purolite® A-520E (see Table 1), which is currently being used to remove pertechnetate from groundwater at DOE's Paducah facility.

Invention Disclosure Submitted

An invention disclosure was submitted describing the synthesis and characterization of the new class of anion exchange resins. Eichrom Industries, Inc., has expressed interest in this resin to complement other Tc-selective materials in their product lines.

Field Tests at Monitoring Well #106 in the ORNL Pits and Trenches Area

This field test was conducted in the pits and trenches area at the DOE Oak Ridge Reservation. Groundwater in this area is contaminated with ^{99}Tc (as TcO_4^-). Monitoring well #106 was selected as our test site because the groundwater contains a relatively high ^{99}Tc concentration but relatively low concentrations of other contaminants such as ^{60}Co, ^{3}H, ^{90}Sr, and ^{137}Cs. However, the groundwater contains a relatively high concentration of NO_3^- and SO_4^{2-} (>100 mg/L). The TcO_4^- concentration in the groundwater varied from ~1000 to 5000 pCi/L during the test period because of rainfall events.

Results indicated that no significant breakthrough of ^{99}Tc was observed during the first 5 days of operation. At day 7 (or after ~56,000 bed volumes of groundwater passed through the column), we observed ~2% breakthrough of TcO_4-. The column was continuously operated for 31 days, and by an observed color change, the column appeared to pick up a coating of organic materials on the resin that did not appear to significantly reduce the performance of the synthetic resin. The performance of this resin in this test (see data in Table 1) indicates that it is at least an order of magnitude more selective than any other sorbent that has been tested for Tc sorption including iron filings,[5] other resins, and activated carbon.[6]

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TTP Number OR16C311 [3TEU]

Table 1. Column breakthrough data for pertechnetate sorption from groundwater test solution for Purolite® A-520E and VP02-217 resins at two different flow rates, and breakthrough data for VP02-217 field trial at monitoring well #106 for comparison.

Property	Purolite® A-520E "slow" flow rate	Purolite® A-520E "fast" flow rate	VP02-217 Laboratory "slow" flow rate	VP02-217 Laboratory "fast" flow rate	VP02-217 Field Trial "intermediate" flow rate
24-h Batch-equilibrium K'_d (mL/g) (±5%)	12,800		48,400		
Resin Bed Volume (mL)	3.0	3.0	3.0	3.0	3.1
Void fraction (interstitial volume in mL/ resin)	0.31	0.31	0.31	0.31	0.31
Resin Pore Volume Bed Vol x Void fraction (mL)	0.93	0.93	0.93	0.93	0.96
Actual Flowrate (BV/min)	3.26 ± 0.10	10.84 ±0.44	3.52 ± 0.06	11.12 ± 0.09	5.7
Interstitial velocity (cm/min)	40 ± 1	134 ± 5	43 ± 1	136 ± 1	73
Bed Volumes at 0.1% Breakthrough	<10	<<10	400	80	Not determined*
Bed Volumes at 1.0% Breakthrough	33	<10	1250	330	40,000
Bed Volumes at 2.0% Breakthrough	90	<10	1800	500	56,000
Bed Volumes at 10.0% Breakthrough	550	50 est. (11.5% at 67 BV)	3700-4000 est. (4% at 2440 BV)	1540	143,000

* Not determined because of the variation of the background data.

Electrically Switched Ion Exchange

Michael A. Lilga*, Pacific Northwest National Laboratory; Daniel T. Schwartz, University of Washington; and David Genders, The Electrosynthesis Company, Inc.

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

Technology Need

A variety of waste types containing radioactive ^{137}Cs are found throughout the DOE complex. These waste types include water in reactor cooling basins, radioactive high-level waste (HLW) in underground storage tanks, and groundwater. Safety and regulatory requirements and economics require the removal of radiocesium before these wastes can be permanently disposed of.

Because of the high cost of vitrifying HLW, the radionuclides need to be separated and concentrated to minimize the HLW volume so that most of the waste may be disposed of less expensively as low-level waste (LLW). Based on the concentration of cesium in tank waste (about 10^{-4} *M*) and the needed level of decontamination, the separation process must have a decontamination factor of at least 5500. The separation must also be selective for cesium in the presence of sodium concentrations that can be 10^5 times higher.

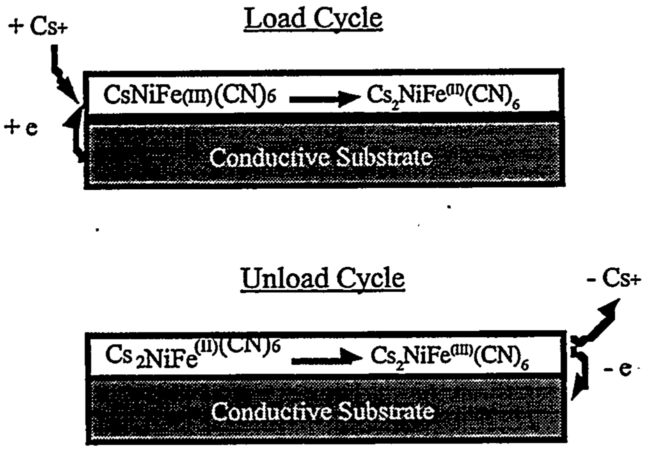

Figure 1. The ESIX concept for metal ion loading and unloading

Radioactive cesium concentrations in spent nuclear fuel storage basins (10^{-10} *M*) and groundwater (10^{-7} *M*) are much lower than that found in tank waste. A method of removing cesium is needed that avoids transuranic loading of the ion exchange material and does not generate large quantities of secondary waste, including spent ion exchange material.

The most accepted option for cesium separation before final disposal is conventional ion exchange (IX). Both inorganic and organic ion exchangers are under consideration. Unfortunately, for regenerable IX materials, a large amount of secondary waste is generated because of the numerous process steps required (acid elution, exchanger water rinse, and sodium loading of the exchanger). Neutralizing the acidic eluant typically adds sodium to the waste, restricting the choice of waste form and limiting the amount of waste that can be incorporated. In addition, it has been reported 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 must also be disposed of as another form of secondary waste.

Technology Description

Electrically Switched Ion Exchange (ESIX) is an approach for radioactive cesium separation that combines IX and electrochemistry to provide a selective, reversible, and economic separation method that also produces little or no secondary waste. In the ESIX process, an electroactive IX film is deposited electrochemically onto a high-surface area electrode, and ion uptake and elution are controlled directly by modulating the potential of the film (Figure 1). For cesium, the electroactive films under investigation are ferrocyanides, which are well known to have high selectivities for cesium in concentrated sodium solutions. 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 loaded). Conversely, if an anodic potential is applied, a cation must be released from the film (i.e., Cs^+ is unloaded). Therefore, to load the film with cesium, the film is simply reduced; to unload cesium, the film is oxidized.

Benefit to DOE/EM

ESIX is a regenerable ion exchange process that has great potential to minimize secondary waste and produce a low-sodium, cesium-rich waste stream. A potential advantage of the ESIX process is that it may be possible to elute cesium into the same elution solution after several load cycles, because the unload step is conducted electrochemically without added chemicals and independent of the soluble cesium concentration. This improved process would result in the generation of a waste stream with a very low sodium concentration and a cesium concentration that is limited only by solubility, radiation, and heat generation. Such a HLW feed stream could allow consideration of a broader range of final waste forms, including those that cannot tolerate sodium. This process also should not produce significant amounts of secondary waste requiring disposal as LLW, because the elution, wash, and regeneration cycles typical of standard IX are not necessary. A small amount of wash solution may be necessary after the unload cycle, but this solution could be used in subsequent cycles for unloading the exchanger. Ratios of the volume of generated secondary waste to the volume of processed waste are estimated to be as low as 0.0006 for the ESIX process, or about two orders of magnitude lower than for a typical process using Rohm & Haas CS-100 IX resin.

Technology Transfer/Collaborations

Pacific Northwest National Laboratory (PNNL) researchers are collaborating on this work with the University of Washington (Dr. Daniel Schwartz), the Electrosynthesis Company, Inc. (Dr. David Genders), and Columbia University (Dr. Alan West). The University of Washington provides expertise in the area of thin-film characterization using Raman spectroscopy. The Electrosynthesis Company will aid in bench-scale unit design and testing, in pilot-scale design, and will also help transfer the technology to DOE and industrial clients. Columbia University prepared a model of the ESIX process that will be validated in future testing. PNNL is working to prepare and optimize the IX film, design and manufacture a bench-scale continuous flow cell to examine simulant and actual waste, design a pilot-scale system, and coordinate all research efforts.

Scientific Background

The combination of IX and electrochemistry has been attempted previously. The most successful attempt has been the electrochemical ion exchange (EIX) technology developed by AEA Technology, United Kingdom. In EIX, the IX properties of an exchanger/electrode are controlled by generating acid and base locally by water electrolysis. ESIX differs significantly because the uptake and elution of ionic species in a modified electrode or IX film are controlled by modulating the potential of the film directly without changing the local interfacial pH. Furthermore, the potentials used in this method do not result in the electrolysis of water, leading to more efficient use of electrical energy and eliminating the safety issues associated with hydrogen evolution.

Modification of electrode surfaces with electroactive films has been studied extensively, and the preparation and characteristics of ferrocyanide films have been reported by several groups. Nickel ferrocyanide films, $M_2NiFe(CN)_6$ (M = Na, K), are most commonly prepared by electrochemically oxidizing a nickel electrode in a $Fe(CN)_6^{-3}$ solution, precipitating the active film on the electrode surface. Electrochemical deposition gives the most reproducible films with reversible behavior. Redox potential, electron transfer properties, and selectivities of the films depend on the alkali metal cation present in the supporting electrolyte, with the cesium ion greatly affecting the observed behavior. Selectivity is believed to be dependent on metal ion size. In addition, cation loading and unloading apparently require solvent transport.

Technical Approach

Work in FY 1996 to develop this technology focused on deposition of films with improved capacity and stability. In FY 1997, bench-scale flow reactors will be tested using high-surface-area electrodes.

Typically, deposition is accomplished by applying an anodic potential to a nickel electrode in an aqueous ferricyanide solution. The insoluble alkali metal nickel ferricyanide precipitates on the electrode surface to form the electroactive film. The thickness and stability of the film depends on the method of deposition. Three different ferrocyanide film deposition procedures were used. One procedure was similar to that of Bocarsly and Sinha, where a nickel electrode was exposed to a solution of 5 mM $K_3Fe(CN)_6$ and 0.1 M KNO_3 and a 1.0-V potential versus saturated calomel electrode (SCE) was applied to the nickel electrode for 300 s. This method is designated the "literature" procedure. The other procedures were PNNL proprietary methods designated as PNNL-1 and PNNL-2. A nickel sponge electrode (The Electrosynthesis Co., Inc.) with a nominal surface area per volume of 13 cm^2/cm^3 (20 pores per inch, ppi) was also coated with a nickel hexacyanoferrate film using the literature procedure.

The characteristics of the films were determined with use of cyclic voltammetry and chronocoulometry. Cyclic voltammetry was typically conducted in 1 M $NaNO_3$ or 1 M $CsNO_3$ solutions starting from an applied potential of 0.25 V, scanning anodically to 0.8 V, then cathodically to -0.1 V, returning to 0.25 V at a scan rate of 50 mV/s. Chronocoulometry was conducted by stepping to 0.25 V to load the film and to 0.5 V to unload the film, typically in 0.5 M Na_2SO_4.

Cyclic voltammetry shows that the ferrocyanide film may be oxidized to the ferricyanide form (metal ions unloaded), which may in turn be reduced back to the ferrocyanide form (metal ions loaded). This chemical reversibility is clearly illustrated in the typical voltammograms for the three film preparations, shown in Figure 2. This figure also shows that there are differences in capacity and rate of metal ion uptake for the three preparations.

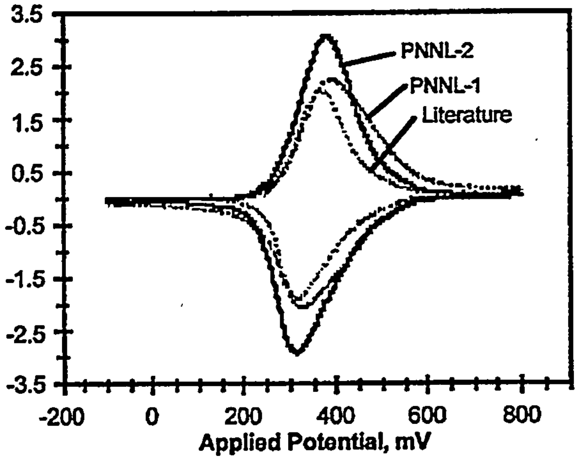

Figure 2. Cyclic voltammetry in 1 M $NaNO_3$ of hexacyanoferrate films prepared by three different methods (Cycle #2)

Accomplishments

This research has demonstrated the viability of ESIX for metal ion separations. Ion loading and unloading is easily controlled by modulating the electrode potential. The use of metal hexacyanoferrates, which are known cesium ion exchange materials, gives high selectivity for cesium over sodium. Films are relatively easy to prepare, but modifications to the reported procedures can generate films with significantly improved capacity and stability.

Films prepared by modified procedures (PNNL-1 and -2) have higher capacity and stability than those previously reported (Figure 3). The best films prepared to date using new procedures have almost twice the capacity of previously reported films and lose less than 20% of their capacity after 2000 load/unload cycles. In contrast, a literature film lost 50% of its capacity after the same cycling. Films on the 20-ppi high-surface-area nickel electrodes, prepared by the literature procedure, had stabilities more like the PNNL-2 films, losing less than 10% of their capacity after 400 cycles.

The high affinity of hexacyanoferrates in the film for cesium is demonstrated by cyclic voltammetry. A film initially in the sodium form converts readily to the cesium form before the second potential cycle in 1 M $CsNO_3$ (Figure 4). Displacement of sodium by cesium occurs during electrochemical cycling as well as by chemical ion exchange,

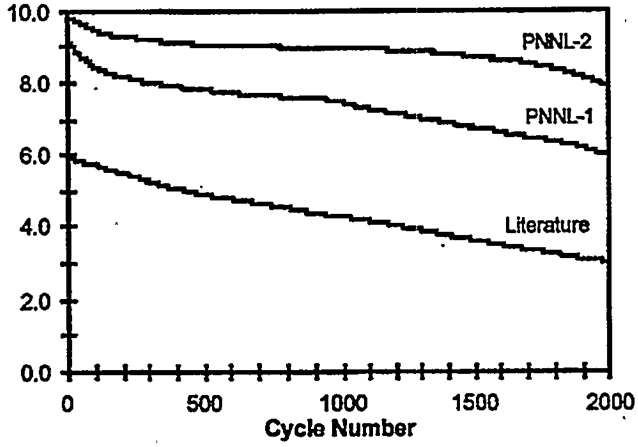

Figure 3. Charge passed as determined by integration of a single potential cycle (Cycle #2) for three film preparations

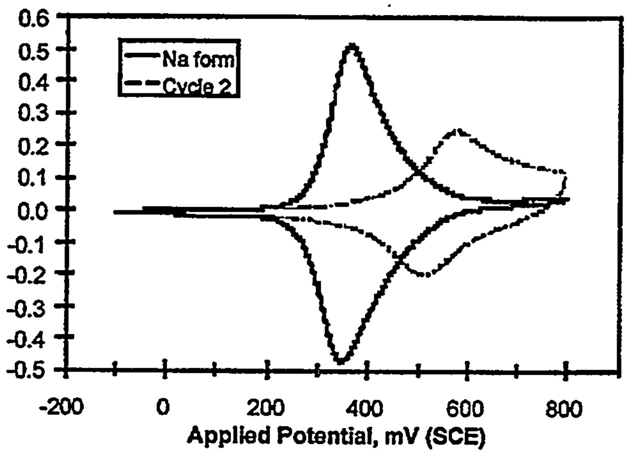

Figure 4. Cyclic voltammetry of a film in the sodium form and after two potential cycles in 1 M $CsNO_3$

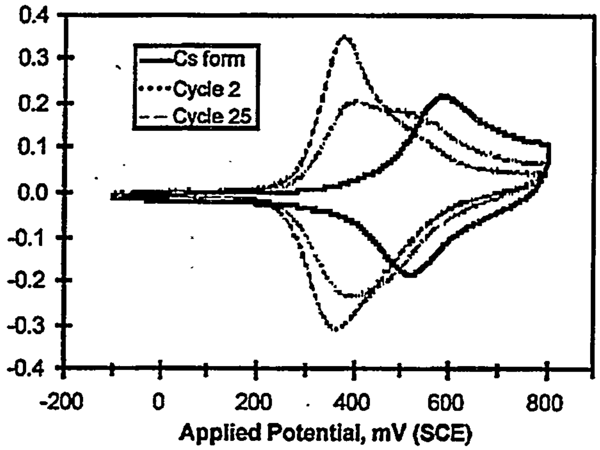

Figure 5. Cyclic voltammetry for a film in the cesium form and after two and 25 potential cycles in 1 M $NaNO_3$

as in a conventional ion exchange column. In other testing, it has been shown that as little as 5 m*M* cesium added to a 1 *M* $NaNO_3$ solution converts most of the sodium form to the cesium form. Figure 4 shows that, like sodium ion, cesium ion uptake and release is also chemically reversible. However, cesium peaks are much broader and shifted anodically. The practical consequence is that in a process for cesium separation, loading of the film with cesium requires a higher applied potential than sodium loading. It is possible that selectivity for cesium over sodium could be enhanced by applying the appropriate potential; the applied potential is an additional driving force to increase the Cs/Na separation factor.

Conversion of the cesium form to the sodium form requires repeated cycling in 1 *M* $NaNO_3$. Figure 5 shows this transformation. After two potential cycles in the unstirred solution, only about half of the film is in the sodium form. The peak for the sodium form increases upon cycling, but the affinity of the film for cesium is large enough that even after 25 cycles in initially pure 1 *M* $NaNO_3$, a peak associated with cesium uptake is still observed. The only cesium in this experiment is that initially in the film, estimated to be about 1.6×10^{-8} *M* for a 1.27-cm-diameter electrode with a surface coverage of 6.5×10^{-9} *M*/cm^2. These results show that low cesium concentrations compete with high sodium concentrations for ion exchange sites in the film.

Potential step data, which are not complicated by a potential scan, indicate that the films have about the same capacity for cesium as they do for sodium. The charge that flows during electrochemical loading of sodium ion into a film in the sodium form and of cesium ion into the same film in the cesium form, at an applied potential of 0.25 V, is shown in Figure 6. Charge flows until the film is completely loaded. Both sodium and cesium loaded into the film to nearly the same extent. The potential step experiments more closely approximate how a process based on ESIX would operate.

The behavior of the films is being studied with use of Raman spectroscopy. Raman spectroscopy is a sensitive probe of the oxidation state of the film and is a good diagnostic tool for in situ investigations of the behavior of metal hexacyanoferrate films during redox reactions. Ferro- and ferricyanide have been distinguished on potential cycling of films with thicknesses as low as about 100Å (10 unit cells thick) (Figure 7). Imaging Raman spectroscopy shows that the thin-film redox reactions occur uniformly across the film rather than in isolated regions. These results are important for the design of a practical ion separation system and in maintaining as uniform a current distribution as possible at a high-surface-area electrode.

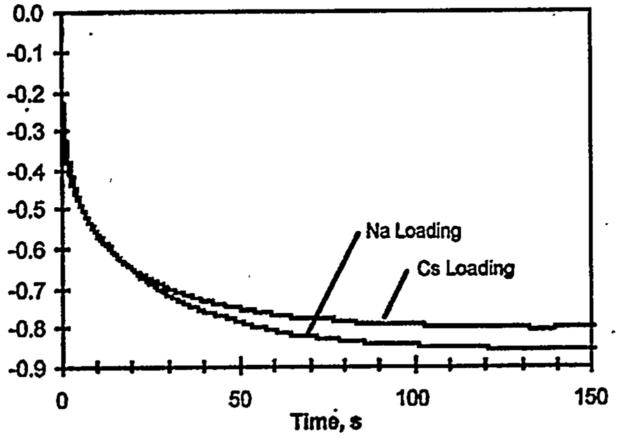

Figure 6. Loading of a film with sodium and cesium. Potential step to 0.25 V

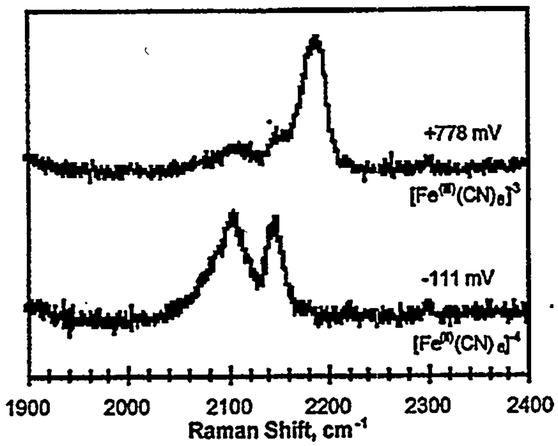

Figure 7. Raman spectra of hexacyanoferrate films on a nickel wire as a function of applied potential

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Sequestering Agents for the Removal of Actinides from Waste Streams

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

Technology Need

The treatment of nuclear waste at DOE's Hanford Site presents many challenging separation problems. One of the most challenging issues faced by DOE is the separation of parts-per-million concentrations of the generally long-lived actinide isotopes from the larger volumes of nonradioactive chemical waste, and the removal of radionuclides from the approximately 1% of the high-level waste (HLW) that will remain in large storage tanks. To address these issues, new separation technologies are needed. To be applicable, these new technologies should be inexpensive, selective for actinide ions, stable and functional under both high and low ionic strength and pH conditions, be a stronger chelator than chelators already present in the waste solutions (i.e., ethylenediaminetetraacetic acid [EDTA]), introduce no hazardous chemicals into the environment during the separation process, and prove practical for potential scale-up.

Technology Description

The goal of this project is to take a biomimetic approach toward developing new separation technologies for the removal of radioactive elements from contaminated DOE sites. To achieve this objective, we are investigating the fundamental chemistry of naturally occurring, highly specific metal ion sequestering agents and developing them into liquid/liquid and solid supported actinide extraction agents.

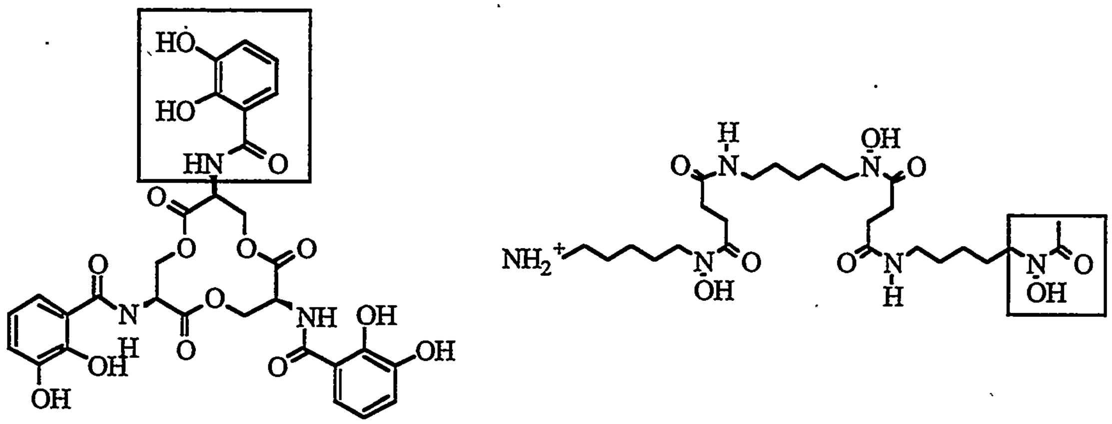
Nature produces siderophores (e.g., *Enterobactin* and *Desferrioxamine B*) to selectively sequester Lewis acidic metal ions, in particular Fe(III), from its surroundings.[1] These chelating agents typically use multiple catechols or hydroxamic acids to form polydentate ligands that chelate the metal ion forming very stable complexes (Figure 1). We are investigating and developing analogous molecules into selective chelators targeting actinide(IV) ions, which display similar properties to Fe(III). By taking advantage of differences in charge, preferred coordination number, and pH stability range, the transition from nature to actinide sequestering agents has been applied to the development of new and highly selective actinide extraction technologies.

Additionally, we have shown that these chelating ligands are versatile ligands for chelating U(VI). In particular, we have been studying their coordination chemistry and fundamental interactions with the uranyl ion $[UO_2]^{2+}$, the dominant form of uranium found in aqueous media. With an understanding of this chemistry, and results obtained from in vivo uranium sequestration studies, it should be possible to apply these actinide(IV) extraction technologies to the development of new extraction agents for the removal of uranium from waste streams.

Benefits to DOE/EM

This work has developed highly selective and efficient chelating ligands that complex actinide ions over a wide range of solution compositions (ionic strength and pH). These ligands have been incorporated into liquid/liquid and solid supported actinide extraction agents. Because these extraction agents are covalently bound derivatives of naturally occurring siderophores, they are nontoxic and eliminate any threat to the environment. Simulated waste testing involving the uptake of Pu(IV) from variable solution composition shows very promising potential for measurably reducing the volume of HLW and low-level waste from waste streams, thus reducing the cost of long-term storage in a geologic repository. In addition, these new extraction agents have promise for addressing the difficult task of removing the small amounts of HLW that will remain in the large storage tanks remaining at DOE sites.

The applicability of these liquid/liquid and solid-supported extraction technologies can now be expanded to extend to the sequestration of uranium and potentially other actinides such as $[NpO_2]^+$. Through reducing the cost associated



Enterobactin

$\log K_f = 49$

Desferrioxamine B (DFO) Desferal®

$\log K_f = 30.6$

Figure 1. The catecholate and hydroxmate binding sites found in the natural siderophores Enterobactin and Desferrioxamine B

with the synthesis of the solid-supported extractants, scale-up investigations can be realized.

Technology Transfer/Collaborations

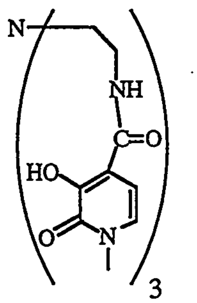
This work is a collaboration between Lawrence Berkeley National Laboratory-University of California, Berkeley; and the Glenn T. Seaborg Institute for Transactinium Science at Lawrence Livermore National Laboratory. An additional collaboration with Dr. Gordon Jarvinen's group at Los Alamos National Laboratory (LANL) begins this year in which we will couple our ligands to LANL's water-soluble polymers.

Technical Approach/Accomplishments

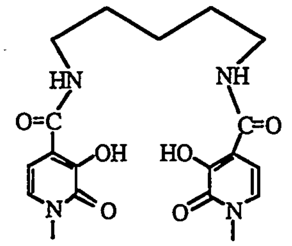
In vivo animal tests show that the hydroxypyridinate ligands display an enhanced ability to effectively remove uranium from mice compared to the more common metal ion sequestering agents such as EDTA and diethylenetriaminepentaacetic acid (DTPA) (Figure 2). Following up on that lead, we are studying the coordination chemistry of hydroxypyridonates (HOPOs) for $[UO_2]^{2+}$. Through these fundamental investigations, we are deriving a knowledge of these basic binding interactions allowing the design of ligands with increased specificity for $[UO_2]^{2+}$. Furthermore, the information gained from uranyl structural determinations is being applied to developing new and fine-tuning our existing chelators for actinide(IV) ions.. These studies are providing further insight into the chelating properties and interactions taking place at the interface between the aqueous solutions of actinide(IV) ions and the chelators attached to our newly developed solid-supported extraction agents.

Plutonium likely exists in the 4+ oxidation state in aqueous solutions containing high concentrations of acid and nitrates, conditions apt to be encountered in the remediation of the Hanford storage tanks.[2] Pu(IV) shares many similarities with Fe(III) (Figure 3).[3] The charge to ionic ratio is nearly the same: 0.46 for 6-coordinate Fe(III) and 0.42 for 8-coordinate Pu(IV). Both metal cations are "hard" metal ions preferring the interaction of "hard" donor ligands such as negatively charged oxygen as found in the naturally produced siderophores. Likewise, both Pu(IV) and Fe(III) have similar hydrolysis constants.

We have synthesized a series of liquid/liquid extractants based on catecholamide, hydroxypyridonate, and terephthalamide derivatives as shown in Figure 4. Thermodynamic measurements have been made to ensure that these bidentate chelators show selectivity for actinide(IV) ions over Fe(III) forming 1:4 complexes with Th(IV). By employing modifiable side chains to these strong chelators, the distribution between aqueous and organic phases has been determined for several organic solvents commonly used in separation technologies.



TREN3,2-HOPO



5LI-Me-3,2-HOPO

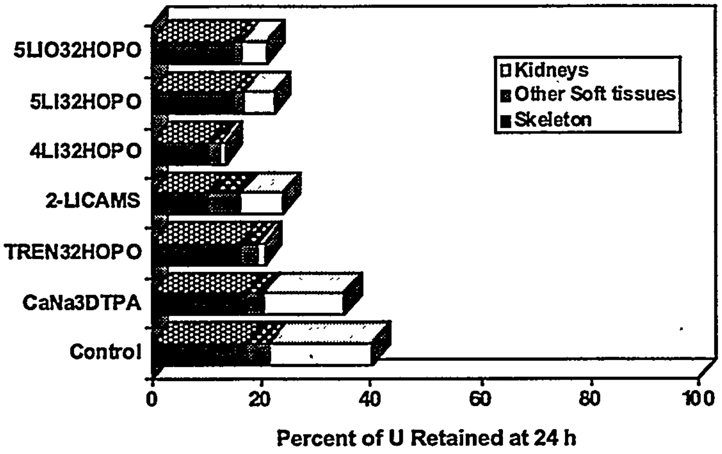


Figure 2. Removal of U(VI) from mice by multidentate HOPO ligands

$$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^- \qquad K \sim 10^{-38}; \quad 10^{-12.6} \text{ per } OH^-$$

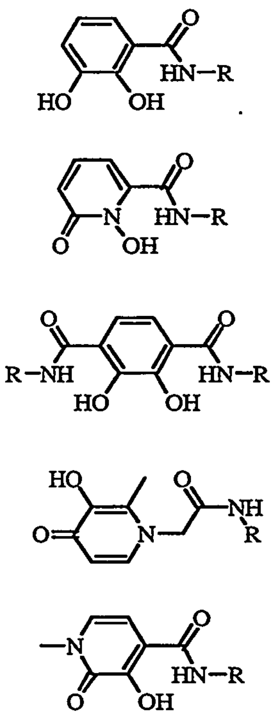
$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+ \qquad K = 0.0009$$

$$Pu(OH)_4 \rightleftharpoons Pu^{4+} + 4OH^- \qquad K \sim 10^{-55}; \quad 10^{-13.7} \text{ per } OH^-$$

$$Pu^{4+} + H_2O \rightleftharpoons Pu(OH)^{3+} + H^+ \qquad K = 0.0301$$

Figure 3. A comparison of properties between Fe(III) and Pu(IV)

Several of these extractants display low water solubility and have been tested under simulated waste stream conditions for their ability to selectively extract Pu(IV) from aqueous phase. These extraction agents display very encouraging results. Pu(IV) extractions were performed for both low and high ionic strength solutions at pH = 1. The 1,2-HOPO extractants performed exceptionally well, extracting greater than 99% of the Pu(IV) from the aqueous phase. Additionally, plutonium uptake studies show that Pu(IV) is selectively extracted from up to a thousand-fold excess of Fe(III), one of the potentially more difficult competing ions likely to be encountered in the waste tanks. Likewise, in competition studies with EDTA, 1,2-HOPO derivatives selectively sequester Pu(IV) with high efficiency.



Catecholamides
R = propyl, hexyl, octyl, decyl, octadecyl, phenylpropyl

1,2-HOPO's
R = propyl, hexyl, octyl, decyl, octadecyl, phenylpropyl

Terephthalamides
R = propyl, hexyl, octyl, octadecyl, phenylpropyl

3,4-HOPO's
R = propyl, hexyl, octyl, octadecyl, phenylpropyl

3,2-HOPO's
R = propyl, hexyl, octyl, octadecyl

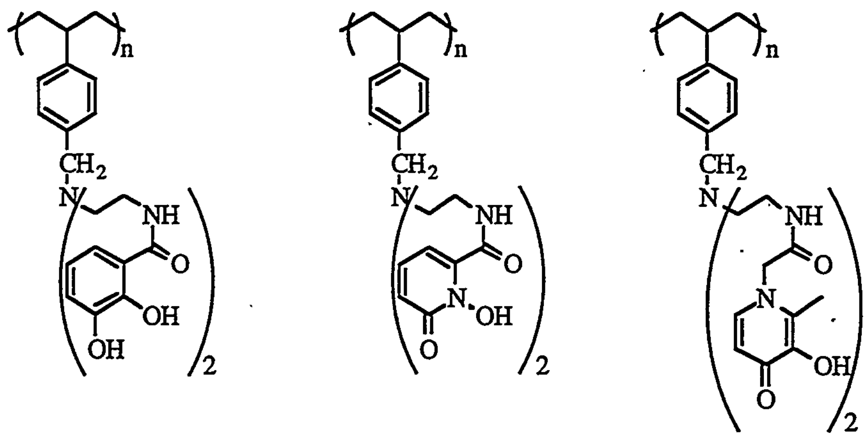
Figure 4. Liquid/liquid extractants based on HOPO, catecholamide, and terephthalamide derivatives

We are currently examining the addition of several new side chains to these chelators that should display enhanced plutonium uptake properties.

The 1,2-HOPO-, 3,4-HOPO-, and catecholamide binding groups have been incorporated into solid supports by immobilizing them onto polystyrene beads (Figure 5). In addition to the liquid/liquid extractants, these solid-supported extractants show excellent kinetics for the uptake of Th(IV), have a high loading capacity, and perform well in the presence of competitive chelators. To further exemplify their effectiveness, these resins have undergone Pu(IV) uptake studies from simulated waste streams. The 1,2-HOPO resin displays excellent Pu(IV) uptake from strong acid solutions, and from weak to strong ionic strength solutions up to 5 *M* in $NaNO_3$. The selectivity of the chelating resins was also demonstrated by the high degree of selectivity for Pu(IV) from aqueous solutions containing up to a thousand-fold excess of Fe(III).

While continuously investigating the fundamental aspects of ligand design and studying their interactions with metal cations for developing new extraction agents, we are constantly refining the synthesis of our extractants in terms of cost, effectiveness, and potential for scale-up. To this end, we have developed new synthetic procedures for the preparation of our solid supports, thus enabling us to substantially reduce the cost associated with preparing the resin. Furthermore, this new approach reduces the overall preparation time and avoids the use of expensive and unrecoverable starting materials. In addition, analysis indicates a slight increase in the overall incorporation of binding sites within the polymer support. Future studies will involve the investigation of other solid supports, both commercially available and those available through simple synthetic means. By combining our chelating ligands with several solid supports, further reductions in cost are foreseeable and potentially allow applications under an even wider range of conditions and waste streams at DOE sites.

The hydroxypyridinones have also been applied toward the recognition and chelation chemistry of uranium. The isolation and structural characterization of several 3,2-HOPO complexes with the uranyl ion have been obtained. The ligands 3LI-Me-3,2-HOPO and 4LI-Me-3,2-HOPO (Figure 6) form complexes with the uranyl ion in which the tethered HOPO ligands occupy positions within the



BISCAM 1,2-HOPO 3,4-HOPO

Figure 5. 1,2-HOPO-, 3,4-HOPO-, and catecholamide chelators bound to the solid support

equatorial plane of the $[UO_2]^{2+}$ ion. The complexation and solution thermodynamics of $[UO_2]^{2+}$ with 1,2-HOPO-, 3,4-HOPO, and catecholamide derivatives are under investigation.

Refinements in the synthesis of HOPO, catecholamide, and terephthalamide ligands are being investigated for scale-up possibilities, as well as the possibility of incorporating additional functionality into the chelating ligands to further modify their extraction properties.

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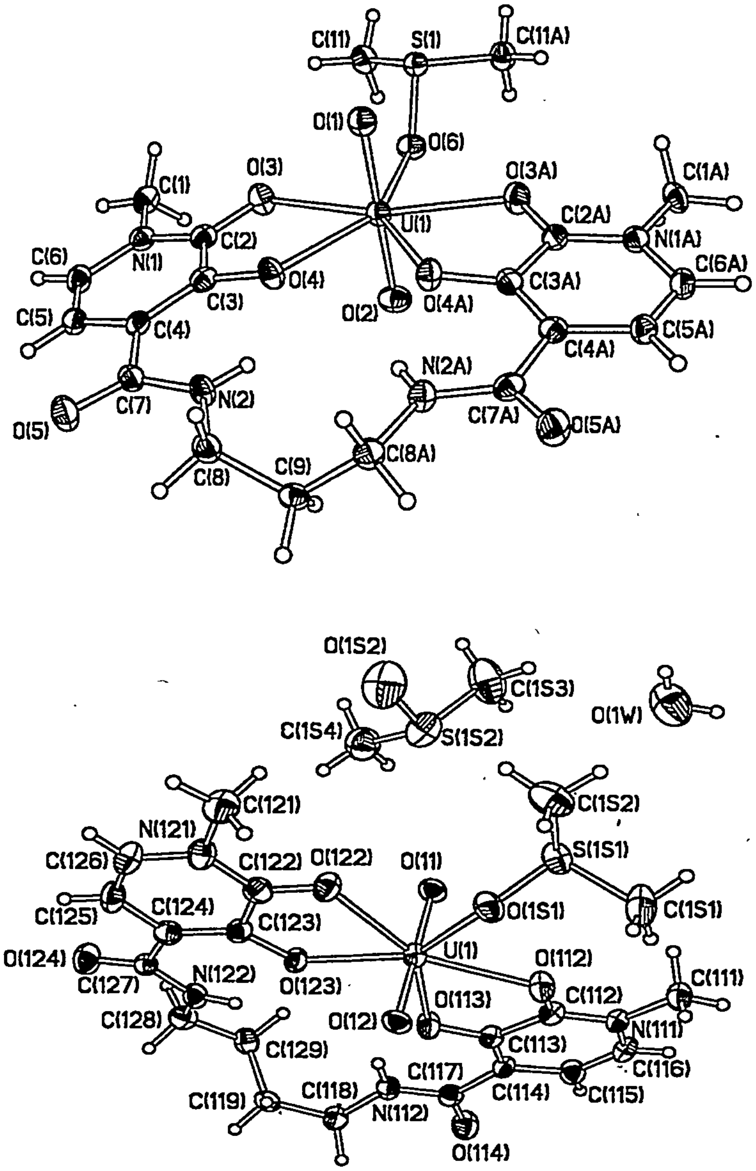

Figure 6. Molecular structures of 3LI-Me-3,2-HOPO and 4LI-Me-3,2-HOPO uranyl complexes

Evaluation and Testing of Sequestering Agents for the Removal of Actinides from Waste Streams

Darleane C. Hoffman, Vadim V. Romanovski*, Alan C. Veeck, and Pihong Zhao, Glenn T. Seaborg Institute for Transactinium Science, Lawrence Livermore National Laboratory

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

Technology Need

A variety of options for waste treatment protocols and corresponding flow sheets has been proposed and is currently being considered for remediation needs at the various DOE sites. In most of the proposed waste treatment schemes there are junctures where it would be advantageous to use highly selective complexing agents to remove plutonium and perhaps other transuranic elements from high ionic strength solutions that may vary widely in pH depending on the exact flowsheet. Our technology is designed to treat primary or secondary waste streams containing low concentrations of actinide ions.

Technology Description

The purpose of this project is to evaluate and test the complexing ability of a variety of promising new complexing agents synthesized by Professor Kenneth Raymond's group at the University of California, Berkeley (ESP-CP TTP Number SF16C311). Some of these derivatives have already shown the potential for selectively binding Pu(IV) in a wide range of solutions in the presence of other metals.

Professor Raymond's group uses molecular modeling to design and synthesize ligands based on modification of natural siderophores, or their analogs, for chelation of actinides. The ligands are then modified for use as liquid/liquid and solid/liquid extractants.[1] Our group at the Glenn T. Seaborg Institute for Transactinium Science (ITS) at Lawrence Livermore National Laboratory determines the complex formation constants between the ligands and actinide ions, the capacity and time dependence for uptake on the resins, and the effect of other metal ions and pH.

Benefit to DOE/EM

We have shown that the chelating ligands are highly selective and efficient for complexing Pu(IV) over a wide range of solution compositions. They can be used in liquid/liquid or resin column separations. The applicability of these liquid/liquid and solid-supported extraction technologies can now be expanded to the sequestration of uranyl $[UO_2]^{2+}$, neptunyl $[NpO_2]^{+}$, and possibly other actinide ions.

Successful development and characterization of such complexing agents could be instrumental in designing a process for removing plutonium (and possibly other actinides) from actinide-containing waste streams. This would help reduce large volumes of liquid waste and permit their disposal as low-level waste. Removing and concentrating the plutonium can also help minimize the volume of transuranic waste to be disposed of in a geologic repository. In addition, these derivatives are relatively inexpensive, biodegradable, and would not involve the addition of significant toxic chemicals during their use. The task is cross-cutting in its scope and is not limited to a given Focus Area. It can be used wherever low-level actinide-contaminated organic or aqueous waste streams are encountered.

Technology Transfer/Collaborations

This project is a collaboration between ITS and the Department of Chemistry at the University of California, Berkeley. The collaboration combines the synthetic expertise of Dr. Raymond's group with the ability of Dr. Hoffman's group to handle actinides and make measurements to evaluate and test the synthesized sequestering agents.

Though we as yet have no industrial collaborators, discussions have taken place with the following companies concerning application of our sequestering agents: Lockheed Environmental Systems and Technologies Co. (Las Vegas, NV) ICET, Inc. (Norwood, MA), and ChromatoChem, Inc. (Missoula, MT).

We continue to try to identify suitable "real" waste solutions on which to test our best resins and liquid extractants. Some 5.6 million L of waste containing both Pu(IV) and Pu(VI) in $NaNO_3 + HNO_3$ solution exist[2] at Idaho National Engineering Laboratory (INEL). We believe our sequestering agents should be effective in removing both Pu(IV) and Pu(VI) from such solutions and are discussing with staff at Westinghouse Idaho Nuclear Company, Inc., the possibility of performing tests on samples of these wastes.

Scientific Background

Plutonium exists in the 4+ oxidation state at high concentrations of acids and nitrates.[3] Plutonium(IV) shares many chemical properties with Fe(III). Both Fe(III) and Pu(IV) are "hard" Lewis acid metal cations, carrying a large amount of charge and having a relatively small ionic radius:

$$\text{Fe(III): charge(Z)/radius(A°)} = 3/0.65 = 4.6$$

$$\text{Pu(IV): charge(Z)/radius(A°)} = 4/0.96 = 4.2$$

They also behave similarly in water with very low free metal ion concentrations at near neutral pH:

$$Fe(OH)_{3\,(s)} \text{ Æ } Fe^{3+} + 3OH^-;\ K_{sp}=10^{-38}$$

$$Pu(OH)_{4\,(s)} \text{ Æ } Pu^{4+} + 4OH^-;\ K_{sp}=10^{-55}$$

Biological properties of Fe(III) and Pu(IV) are also similar. Pu(IV) is transported in the blood plasma of mammals as a complex of transferring, the normal transport agent of Fe(III). Pu(IV) binds at the same site as Fe(III).

In nature, bacteria and other microorganisms produce siderophores, low-molecular-weight multidentate iron chelators, to scavenge ferric ion from their environments. Nature has finely tuned siderophores to form highly stable complexes with the Lewis acidic metal ion Fe(III). Both Fe(III) and Pu(IV) are bound by basic ligands that can provide electrical charge, such as negatively charged oxygen donors. Because of its larger size and charge, Pu(IV) is eight-coordinate instead of six-coordinate, like Fe(III). Differences in charge, preferred coordination number and range of pH stability can be used to make the transition from Fe(III)-specific chelators to those that are specific for actinide(IV) ions.

Many binding groups are employed by siderophores, but the strongest siderophores use catechol, 1,2-hydroxypyridinone (HOPO) and hydroxamic acid. These bidentate chelating groups are strong Lewis bases and show remarkable selectivity for Lewis acidic metal ions including Pu(IV) and Th(IV). These chelating groups can be incorporated into insoluble polymers for use as ion exchange resins or into molecules appropriate for use as liquid/liquid extractants.[1]

Technical Approach

Currently, three polystyrene-based chelating ion exchange resins and more than 16 liquid/liquid extractants with different structures[1,4] have been tested to determine the ability of these materials to remove actinide(IV) ions from solution.

For sorption experiments, batch studies were carried out by stirring the resin with the aqueous phase containing natural thorium or ^{242}Pu. In general, the duration of the kinetic experiments was 1 or 2 h. At certain time intervals, 0.5 mL of aqueous phase was removed, the resin separated by centrifuging (1 min), and a sample of supernatant was taken. Th(IV) concentrations in the aqueous phases were determined by the Arsenazo III Method using UV/VIS spectrometry. ^{242}Pu was analyzed by liquid scintillation counting.

Solvent extraction studies of ^{242}Pu(IV), ^{242}Pu(VI), and ^{55}Fe(III) were carried out by shaking 0.5 mL of each organic and aqueous phase in a centrifuge cone. The phases were separated by centrifuging and aliquots of each phase were taken for liquid scintillation counting. Liquid scintillation counting was used for ^{55}Fe and ^{242}Pu analysis.

The kinetics of Th(IV), Pu(IV), and Pu(VI) sorption by catechol resin, 1,2-HOPO resin, and 3,4-HOPO resin have been studied using various aqueous media in the presence of univalent (Na), bivalent (Zn), and trivalent (Fe) metal ions, and the complexing agent ethylenediaminetetraacetic acid (EDTA). EDTA or other competing agents are possible components of radioactive waste streams.

The solvents kerosene, toluene, chloroform, dodecane, octanol-1, and methyl-isobutyl ketone (MIBK) were investigated for dissolution of the synthesized extractants.

Accomplishments

The catechol, 1,2-HOPO, and 3,4-HOPO resins have been shown to remove low concentrations (<10 mM) of actinide(IV) ions from acidic aqueous solutions. The ability of these resins to extract Th(IV) and Pu(IV) was compared with the commercially available Chelex 100 resin.

The Chelex 100 resin showed no detectable sorption of these tetravalent actinides from acidic media. All three of our resins showed appreciable sorption, with the 1,2 HOPO-resins showing >98% sorption (Figures 1 through 4).

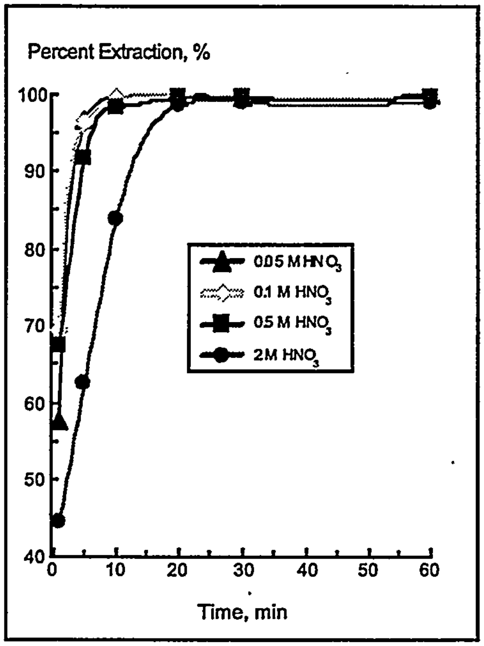

Figure 1. Pu(IV) uptake by 1,2-HOPO resin from acidic solutions, 10 mg of resin/10 mL of 1.8 x 10^{-5} M Pu(IV)

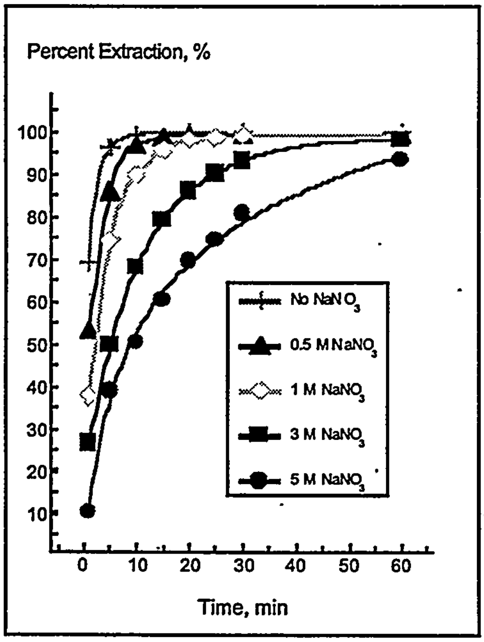

Figure 2. Pu(IV) uptake by 1,2-HOPO resin from 0.1 M HNO_3 in the presence of $NaNO_3$, 10 mg of resin/10mL of 1.8 x 10^{-5} M Pu(IV)

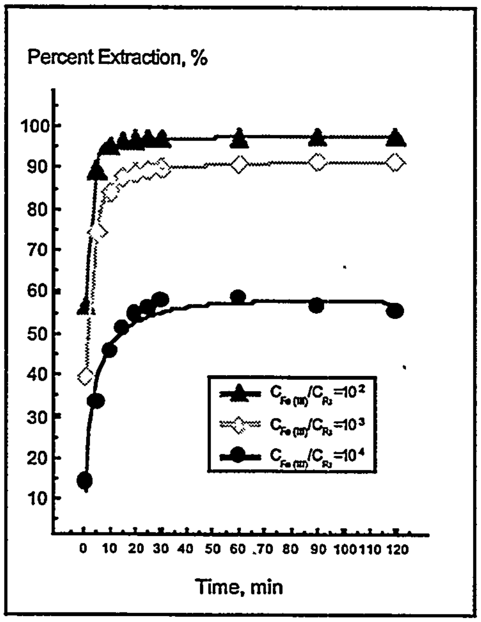

Figure 3. Pu(IV) sorption from 0.1 M HNO_3 by 1,2-HOPO resin, 10 mg of resin/10 mL of 1.8 x 10^{-5} M Pu(IV)

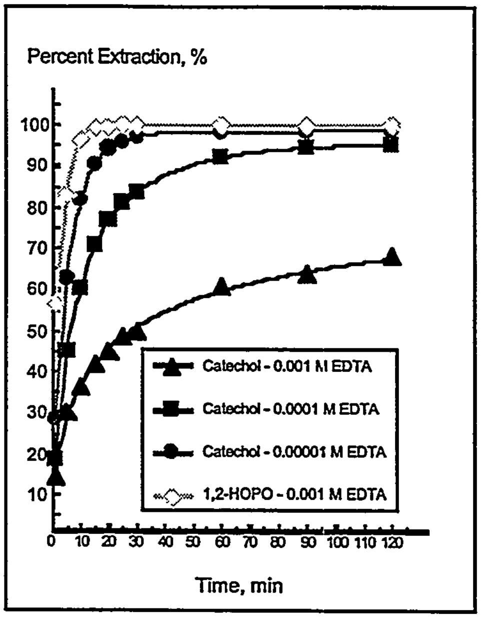

Figure 4. Pu(IV) uptake by catechol and 1,2-HOPO resins from 0.1 M HNO_3, 10 mg of resin/10 mL of 1.8 x 10^{-5} M Pu(IV)

The best extractant solvents appeared to be octanol-1 and MIBK. Of 16 extractants, 12 of the hydroxypyridinone derivatives (alkyl-3,4-HOPO, alkyl-3,2-HOPO, and alkyl-1,2-HOPO) in octanol-1 and MIBK have been tested for extraction of Fe(III) and Pu(IV) from nitrate media.

Our results for the resin separations and solvent extractions can be briefly summarized.

Resin Separations

- 1,2-HOPO resin showed excellent sorption ability for Pu(IV) from nitric acid solutions; it extracts Pu(IV) very well even from 2 *M* nitric acid (Figure 1).
- 1,2-HOPO can bind Pu(IV) in the presence of competitive metal ions (Figures 2 and 3).
- Pu(IV) extraction by 1,2-HOPO is still possible from the solution with 10^4-fold excess of Fe(III), one of the most competitive ions for Pu(IV) sorption (Figure 3).
- Pu(IV) sorption was studied in the presence of the complexing agent EDTA in the aqueous phase: 1,2-HOPO resin extracts Pu as though there is no competition from EDTA. However, uptake by catechol resin is affected by EDTA at the higher concentrations (Figure 4).
- 1,2-HOPO resin can sorb Pu(VI), although the uptake from high acid solutions was less than for Pu(IV).

Solvent Extractions

- The 1,2-HOPO amides performed the best for Pu(IV) and Fe(III) extraction, followed by the 3,2-HOPO amides and 3,4-HOPO amides.
- Extraction of Pu(IV) and Fe(III) from the higher ionic strength aqueous phase was favored over extraction from the lower ionic strength aqueous phase.
- The kinetics for the Pu(IV) extraction were much faster than for the Fe(III).
- 1,2-HOPO amide was able to remove 95% to 99.99% of Pu(IV) in competition studies with Fe(III) and EDTA: C_{Fe}/C_{Pu}=100 (99%); C_{Fe}/C_{Pu}=1000 (98%); C_{EDTA}/C_{HOPO}=3 (95%).
- 1,2-HOPO octyl amide extracted Pu(VI) from nitrate media; distribution coefficients were 1 to 2 orders of magnitude less than Pu(IV).

Additional experiments are in progress to evaluate the ability of the resins and liquid extractants to remove Pu(VI), which can sometimes be present together with Pu(IV) as in the waste solutions located at INEL.

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Water-Soluble Chelating Polymers for Removal of Actinides from Wastewater

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EM Focus Areas: decontamination and decommissioning; subsurface contaminants; mixed waste characterization, treatment, and disposal

Technology Need

Alternative technologies are needed for treating 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. More specifically, this project addresses the need to replace precipitation methods that generate large volumes of radioactive sludge at Los Alamos and other DOE sites, and reduce transuranic (TRU) wastes that will be generated from processing the multitude of actinide-containing residues that exist at DOE facilities.

Sludge handling and disposal are becoming more expensive as burial requirements increase and the availability of approved burial sites decreases. More stringent discharge regulations have been enacted by DOE, the U.S. 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 Los Alamos National Laboratory (LANL) Waste Treatment Facility. Precipitation technology cannot consistently meet today's discharge requirements for some metals. Even lower discharge limits are anticipated in the future. The long-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 wastewater of concern is 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 the toxic metals to levels below regulatory concern could generate a much smaller mixed-waste stream and a separate radioactive waste stream that can be treated by other technologies that are better established from a regulatory viewpoint. Technology development for treating mixed wastes is being driven at most DOE sites by schedules established in the various Federal Facility Compliance Agreements (FFCAs) between the EPA and DOE.

Technology Description

Polymer filtration is a technology under development to selectively recover valuable or regulated metal ions from process or wastewaters. The technology uses water-soluble chelating polymers that are designed to selectively bind with metal ions in aqueous solutions. The polymers have a sufficiently large molecular weight that they can be separated and concentrated using available ultrafiltration (UF) technology. The UF range is generally considered to include molecular weights from about 3000 to several million daltons and particle sizes of about 2 to 1000 nm. Water and smaller unbound components of the solution pass freely through the UF membrane as shown in Figure 1. The polymers can then be reused by changing the solution conditions to release the metal ions that are recovered in concentrated form for recycle or disposal.

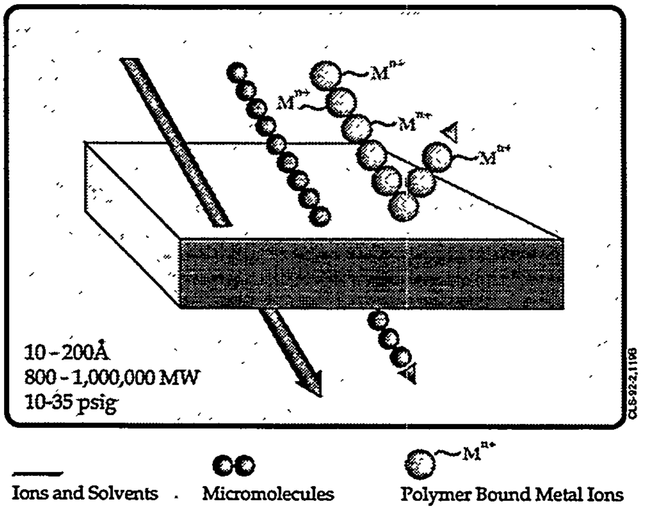

Figure 1. Metal ions bound to the chelating water-soluble polymer are retained by the ultrafiltration membrane; water and other small solute species pass freely through

Some of the 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, nuclear power plant cooling water; remediation of contaminated soils and groundwater; removal of mercury contamination; and textile, paint and dye production.

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 preparation of the water-soluble chelating polymers; small-scale testing of the chelating polymer systems for the required solubility, UF properties, selectivity and binding constants; followed by an engineering assessment at a larger scale to allow 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 LANL. Potential applications at other DOE facilities are also apparent.

Benefits to DOE/EM

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 at the Waste Treatment Facility by using improved extraction technology to greatly reduce the TRU element content of waste streams from the Plutonium Facility and other locations with actinide processing operations. The polymer filtration technology is one of the advanced extraction technologies under evaluation in this effort. Applications for these systems at Idaho National Engineering Laboratory, the Hanford Site, and other DOE facilities are also apparent. For example, bench-scale tests have shown the potential for polymer filtration to remove technetium from groundwater at DOE sites such as Paducah, Kentucky. The Subsurface Contaminants Focus Area is evaluating a proposal to develop polymer filtration for this application.

New collaborative efforts have grown out of the work in this ESP-CP project. A project to develop polymer filtration for removal of RCRA metal ions from various DOE mixed wastes has been started under the ESP-CP this year. The Mixed Waste Focus Area is considering co-funding of this effort with mercury as the primary target metal. A preliminary flowsheet has been developed for recovering valuable metals from the Berkeley Pit acid mine drainage waters and further development of the use of polymer filtration for this type of application is in progress with industrial partners. Water-soluble polymers related to those prepared for this project have shown promise for removing lead from soils at Superfund sites. Ongoing projects at LANL are evaluating polymer filtration for removing metal contaminants from solid wastes generated during experimental tests and decontamination and decommissioning operations.

Technology Transfer/Collaborations

Specific near-term customers for this technology are the LANL Waste Treatment (an EM-30 operation) and various Department of Defense Programs projects at LANL that must reduce TRU or mixed-waste generation from aqueous processing. As noted above, we are testing polymer filtration units for potential applications at one of the wastewater treatment buildings at LANL and at the Plutonium Facility. The program administered by EM-66 to stabilize plutonium-containing residues and wastes at DOE facilities as a result of the Defense Nuclear Facility Safety Board's Recommendation 94-1 may also be a customer for this technology.

Additional projects at LANL are also evaluating the potential of the polymer filtration technology for industrial applications. In 1995, members of this project team and collaborators at Boeing Aerospace received an R&D 100 Award for the application of polymer filtration to recycle metals from electroplating operations. Micro-Set, Inc. (Landisville, NJ), has licensed the technology for the electroplating field-of-use and some related areas. 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 at wastewater treatment facilities in DOE facilities or within the glove box environment at the LANL Plutonium Facility.

Several other companies are working with LANL to help commercialize this technology. Four patent applications were filed in 1995 that cover a variety of polymer filtration applications, including removal of radioactive metal ions from wastewater streams. Three licenses have been signed by industrial partners to develop various applications of polymer filtration. These include cleanup of environmental waters, 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.

Scientific Background

Removal of 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 waters. 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.

The application of *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 Tubingen, 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 an acid elution or electrodeposition process.

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. 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 recycled for further metal-ion recovery. One advantage of this separation technology for dilute metal-ion solutions is in the rapid kinetics due to the homogeneity of the process. Also, by careful selection of the chelating functionality, selective metal-ion complexation can be obtained.

Technical Approach

This project involves preparation of the chelating water-soluble polymers, small-scale testing of the chelating polymer systems for the required solubility, ultrafiltration properties, selectivity and binding constants, followed by an engineering assessment at a larger scale to allow comparison to competing separation technologies. Reducing the concentration of a target metal ion to extremely low levels will require that the water-soluble chelating polymer 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 if the target metal ion is to overcome the competition from these 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 like 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.

Several systematic series of water-soluble chelating polymers have been prepared in this project. Most 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.

We have been collaborating during the past year with Professor A. Gopalan and his group at New Mexico State University to prepare some polymers derivatized with hydroxamic acid chelating groups. We are also beginning work in FY 1997 with Professor Ken Raymond and coworkers at the University of California, Berkeley, to attach some of their very selective and strongly binding chelators for plutonium to water-soluble polymers. We expect that a new generation of improved actinide chelating polymers will grow out of these efforts with the university groups.

Accomplishments

As described above, several 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 0.01 to 1%, and the solution is filtered through an ultrafiltration membrane with the appropriate molecular weight cutoff.

To date, the polymer that has shown the best properties for removing plutonium and americium in the target solutions has been designated Metal-Set-M by our industrial partner. Therefore, the demonstration tests continuing in FY 1997 will use Metal-Set-M. In FY 1996 we continued to optimize the polymer properties by varying the degree of functionalization and carefully controlling the synthesis conditions to obtain polymers that perform consistently. The preparations were also scaled up substantially to produce sufficient material for the demonstration tests.

We have used a series of polymer filtration units for tests on actual waste solutions in the LANL Plutonium Facility. The first tests were done with 10-mL stirred cell units, and we progressed to using hollow-fiber cartridge units with a throughput of 5 to 20 mL/min in FY 1995. In FY 1996 we designed and built a pilot-scale unit for use in a glove box environment that has a throughput of 0.5 to 1 L/min. This pilot-scale unit was designed to allow two stages of polymer filtration to give larger decontamination factors in each pass of solution through the unit. The unit was also designed to operate in a glovebox environment, and is shown in Figure 2 just before installation.

The pilot-scale unit was initially tested with neodymium nitrate solutions. These neodymium solutions are a reasonable surrogate for americium in the process and wastewaters. The two-stage polymer filtration process that we built into this apparatus worked as expected. One gram of polymer was employed in the first 10-L reservoir and 0.1 g in the second 2-L reservoir. The initial neodymium level of 14 ppm dropped to less than 10 ppb (detection limit for the ICP-AES analysis) during processing of the first 10-L batch, which loaded the polymer to about 20% of "capacity" (assuming a 1:1 mole ratio of chelating groups to neodymium ions). The mole ratio of chelating groups to the Nd(III) ion may be 2:1 or 3:1 in the actual polymer/metal ion complex. The loading of the polymer was continued with two additional 10-L batches of neodymium solution to observe the expected "break through" of neodymium. This gave us further information on the capacity of the water-soluble chelating polymer system.

The pilot-scale unit was installed in a glove box in the LANL Plutonium Facility and tested with one 10-L batch of feed from the nitric acid evaporator operation. The results from this test were not very useful because the feed was heavily contaminated during transfer through the process piping to the sampling location. The initially clear solution became green during the transfer and a voluminous precipitate resulted after addition of the polymer and adjustment of the pH of the solution to 4 to 5. The green color and the precipitate were not observed in earlier tests on similar process solutions collected by a different method. It was noteworthy, however, that the precipitate did not noticeably slow the ultrafiltration operation. Further tests with actual waste streams using this pilot-scale unit are in progress for FY 1997.

The Metal-Set-M polymers have been used to remove plutonium and americium 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. Efficient removal of the alpha activity was observed even though the solution contains a variety of other metal ions and anions in much higher concentration that could compete with the actinide metal ions for polymer binding sites, including Fe(II), Cu(II), Ca(II), Mg(II), Zn(II), Ni(II), fluoride, phosphate, nitrate, and chloride.

Additions of ferric nitrate to simulant solutions showed that Fe(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

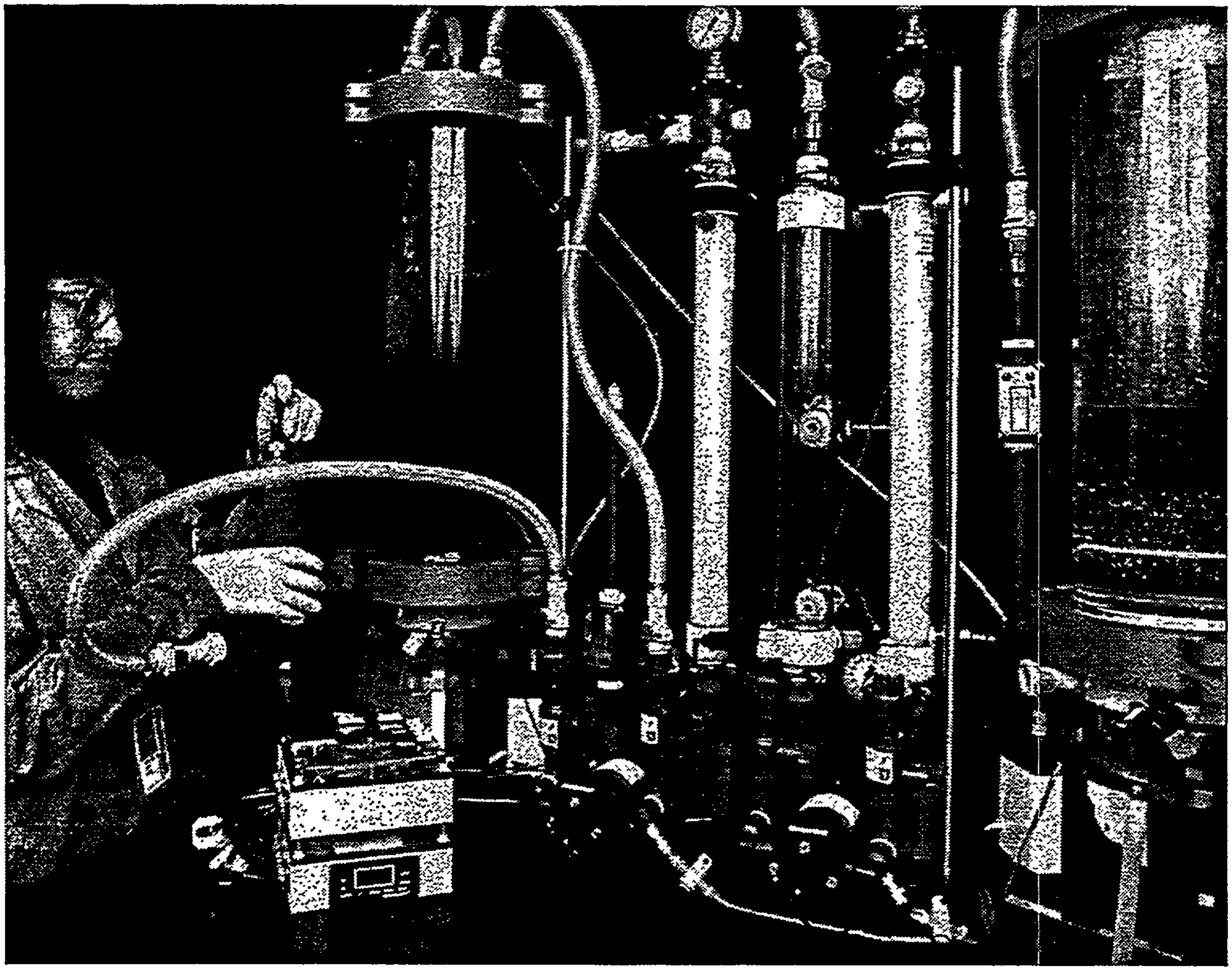

Figure 2. Polymer filtration unit designed for a glovebox environment

potentially competing cations and anions that are commonly present in waste streams.

A second pilot-scale polymer filtration unit has been constructed for tests at the TA-21 wastewater treatment building at LANL. These tests will generate the engineering data needed to allow design of full-scale equipment. This unit will process much larger volumes of water (100 to 250 gal) than the Plutonium Facility operation. The goal is to remove alpha activity (primarily plutonium and americium) to levels less than 30 pCi/L. Bench-scale tests have shown that the water-soluble polymers are effective at reducing the alpha activity to this level. The construction of this unit was funded by the EM-30 Pollution Prevention Program Office at Los Alamos, but the test runs will be conducted by personnel funded by this ESP project.

The main elements of the pilot test unit are three batch tanks, a bag filter, and an UF process skid. The UF process skid uses both an open tubular ceramic ultrafilter unit and a hollow-fiber ultrafilter. The ceramic ultrafilters are expected to be more resistant to fouling by particulates in the waste stream and that is one parameter that will be tested. The first 275-gal tank receives the raw feed from the TA-21 system and acid or base is added to adjust the pH, if necessary. The water-soluble polymer is then added and the solution is pumped through the bag filter to remove large particulates (if needed) into the 275-gal UF feed tank. The solution is then pumped to the ceramic UF unit and the permeate collected in the third tank for sampling before pumping into the hollow-fiber UF system. The permeate from the second UF operation is sampled before discharge back to the large TA-21 waste tanks. The concentrate containing the polymer and suspended solids will be left in the UF system until performance degrades sufficiently to require disposal. At this point, the concentrate will be discharged to a 55-gal waste drum for eventual solidification and disposal as low-level waste. The results of these test runs will be used in decisions about whether to deploy polymer filtration as one of the treatment technologies in wastewater treatment operations at LANL.

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TTP Number AL16C322

Selective Removal/Recovery of RCRA Metals from Waste and Process Solutions Using Polymer Filtration™ Technology

Barbara F. Smith, Los Alamos National Laboratory

EM Focus Areas: mixed waste characterization, treatment, and disposal; decontamination and decommissioning; subsurface contaminants

Technology Need

Resource Conservation and Recovery Act (RCRA) metals are found in a number of process and waste streams at many DOE, U.S. Department of Defense, and industrial facilities. RCRA metals consist principally of chromium, mercury, cadmium, lead, and silver. Arsenic and selenium, which form oxyanions, are also considered RCRA elements. Discharge limits for each of these metals are based on toxicity and dictated by state and federal regulations (e.g., drinking water, RCRA, etc.). RCRA metals are used in many current operations, are generated in decontamination and decommissioning (D&D) operations, and are also present in old process wastes that require treatment and stabilization. These metals can exist in solutions, as part of sludges, or as contaminants on soils or solid surfaces, as individual metals or as mixtures with other metals, mixtures with radioactive metals such as actinides (defined as mixed waste), or as mixtures with a variety of inert metals such as calcium and sodium.

The crosscutting nature of RCRA metals render them of interest to all the EM-50 Focus Areas: subsurface contaminants (groundwater, soil spills), D&D (removal from facilities), mixed waste (RCRA metals in the presence of actinides), tanks (RCRA metals in Hanford tanks), and plutonium (transuranics and RCRAs together as a result of certain processing and secondary waste issues). Therefore, the need exists to selectively concentrate and remove RCRA metals from a variety of waste or process streams, both solid and solution, to meet discharge limits of a process solution, soil decontamination requirements, or to have sludges pass Toxic Characteristic Leaching Procedure (TCLP) testing for proper waste management. In cases where RCRA metals are valuable, it would be desirable to recover the metals for market value. Thus, the capability to not only remove and concentrate metals in general is important, but to recover a metal in relatively pure form is value added. Some specific examples of waste types and sites are described below.

Mercury (Hg)

Past processes in DOE facilities often incorporated mercury. Currently, many waste streams exist from which the recovery or removal of mercury metal (Hg^0) would be desirable; for example, soil contamination from Hg spills, equipment contamination from the use of Hg in industrial processes, contamination of DOE facilities such as Y-12 in Oak Ridge, and D&D processes that generate Hg in aqueous streams. Major feedstock for Hg recyclers include batteries, thermometers, switches, thermocouples, chloralkali wastes, fluorescent lamps, and residues from remediation activities.

Mercury can also exist in process streams already in the ionic form as Hg(II). In this case, concentration and removal of the metal ion is needed. The current approaches to Hg ion removal and concentration from aqueous streams include ion exchange, precipitation, and electrorecovery. Reaching the low levels required for discharge has been difficult to achieve cost effectively.

Chromium (Cr)

Chromium usually exists as Cr(VI) or Cr(III) in various wastes or process streams. The Cr(VI) is considered to be the hazardous form (a known carcinogen). Chromium occurs in a variety of media from past cleaning operations to current electroplating operations. It is used in cooling towers to reduce scale/corrosion, occurs in paints from D&D operations, and often gets into waste streams from corrosion of steel and deterioration of treated wood. In industrial processes, Cr appears in electroplating waters, cooling tower water, and as corrosion products.

Silver (Ag)

Silver is currently used at many DOE facilities and in much of the industrial sector. Many facilities have photofinishing operations, hospitals produce x-rays, and DOD produces aerial photos. Each of these processes produce Ag waste streams. Because Ag is both a valuable metal and a RCRA metal, a recovery industry has been built that can readily recover Ag to the 5-ppm level using metal exchange canisters (Ag is exchanged for Fe). The main issue now is that the new federal discharge levels cannot be readily met, and many states require even lower discharge levels.

Technology Description

We have successfully completed a preliminary proof-of-principle evaluation of Polymer Filtration™ (PF) technology for the dissolution of metallic mercury and have also shown that we can remove and concentrate RCRA metals from dilute solutions for variety of aqueous solution types using PF technology. In addition, we have shown that the PF technology can remove lead from Superfund soils. Another application successfully demonstrated is the dilute metal removal of americium and plutonium from process streams. This application was used to remove the total alpha contamination to below 30 pCi/L for the wastewater treatment plant at TA-50 at Los Alamos National Laboratory (LANL) and from nitric acid distillate in the acid recovery process at TA-55, the Plutonium Facility at LANL (ESP-CP TTP AL16C322). This project will develop and optimize the PF technology for specific DOE process streams containing RCRA metals and coordinate it with the needs of the commercial sector to ensure that technology transfer occurs.

The objectives of this project are to 1) develop and optimize the selective dissolution of Hg^0 from solid surfaces; 2) optimize the concentration, removal, and recovery of Hg from aqueous solutions produced by dissolution of Hg^0; 3) optimize PF for concentration, removal, and potential recovery of Cr and Ag from aqueous solutions that represent DOE aqueous waste/process solutions to meet discharge limits of wastewater for RCRA metals; and 4) identify and evaluate comparable wastes in the private sector that can be treated using PF to aid with technology transfer. The long-term goal is to obtain the fundamental scientific information to perform a full demonstration for the Subsurface Contaminant, D&D, and/or Mixed Waste Focus Areas at actual contaminated sites.

Benefit to DOE/EM

PF has the potential to reduce costs, improve treatment schedules, reduce ES&H concerns and, because of the state of technology development, has low technical risk (e.g., PF is being commercialized for the electroplating industry to recover nickel and zinc from rinse solutions with our industrial partner, Micro-Set, Inc., Landisville, NJ).

Separations Performance, Reliability, and Robustness

Our PF system has many advantages compared to resin-based ion exchange or chelating resin technology, the technology most closely aligned to PF.

- **Processing Speed.** Binding kinetics are more rapid with the PF system because they occur in a single, aqueous phase (homogeneous reaction). With chelating ion exchange, two phases are involved: aqueous and solid resin. The metal ions are transported from the solution onto the organic resin and then into the resin pores (heterogeneous reaction). This process is relatively slow in both the metal-ion binding and regeneration steps. Thus, column flow rates have to be optimized to allow for slower binding and release. Because of this slowness the amount of regeneration solution required to recover the metal ions is large. PF significantly reduces processing times and process volumes.
- **Loading Capacity.** Our polymers generally have loading capacities 3 to 8 times greater than that of any chelating ion exchange resin because they have more binding sites. Chelating resins are organic solids that use some of their chemical structure to maintain mechanical stability, thus leaving fewer binding sites available for the metal ions on a weight basis. Also, resin beads must be large enough to avoid hydraulic backpressure in the column. Binding sites at the centers of large beads often are not easily accessed.
- **Selectivity.** Because our polymers use chelation bonding, we can tailor a polymer's structure and chelating groups to select specific metal ions, rejecting benign impurities such as calcium, potassium, and other salts. With PF, it is possible to easily develop formulations (mixtures) of polymers with different chelators to

recover metal ion mixtures and separate them as needed. Chelex 100 and IRC-718, as examples of commercially available chelating resin, have only one type of chelator, making them selective for fewer metal ions; however, new chelating resins are under development.

- **System Size.** The PF system can be very compact. Scale-up is easy, however, so the system can be used in all sizes. Resin ion-exchange equipment requires more space because of its multiple columns of resin beads.
- **Metal-Ion Recycle.** PF can recover metal-ion concentrate in a small volume for proper waste management all in a single unit.

The PF system also improves on other conventional metal concentration processes. In contrast with reverse osmosis, PF is operated at low pressure (equal to or less than 25 lb/in.^{2}). Unlike evaporation, PF is a low-temperature, and therefore, a low-energy process. Reverse osmosis and evaporation, as compared to PF, are nonselective, recovering all waste stream salts and materials, including metal ions that are impurities. Advanced precipitation approaches produce large amounts of waste, which is particularly expensive if it is hazardous or mixed waste. Unlike liquid-liquid extraction, PF is a single-phase, aqueous-based reaction and does not require organic solvent diluents.

Cost Benefits

Each waste type, aqueous process, or solid stream will vary in size and difficulty and will require a different polymer formulation. Different polymers with specialized chelators will have different costs. But for the electroplating industry where dilute rinse waters have been treated to selectively concentrate and recover nickel and zinc, operation expenses for PF are estimated at $0.01/gal compared to $0.25/gal for evaporation, and $0.025/gal for reverse osmosis. Operating expenses for ion exchange are similar to PF, but the equipment size and cost are less for PF technology based on equal feed throughput. Polymer costs are very competitive with currently available chelating ion-exchange materials.

Technology Transfer/Collaborations

We will be working closely with industrial partner Micro-Set, Inc., to provide partial support in marketing and engineering and in polymer production once the optimum polymers are developed. It is important to the commercialization effort that there be both a DOE market and a private sector market for the technology application. Our goal is to transfer the technology to the private sector so that it will be commercially available. All RCRA metals were chosen such that there is a reasonable commercial market for the technology.

Once new polymeric materials are developed, they will be evaluated and tested both at LANL and by collaborators at the University of Massachusetts Chemistry Department, using its unique capabilities and facilities.

The end users include DOE sites such as Oak Ridge at Y-12, LANL, Hanford, and other industries that use these RCRA metals and generate aqueous waste streams containing them.

Scientific Background

PF uses water-soluble metal-binding polymers to sequester metal ions in dilute solution. The water-soluble polymers have a sufficiently large molecular size that they can be separated and concentrated using commercial ultrafiltration (UF) technology. Water, small organic molecules, and unbound metals pass freely through the UF membrane while concentrating the metal-binding polymer. The polymers can then be reused by changing the solution conditions to release the metal ions. The metal ions are recovered in concentrated form for recycle or disposal. The water-soluble polymer can be recycled for further aqueous-stream processing.

Though the concept of using water-soluble metal-binding polymers for metal ion recovery and concentration from aqueous solutions has been in the literature for more than 20 years (Geckeler, Env. Sci. &Tech., *30(3)*, 725, 1996), it has never been applied on an industrial scale or used as an engineered unit, even though UF is commonly used in industrial operations. The LANL Separations Team developed this PF technology (four patents pending) for real-world applications and received a 1995 R&D 100 award for developing and demonstrating a pilot-scale system for application to the electroplating industry. An international review panel selected PF as one of the top 100 technologies made commercially available in 1995.

Technical Approach

The RCRA metal field is so large that this task focuses on only a few metals and several waste streams. We are starting with mercury because it is the primary RCRA metal problem at DOE facilities. We will evaluate removal of Hg metal from solid surfaces representing pipes at Oak Ridge. Once we establish that Hg can be removed from different materials with a high degree of selectivity, different configurations will be tested, such as inside straight pipes, curved pipes, crevices, and other difficult-to-reach places. Crushed fluorescent lighting materials containing Hg will also be evaluated to ensure that the technology can be readily transferred to industry.

Initial proof-of-principle experiments indicate that mercury dissolution is quite rapid under the harsh conditions tested (from 6 to 2 *M* HNO_3), but slowed as the conditions became milder (polymer plus 1 *M* HNO_3). Future tests will include evaluating different water-soluble metal-binding polymers with different concentrations, mixing conditions, temperatures, and acids. Non-salt-forming oxidizers will also be evaluated. This will be followed by optimizing the mercury and polymer recycle conditions by looking at polymer selectivity, optimum metal stripping conditions as a function of pH, temperature, ligand competition, and reductants. Our goal will be to reach the EPA-promulgated treatment standard of 0.03 mg/L for wastewater and 0.2 mg/L for solids as measured by TCLP.

We will also evaluate removal of RCRA metals from aqueous processes such as condenser-scrubber liquids produced by waste destruction and stabilization operations. Chromium and silver are the two main target metals. Chromium is particularly difficult as it has several different oxidation states that can be either cationic or anionic. Silver exists as a cation or as an anionic complex in many wastes. A systematic evaluation of a series of polymers for extraction of Ag(I), Cr(III), and Cr(VI) from a broad range of solution types will be performed. A key component of this series of studies is the evaluation of a carefully selected set of metal-binding polymers containing the appropriate donor atom sets for binding of both anions and cations. The matrix will be varied to reflect the variable matrix that exists in real wastewater. The technology will then be tested on LANL wastewater to determine its ultimate effectiveness.

Metals that represent RCRA and other metals will be tested for polymer selectivity. While we may not focus on certain metals, information about their binding will result from the selectivity studies. These could include lead and cadmium to represent other RCRA metals; iron, calcium, and aluminum as they exist in matrix materials; and some transition metals to represent competing metal ions.

Accomplishments

This a new task in FY 1997. Project planning meetings have been held with the technical team members and work is under way. Some starting materials and small equipment supplies have been ordered, and backbone water-soluble polymer is being prepared. We are building a polymer processing unit to prepare water-soluble polymers on a larger scale. By preparing one large batch of starting material (polydisperse polyelectrolytes) we can achieve continuity for a series of tests. A new multi-element ICP-AEC was installed, and training of appropriate personnel has begun. This will be used for total analysis of certain RCRA metals (Cd, Pb, Ag, Cr, etc.). A stand-alone mercury analyzer is being installed. The separate analyzer is required as mercury often leaves residue in the ICP instrument causing background problems. A new detector for the ion chromatography system was installed and tested and is being used for chromium speciation determinations.

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TTP Number AL17C331

Decontamination of Soils and Materials Containing Medium-Fired PuO_2 Using Inhibited Fluorides with Polymer Filtration Technology

Donald J. Temer*, Robert Villarreal, and Barbara F. Smith, Los Alamos National Laboratory

EM Focus Areas: subsurface contaminants; mixed waste characterization, treatment, and disposal; decontamination and decommissioning

Technology Need

An effective and efficient methodology is needed to decontaminate soils and/or materials containing medium-fired Pu and Am oxides in various forms without dissolution of greater than 10% of the matrix. Also needed is a process that reduces the volume of secondary waste by allowing reuse of the original decontamination solution.

Technology Description

The decontamination of soils and/or materials from medium-fired plutonium oxide (PuO_2) with an effective and efficient decontamination agent that will not significantly dissolve the matrix requires a new and innovative technology. After testing several decontamination agents and solutions for dissolution of medium-fired PuO_2, the most successful decontamination solutions were fluoride compounds, which were effective in breaking the Pu-oxide bond but would not extensively dissolve soil constituents and other materials. The fluoride compounds, tetra fluoboric acid (HBF_4) and hydrofluorosilicic acid (H_2F_6Si), were effective in dissolving medium-fired PuO_2, and did not seem to have the potential to dissolve the matrix. In both compounds, the fluoride atom is attached to a boron or silicon atom that inhibits the reactivity of the fluoride towards other compounds or materials containing atoms less attracted to the fluoride atom in an acid solution. Because of this inhibition of the reactivity of the fluoride ion, these compounds are termed inhibited fluoride compounds or agents.

Both inhibited fluorides studied effectively dissolved medium-fired PuO_2 but exhibited a tendency to not attack stainless steel or soil. The basis for selecting inhibited fluorides was confirmed during leaching tests of medium-fired PuO_2 spiked into soil taken from the Idaho National Engineering Laboratory (INEL). When dissolved in dilute HNO_3, HCl, or HBr, both inhibited fluoride compounds were effective at solubilizing the medium-fired PuO_2 from spiked INEL soil.

The work to be conducted in this task

- optimizes the concentration of inhibited fluoride
- selects the most effective host acid
- optimizes concentration of the host acid
- establishes the most effective pretreatment process for soils
- establishes optimum heating temperature and time
- tests the effectiveness of the decontamination solution (inhibited fluoride and acid conditions) on pretreated soil
- establishes the percentage of solid dissolved by the decontamination solution
- optimizes decontamination solution to maximize solubility of PuO_2 and minimize dissolution of soil
- tests optimized decontamination solution on other materials
- proceeds with metathesis of Pu from decontamination solution with polymer filtration that allows concentration of the extracted Pu and reuse of the original decontamination solution.

Once the optimum conditions for solubilizing the medium-fired PuO_2 with the decontamination solution containing inhibited fluorides are established, then a concerted effort will be made to optimize the soil washing process. As a target, a process is preferred that is simple, does not require complex mixing, and can be accomplished in a relatively short timeframe. A simple polishing step will be established to ensure any solubilized PuO_2 will be washed from the soil. An effort must also be pursued to study the characteristics and fate of ^{241}Am through the decontamination process.

Benefit to DOE/EM

This new methodology will establish a new, economical baseline technology that does not currently exist for decontamination of medium-fired PuO_2 from soils and materials. Once demonstrated successfully, this technology can be applied to other materials that are similarly contaminated, such as pyrochemical salts, treatment residues, and ashes. Optimizing this decontamination methodology could provide the only means for decontaminating medium-fired PuO_2 from soils and materials without significantly dissolving the matrix to be decontaminated. Further, by integrating a means of extracting and concentrating Pu from the decontamination solution without modifying the acidity (so the decontamination solution can be reused) will minimize the waste generated during the decontamination process.

Technology Transfer/Collaborations

This methodology was initially conceived and tested to specifically provide an alternative method for soil cleanup at the PIT-9 waste storage site at INEL. Lockheed-Martin Advanced Environmental Services Corporation (LMAES) is contracted to complete the cleanup of the site and is our primary contact for applying this methodology. Initial presentations to LMAES on this methodology were received favorably, but they felt the methodology lacked maturity. We will continue to communicate with LMAES on the progress and success of this methodology. If successful, the methodology will also be made available to Los Alamos National Laboratory (LANL) and Rocky Flats engineers as it is optimized and matured.

Scientific Background

This methodology addresses a need presented to LANL by LMAES for INEL wastes and soils in PIT-9 that were potentially contaminated with medium-fired Pu-Am oxides and other radionuclides. The challenge presented to LANL was to solubilize and remove refractory PuO_2 spiked into INEL soils without dissolving more than 10% of the pretreated soil.

A large number of potential and established decontamination agents that previously showed success in decontaminating non-fired PuO_2 from soils were tested on the medium-fired PuO_2 and were totally ineffective for solubilizing it. These tests confirmed that dissolution of medium- or high-fired PuO_2 requires a strong acid with an oxidizing agent or the presence of hydrofluoric acid, which can break the Pu-oxygen bond because of its greater electronegativity as compared to oxygen. Concentrated nitric acid alone will not dissolve medium- or high-fired PuO_2. However, if nitric acid in concentrations greater than 3 *M* are used with addition of HF to enhance the dissolving potential of the mixture, the matrix to be decontaminated will also be dissolved. Consequently, several tests were conducted with low acid concentrations of HNO_3, HCl, and HBr with added compounds containing fluoride that was associated with an atom that is chemically bound to the fluoride and will mask the activity of the fluoride ion.

Two of the fluoride-containing compounds that showed potential for solubilizing PuO_2 without dissolving significant quantities of soil and other materials were tetra fluoroboric acid (HBF_4) and hydrofluorosilicic acid (H_2F_6Si). In these two compounds, the fluoride atom is chemically bound to either a boron atom or a silicon atom, which inhibits the reactivity of the fluoride ion. Because the fluoride ion is inhibited from reacting with other silicon atoms (soil) and ferrous materials (stainless steel), these compounds are termed inhibited fluoride compounds.

The decontamination solutions developed and tested by mixtures of the inhibited fluorides with dilute solutions of HNO_3, HCl, and HBr were found to be effective in solubilizing medium-fired PuO_2 without significantly dissolving the pretreated soil or stainless-steel coupons added to the solutions. The success of the decontamination solutions containing inhibited fluorides is the basis of this new methodology that will be optimized according to this developmental project.

Technical Approach

The successful establishment of a new methodology for decontaminating medium-fired PuO_2 without significant dissolution of soils and materials will require an elaborate testing matrix. The basis for this new methodology is the use of inhibited fluorides for dissolution of medium-fired PuO_2. The approach for establishing the new decontamination methodology will be to optimize each major variable through testing on a sequential and iterative basis as shown below.

Major Variables of Decontamination Solution

Active Agent	
inhibited fluoride type	HBF_4 or H_2SiF_6
inhibited fluoride concentration	2%, 4%, 8%
other inhibited fluorides	HSO_3F, H_2PO_3F
Host Acid	
acid type	HNO_3, HCl, HBr
acid concentration	1N, 2N, 4N
Temperature	
temperature range	40°C, 60°C, 80°C
Enhancement Additives	
oxidants	NaOCl, H_2O_2
reductants	N_2H_4, NH_2OH
complexants	oxalic acid

Major Variables of Mixing

Method of Contacting	
free fall	30 cm, 60 cm
stirring	stirring bar
shaking	reversible
ultrasonic	external, internal probe
heap leach	free flow, pressure
contactor	continuous mixing

Major Variables of Matrix

Matrix Characteristics	
soil type	fractionated, sand, clay
soil basicity	highly carbonated, acid
soil permeability	high permeability, low
material type	stainless steel, refractory; aluminum, mild steel

Major Variables of Pretreatment

Pretreatment Processes	
acid type	HNO_3, HCl, HBr
acidity	<0.5 N, 1 N, 2 N

Major Variables of Polishing Process

Polishing Processes	
decontamination polishing solution	HNO_3; inhibited fluoride
number of polishing cycles	1, 2, >3

Major Variables of Decontamination Solution Processing

Decontamination Solution Cleanup/Leachate Recycle	polymer filtration, polymer extraction, precipitation, ion exchange

Major Variables of PuO_2 Forms

PuO_2 Forms	low-fired, medium-fired, high-fired
AmO_2 Forms	Same as PuO_2

To meet the goal of establishing a new methodology for decontamination of soils and materials from medium-fired PuO_2 without significantly dissolving the matrix with the decontamination solution will require varying the conditions of tests to obtain a final optimum decontamination solution and process. This will be accomplished by establishing a test matrix according to a hierarchy of variable impact. When a final decontamination solution and process is selected, then the success of the decontamination process will be demonstrated on INEL soil spiked with medium-fired PuO_2. The degree of success of this decontamination process will lead to future optimization of the process on a scaled-up version.

Accomplishments

To date, the major accomplishment has been to identify inhibited fluorides as a potential active agent in solubilizing medium-fired PuO_2. The success of these types of solubilizing agents will be the basis for pursuing the technical approach described above.

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TTP Number AL17C322

3. Wednesday Presentations—First Half-Day

- ☐ Oxidation, Characterization, and Separation of Non-Pertechnetate Species in Hanford Wastes
- ☐ Comprehensive Supernatant Treatment
- ☐ Hot Demonstration of Proposed Commercial Radionuclide Removal Technology
- ☐ Chemical Derivatization to Enhance Chemical/Oxidative Stability of Resorcinol-Formaldehyde Resin
- ☐ Technical Liaison with the Institute of Physical Chemistry (Russian Academy of Sciences)
- ☐ Advanced Separations at Savannah River Site
- ☐ Electrochemical Treatment of Liquid Wastes
- ☐ Salt Splitting Using Ceramic Membranes

Oxidation, Characterization, and Separation of Non-Pertechnetate Species in Hanford Wastes

Norman C. Schroeder, Los Alamos National Laboratory

EM Focus Area: high-level waste tank remediation

Technology Need

Under DOE's privatization initiative, Lockheed Martin and British Nuclear Fuels Limited are preparing to stabilize the caustic tank waste generated from plutonium production at the Hanford Site. Pretreatment of Hanford tank waste will separate it into low-level waste (LLW) and high-level waste (HLW) fractions. Both streams will be vitrified; the LLW will be stored on the Hanford Site, and the HLW will be placed in a geologic repository. Cesium and technetium will be separated from the LLW stream and vitrified with the HLW. The reasons for placing technetium in the HLW component are its long half-life (213,000 years) and its ability to migrate in the environment. If left in the LLW, these factors cause technetium to be a major contributor to the long-term hazard associated with the LLW form.

The scope of the technetium problem is indicated by its inventory in the waste: ~2000 kg. Technetium would normally exist as the pertechnetate anion, TcO_4^-, in aqueous solution. However, evidence obtained at Los Alamos National Laboratory (LANL) indicates that the combination of radiolysis, heat, organic complexants, and time may have reduced and complexed a significant fraction of the technetium in the tank waste. These species are in a form that is not amenable to current separation techniques based on pertechnetate removal. Thus, it is crucial that methods be developed to set technetium to pertechnetate so these technologies can meet the required technetium decontamination factor. If this is not possible, then alternative separation processes will need to be developed to remove these non-pertechnetate species from the waste.

Technology Description

The simplest, most cost-effective approach to this problem is to convert the non-pertechnetate species to pertechnetate. Chemical, electrochemical, and photochemical oxidation methods, as well as hydrothermal treatment, are being applied to Hanford waste samples to ensure that the method works on the unknown technetium species in the waste. The degree of oxidation will be measured by determining the technetium distribution coefficient, $^{Tc}K_d$, between the waste and Reillex™-HPQ resin, and comparing it to the true pertechnetate K_d value for the waste matrix. Other species in the waste, including all the organic material, could be oxidized by these methods, thus selective oxidation is desirable to minimize the cost, time, and secondary waste generation. The best and most acceptable technique will be optimized and applied to a small batch of waste and tested for pertechnetate removal by anion exchange using Reillex™-HPQ resin. If these methods fail or are undesirable, it will then be necessary to characterize the technetium species in the waste. Knowing the type of technetium species present could aid the development of an oxidation process and would be necessary to develop separation methods for the species.

Benefits to DOE/EM

Anion exchange using Reillex™-HPQ resin, extractions using crown ethers, and polyethylene glycol resins are some of the technologies being developed to separate technetium from DOE waste streams. All of these methods require technetium to be present as pertechnetate or easily converted to pertechnetate for their success. Failure to address this problem may result in applying a process that is incapable of removing technetium to the required decontamination factor. Development of a technology to determine the scope of a technetium speciation problem would be of value to DOE.

Technology Transfer/Collaborations

Under the Tanks Focus Area (TFA), Pacific Northwest National Laboratory (PNNL) is scheduled to do a large column flow test with Reillex™-HPQ resin in FY 1997 to remove technetium from Hanford waste. We will provide the results of our studies to PNNL to help them adjust their feed for this test. An oxidation protocol is needed by April 1997 to meet their schedule. A similar transfer of information would occur to TFA and PNNL if a separations protocol was developed. LANL's technetium processing group and PNNL staff have had an informal collaboration on the technetium processing problem over the last 18 months.

Scientific Background

We have developed a process to remove technetium, as TcO_4^-, from the Hanford tank waste using Reillex™-HPQ anion exchange resin. This system successfully partitions pertechnetate from simulants that mimic various high-nitrate Hanford wastes. We have also modeled pertechnetate sorption from simpler alkaline nitrate solutions. The fundamental properties of the resin in the presence of the major anions in Hanford wastes, nitrate and hydroxide, are well understood. Figure 1 illustrates the dependence of technetium distribution coefficients, $^{Tc}K_d$, as a function of $[NO_3^-]$ and $[OH^-]$. The measured $^{Tc}K_d$ values are determined as defined in Equation 1.

$$^{Tc}K_d = \frac{\text{Tc on resin (cpm)/ g dry resin}}{\text{Tc in solution (cpm)/ mL of solution}} \qquad (1)$$

If only pertechnetate is present, then the $^{Tc}K_d$ values will be invariant with the phase ratio (volume of liquid/mass of resin) as long as the resin does not approach technetium saturation and there is no rapid equilibrium among the technetium species.

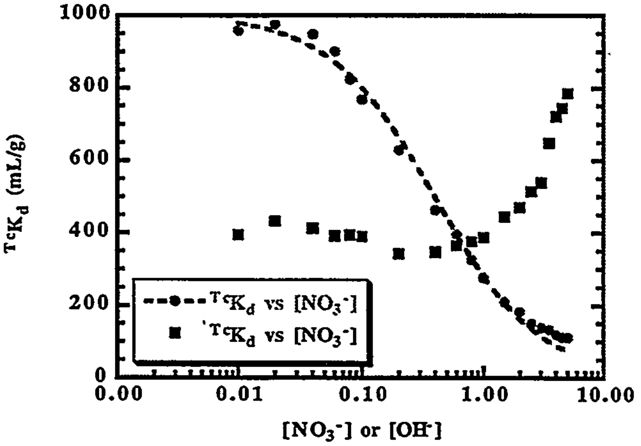

Figure 1. Pertechnetate $^{Tc}K_d$ values as a function of $[NO_3^-]$ and $[OH^-]$

In Figure 1, the dashed line is the least-squares fit of the measured $^{Tc}K_d$ to $[NO_3^-]$ using Equation 2.

$$^{Tc}K_d = \frac{K_1 R_t}{\{K_2 [OH^-] + [NO_3^-]\}} \qquad (2)$$

The resin capacity (R_t) is 3.34 meq/g dry resin. K_1 (117 mL/meq) and K_2 (0.389) are the equilibrium constants for the exchange of TcO_4^- and OH^- for nitrate in the resin, respectively. Figure 1 also shows the $^{Tc}K_d$ as a function of the hydroxide concentration at 1.00 *M* $NaNO_3$. This curve follows the predicted behavior at hydroxide concentrations up to 0.40 *M* $[OH^-]$. Above 0.40 *M* $[OH^-]$ the curve deviates from the predicted behavior. In this region, the $^{Tc}K_d$ values increase, almost doubling their value between 1.00 and 5.00 *M* NaOH. The dramatic increase in the experimental $^{Tc}K_d$ values can be attributed to the strongly hydrated hydroxide ion effectively removing an increasing fraction of the free water in the system, resulting in a dehydration of the weakly hydrated TcO_4^- anion, and consequently increasing the $^{Tc}K_d$ values.

From our understanding of the behavior of Reillex™-HPQ resin in nitrate/hydroxide media, we can accurately predict the pertechnetate $^{Tc}K_d$ values in Hanford-type matrices. The first samples of waste we received were from tanks 101-SY and 103-SY. They contained 3.5 to 3.9 *M* NaOH and ≈1 M $NaNO_3$, and had total organic carbon concentrations of 4.3 and 2.8 g/L, respectively. Figure 1 predicted $^{Tc}K_d$ values of 600 to 700 mL/g for these wastes. However, the actual $^{Tc}K_d$ values measured were 3.99 and 5.16 mL/g for the 101-SY and 103-SY samples, respectively. These results indicate that 65% of the technetium was not present as pertechnetate. Furthermore, these non-pertechnetate species are resistant to oxidation.

We speculate that the radiolytic conditions in the caustic waste have generated solvated electrons that are strong reductants ($E° = 2.86$ V) for metal ions having a reduction potential less than this; this would include the redox potentials for technetium. Reduction of pertechnetate performed in the presence of complexing agents in the waste leads to reduced complexed technetium compounds and prevents the formation and precipitation of TcO_2.

Technical Approach

Our primary objective is to convert the non-pertechnetate species to pertechnetate so that we can apply our anion exchange process using Reillex™-HPQ to separate technetium from Hanford waste streams. The criteria for success will be to obtain a $^{Tc}K_d$ value close to the true pertechnetate $^{Tc}K_d$ value for the waste matrix. The true pertechnetate $^{Tc}K_d$ is easily obtained by removing the residual ^{137}Cs from the waste, spiking the waste with the gamma-emitting isotope ^{95m}Tc added as pertechnetate, and performing a batch contact with Reillex™-HPQ. If a successful method is found it will be optimized and applied to a small batch of waste, which will then be tested with a small column flow study.

The criteria for success here is to achieve 1% breakthrough after >25 column volumes. The ultimate criteria for a full-scale anion exchange system is to produce a LLW stream that will generate a Class A waste form. At this point the feed adjustment chemistry can be transferred to the TFA. A major technical decision to make is whether the conversion to pertechnetate is feasible, efficient, and practical, and if not, then begin developing separation methods for the non-pertechnetate species; this would occur near the end of the first year. If separations are developed for non-pertechnetate species, then the criteria will be to produce a system that will give a Class A waste form.

Chemical oxidation is currently the preferred route to solving this problem. The choice of oxidants is limited by the caustic waste conditions. The oxidant should be adaptable to a flow process and produce minimal secondary waste. The oxidants that can be prepared as solutions are ozone, hydrogen peroxide, sodium peroxydisulfate, potassium permanganate, a combination of hydrogen peroxide and sodium hypochlorite, calcium hypochlorite, and ammonium vanadate. Sodium bismuthate and lead dioxide are solid-phase oxidants. The advantages and disadvantages of each oxidant are recognized. For example, lead compounds produced from PbO_2 would not be acceptable but need to be tried, ozone would have no secondary waste but may not be selective, and hypochlorite would be undesirable because the chloride produced is corrosive. Enhancement of the chemical oxidation may be accomplished by coupling them to electrochemical or photochemical processes. This may save on reagent cost by regenerating the working oxidant. Alternatively, oxidation to pertechnetate could be achieved after hydrothermal destruction of the organics in the waste. If the oxidation techniques are inefficient or unacceptable, then we will develop methods to separate the non-pertechnetate species. This will require some understanding of the chemical nature of the technetium species. Thus we will need to isolate, identify, and characterize these stable non-pertechnetate species. Initially, we need to understand the behavior of the these species toward different separating agents to obtain information about their charge and reactivity; this information alone may lead to a plausible separation. Thus, sorption by a cation or chelating resins, extraction by donor solvents, or removal by water-soluble chelating polymers may indicate whether these species are cationic, neutral, or undergo ligand substitution. After this we will develop schemes to isolate and identify the technetium complexes from samples of actual waste using instrumental techniques.

Capillary electrophoresis/mass spectrometry with an electrospray source is a relatively new method of transferring ions from solution to the gas phase for mass spectrometric determination. In principle, any cation or anion that is stable in solution can be transferred with little or no chemical change into the gas phase by the electrospray source. Experimental conditions for detecting technetium species in tank waste samples will be developed using Hanford waste simulants containing model technetium complexes; this is needed to calibrate electrophoretic times and isotopic patterns for the technetium complexes in the waste.

Based on the separation protocols for the micro amounts of the technetium species, we will then be able to scale to isolation of macro (mg) quantities. With these quantities, we will then be able to use ^{99}Tc NMR, high-field carbon and proton NMR, and x-ray absorption (both EXAFS and XANES) spectroscopy to characterize the technetium species in the tank wastes. All of these methods will rely heavily on the use of model complexes to develop needed baseline data for interpreting the element-specific spectral features that are observed.

Once identified and synthesized in bulk, the actual technetium species in the waste can be used to develop the appropriate separation chemistry. This information will enable the development of separation chemistry that will efficiently remove technetium from the waste. Possible methods could include water-soluble chelating polymers, ion exchange resins, or solvent extraction. Alternatively, electrochemical studies with the actual compounds in the waste may allow us to revisit the oxidation approach for technetium partitioning.

Accomplishments

We have attempted to oxidize the 103-SY tank waste with numerous oxidants. The true pertechnetate $^{Tc}K_d$ value for this waste was measured to be 542 ± 20.9 mL/g. An initial oxidation with an excess of the candidate oxidant is made to oxidize all the reduced species in the waste; non-pertechnetate technetium, nitrite, and the organic material. If the $^{Tc}K_d$ is enhanced by this treatment then the amount of oxidant is reduced to level that is excess of the just the non-pertechnetate species present. Oxidants, such as $NaBrO_3$, CrO_4^{2-} and H_2O_2, that normally take TcO_2 or Tc(V) species to TcO_4^- were ineffective. The most promising oxidants ($^{Tc}K_d$ values>50 mL/g) have been hypochlorite, ozone, peroxydisulfate, a peroxydisulfate/silver mixture, and permanganate. Some selectivity was achieved for the latter three oxidants.

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TTP Number AL17C321

Comprehensive Supernatant Treatment

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EM Focus Area: high-level waste tank remediation

Technology Need

Millions of gallons of radioactive waste are stored in tanks at sites managed by DOE. Sites containing this waste include Hanford, West Valley, Idaho Falls, Oak Ridge National Laboratory (ORNL), and the Savannah River Site. These wastes consist of sludges and supernatants composed predominantly of nonradioactive chemicals. Concentration of the radioactive components by separation from the nonradioactive chemicals would allow the bulk of the material to be handled as low-level waste and reduce the volume of waste required for final disposal. Several technologies are available to treat the supernatant or dissolved sludge from the tanks. However, because of the chemical complexity associated with the tank contents, determining the best technology requires research using actual samples from the tanks.

The tanks contain cesium, strontium, and technetium (Cs, Sr, Tc) radionuclides, which are the major contributors to the radioactivity in the supernatants. Ion exchange has been effectively used for some radionuclide separations. However, these supernatants contain high concentrations of sodium, potassium, chloride, and nitrates that interfere with some separation methods.

Identification of the best sorbents for separating these radionuclides can best be accomplished by conducting tests using supernatant samples from storage tanks. For these studies, supernatant samples were collected from the Melton Valley Storage Tank (MVST) farm at ORNL. These samples were used to evaluate the selected sorbents for removing Cs, Sr, and Tc.

Technology Description

This task involves recovering the liquid (supernatant) portions of ORNL MVST waste in a hot cell and treating the supernatant to separate and remove the radionuclides. The supernatant is used in testing various sorbent materials for removing Cs, Sr, and Tc from the highly alkaline, saline solutions. Batch tests are used to evaluate and select the most promising materials for supernatant treatment to reduce the amount of waste for final disposal. Once the sorbents have been selected based on the results from the batch tests, small column tests are made to verify the batch data. Additional data from these tests can be used for process design.

The sorption tests emphasize evaluation of newly developed sorbents and engineered forms of sorbents. Methods are also evaluated for recovering the radionuclides from the sorbents, including evaluating conditions for eluting ion exchange resins.

A final report will summarize the results and compare the results with those of other investigators, along with recommendations for separating and concentrating radionuclides from DOE storage tank supernatants at Oak Ridge and other sites. Documentation of the data and the significance of the findings will be compared, and recommendations will be provided to likely users of the data in EM-30. This program will also provide input to the supernatant treatment process demonstration projects at ORNL.

Benefit to DOE/EM

Information developed in this program is expected to apply to tank waste supernatants found at most DOE sites,

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especially highly alkaline supernatants with high concentrations of salts. The proposed methods would result in smaller volumes associated with the radioactive component of the waste and thus minimize storage needs. The bulk of the remaining materials could then be treated to remove other components like nitrates and other toxic or hazardous components in the stream with minimal shielding requirements. A final report will be issued summarizing these results, comparing them to other results for the same sorbents, and providing recommendations for unit operations to use for separating and concentrating the radionuclides from DOE storage tank supernatants at ORNL and other DOE sites.

Technology Transfer/Collaborations

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

Scientific Background

Previous studies at ORNL have focused on Cs and Sr separations.[1-4] These studies tested several sorbents to remove Cs from the MVST W-25 supernatant. Sorbents tested included resorcinol-formaldehyde (R-F) resin, Duolite CS-100, crystalline silicotitanate (CST), potassium cobalt hexacyanoferrate (KCoCF), and composite microspheres of hydrous titanium oxide (HTO)/KCoCF, and HTO/sodium cobalt hexacyanoferrate (NaCoCF). Potassium cobalt hexacyanoferrate gave the highest Cs distribution ratio; however, of the commercially available sorbents, the R-F and CST worked best.

We examined the effect of Cs concentration on sorbent effectiveness. Increasing the Cs concentration in the supernatant did not affect the Cs distribution ratios of KCoCF or CST. However, with R-F resin the Cs distribution ratios decreased as the Cs concentration increased. Increasing the potassium concentration resulted in major decreases in Cs sorption on R-F resin. On the other hand, Cs distribution ratios for CST and KCoCF did not appear to be affected by an increase in potassium concentration.

Some of the same sorbents may be used to remove Sr simultaneously with the Cs. Batch tests were conducted using several sorbents to determine how effectively they could remove Sr from MVST W-29 supernatant. The sorbents included R-F, CST, sodium titanate (NaTiO), HTO/polyacrylonitrile (PAN), NaTiO/PAN, titanium monohydrogen phosphate microspheres, Amberlite IRC-718, Duolite C-467, and Chelex 100. The powder forms of the inorganic sorbents removed Sr most effectively. Of the engineered forms tested, the titanium monohydrogen phosphate microspheres were slightly better than the polyacrylonitrile composites. The most effective organic resin tested was the Duolite C-467.

Speciation may determine the extent of Tc removal. The Tc can be present as the pertechnetate anion, or as complexes of Tc in lower oxidation states. Radiolytic effects, organic solvents, and complexants may result in reduction, complexation, and precipitation of Tc.

Batch studies on Tc removal were conducted at Los Alamos National Laboratory by Schroeder et al.[5] and by Marsh, Svitra, and Bowen,[6] in which 17 sorbents were tested. Several sorbents gave Tc distribution ratios between 100 and 1000 mL/g. In batch tests at ORNL, Reillex™-HPQ, Reillex™-402, Amberlite IRA 904, and Amberlite IRA 400 were all effective in removing pertechnetate from MVST W-29 supernatant.

In this program, additional batch tests and some small column tests have been completed to further evaluate the removal of Cs, Sr, and Tc from tank supernatants. Recent tests have focused on Tc and Sr removal using small columns.

Technical Approach

Samples of tank supernatants have been retrieved from various tanks at the MVST farm including W-25, W-27, and W-29. Characterizing these materials has revealed many similarities to supernatants found in tanks at other DOE sites. Removal of Cs, Sr, and Tc from these highly alkaline, saline supernatants will be tested using various sorbents, including R-F resin, CST, NaCoCF, KCoCF, NaTiO, and ion exchange resins such as Duolite CS-100, Amberlite IRC-718, Reillex™-HPQ and -402, and SuperLig®644C. Many of these sorbents have been proposed for waste treatment, but most have not been tested on actual waste solutions.

Initially, batch tests are used to evaluate and select the most promising materials for supernatant treatment. Candidate sorbents for Cs removal include the R-F resin, CST, and hexacyanoferrates. Primary candidates for Sr removal are NaTiO, CST, 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, immobilized crown ethers, and microspheres composed of NaTiO and NaTiO blends, will be tested as they become available. Sodium and potassium compete for Cs removal, and nitrate can compete 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 tests results, small column tests are made on selected sorbents to verify the batch data and to obtain additional data for process design.

Most of the sorption studies have focused on radionuclide removal. Some efforts are directed toward elution or stripping of the sorbed radionuclides.

Accomplishments

The MVST supernatants were used in batch and column studies to evaluate sorbents for removal of Cs, Sr, and Tc (as pertechnetate). For the Sr and Tc batch tests, the Cs was first removed from some of the supernatants by ion exchange. However, for column tests of Tc removal, the Cs was always removed from the supernatants by treatment with ion exchangers. The parameters for the batch tests included the use of various sorbents, mixing times, supernatant to sorbent ratios, and sorbent pretreatment. Some of the results from the batch tests are summarized in Table 1. The distribution ratio is defined as follows: $D = [C_0 - C_t]/C_t][V/m]$, where C_0 is the initial concentration of radionuclide in the supernatant; C_t is the concentration at time, t; V is the volume of supernatant; and m is the mass of sorbent.

The sorbents were selected for Cs removal based on a survey of the literature and included SuperLig®644C, IONSIV®IE-911, R-F, KCoCF, and CST. Supernatants were obtained from tanks W-27 and W-29. Pretreatment of SuperLig®644C and IONSIV®IE-911 with 0.1 *M* NaOH did not affect the Cs distribution ratios, namely 1250 mL/g using "as-received" resin and 1220 mL/g for the sorbent pretreated with 0.1 *M* NaOH. However, these values were still less than the distribution ratio obtained for the potassium cobalt hexacyanoferrate. The Cs distribution ratios for this sorbent were 2350 mL/g after mixing for 0.25 h.

Because of the presence of organic liquids in some of the underground storage tanks, tests were conducted to determine the possible effects of the organic liquids on ion exchangers for Cs removal. In one set of tests, treatment of the R-F resin, SuperLig®644C, and CST sorbents by soaking in tributyl phosphate reduced the Cs distribution ratio from 525 to 75 mL/g for the R-F resin, from 480 to 330 mL/g for the SuperLig®644C resin, and from 1000 to 570 mL/g for the CST.

For Sr removal, the sorbents selected for testing included NaTiO, MERSORB-S, and CST. The granular NaTiO gave Sr distribution ratios ranging from 380 to 1400 mL/g. Results from the MERSORB-S gave Sr distribution ratios ranging from 317 to 520 mL/g. These values were less than the 24,000 mL/g obtained when using CST powder.

Batch contact studies to test sorbent effectiveness for Tc (pertechnetate) removal included use of NUSORB LP70-S impregnated with one of three amines—Aliquat, TEDA, or piccoline; Eichrom ABEC-5000; an experimental anion resin developed by the University of Tennessee; Purolite A-520-E; Amberlite IRA-904; Reillex™-HP and -HPQ; and Amberlite IRA-400. The MVST W-29 supernatant depleted in Cs and Sr and spiked with pertechnetate was used for these tests. The Tc (pertechnetate) distribution ratio obtained for the amine-impregnated NUSORB LP70-S sorbents did not vary greatly, ranging from 380 to 450 mL/g after a 24-h mixing time. Eichrom ABEC-5000 reached a similar value after only 2 h. Subsequent loading tests with ABEC-5000 along with Purolite A-520-E, Amberlite IRA-904, Reillex™-HP and -HPQ, and Amberlite IRA-400 resulted in maximum loading of about 2000 mg of Tc per kilogram of sorbent.

Based on the results obtained from the batch studies, column runs were conducted using Reillex™-HPQ and Eichrom ABEC-5000-XL. The supernatant used was column effluent from which the Cs had been previously removed by column chromatography. Using a column bed of 10.4 cm^3 of Reillex™-HPQ and a flow rate of 6 bed volumes (BV)/h, a 50% Tc breakthrough was observed at approximately 45 BV (Figure 1). Using a solution consisting of 0.017 *M* stannous chloride, 0.1 *M* ethylenediamine, and 0.075 *M* sodium hydroxide, a total of 1.2 mg of Tc was eluted in 7 BV.

Table 1. Distribution ratios (D) for Cs, Sr, and Tc between various sorbents and ORNL MVST supernatant[a]

Sorbent	D_{Cs} (mL/g)	D_{Sr} (mL/g)	D_{Tc} (mL/g)
CS-100	34[b]		
R-F	528	321	
CST (powder)	1190	24,900	
KCoCF (granular)	32,700		
TiHP/NaCoCF ϕ[c]	3150[b]		
HTiO/KCoCF ϕ[c]	2560		
SuperLig®644C	549		
NaTiO (powder)		24,200	
TiHP ϕ[c]		5630	
TiP-PAN		2900	
NaTiO-PAN		3070	
Duolite™ C-467		1120	
Chelex 100		673	
Amberlite IRC-718		857	
Eichrom ABEC-5000			780
Purolite A520E			694
Amberlite IRA-904			620
Reillex™-HPQ			611
Reillex™-HP			460
Amberlite IRA-400			424
Reillex™ 402			786

[a] Solution to sorbent ratio = 200; mixing time = 24 h; MVST W-29 supernatant unless otherwise noted.

[b] MVST W-25 supernatant.

[c] ϕ = microspheres.

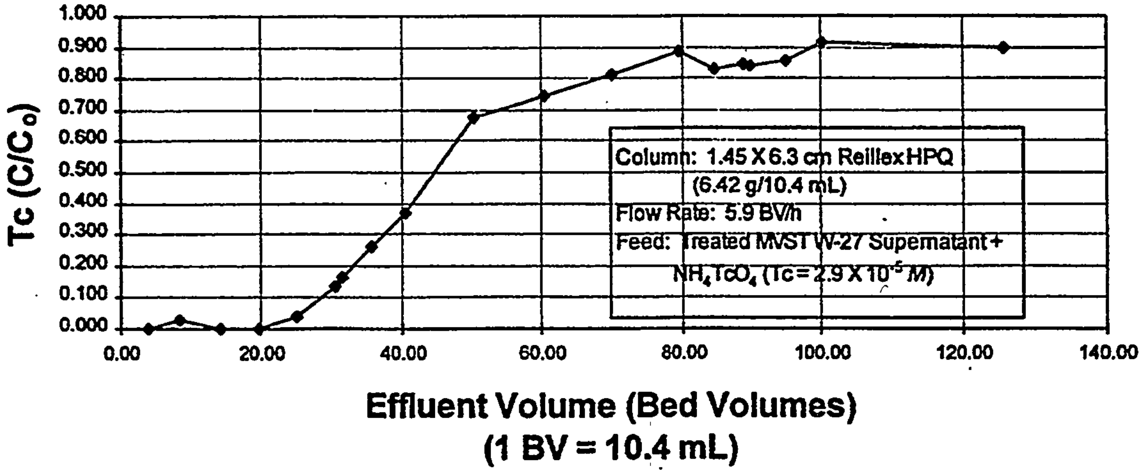

Figure 1. Pertechnetate removal from MVST W-27 supernatant

The column behavior of Eichrom ABEC-5000-XL is still under study. Additional batch and column tests are planned to evaluate sorbents for Sr removal.

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Hot Demonstration of Proposed Commercial Nuclide Removal Technology

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EM Focus Area: high-level waste tank remediation

Technology Need

Cesium, strontium, and technetium radionuclides are a small fraction of the mainly sodium and potassium salts in storage tank supernatants at the Hanford, Oak Ridge, Savannah River, and Idaho sites that DOE must remediate. Radionuclide removal technologies supplied by the ESP-CP have been previously proposed and tested in small batch and column tests using simulated and a few actual supernatants. They must now be tested and the most appropriate ones selected using a flow system of a scale suitable to obtain engineering data that can be applied to the design of pilot-scale equipment.

Technology Description

This task involves operation of an experimental unit designed and constructed to test radionuclide removal technologies during continuous operation on actual supernatants. The equipment diagram, shown in Figure 1, consists of the tanks, pumps, tubing and fittings, filters, and instrumentation for testing radionuclide removal technologies in a continuous-flow system in an Oak Ridge National Laboratory (ORNL) hot cell.

The task provides a test bed for investigating new technologies, such as 3M's SLIG 644 WWL WEB and AEA Technology's EIX electrochemical elution system, and complements ESP's comprehensive supernatant task (TTPOR06C341) by using larger engineering-scale, continuous equipment to verify and expand that task's batch studies. This task complements the Tanks Focus Area's (TFA's) Cesium Removal Demonstration (CsRD) at ORNL by providing sorbent selection information, evaluating and testing proposed sorbents, and providing operational experience and characteristics using the sorbent and supernatant to be used in the demonstration, followed by evaluating and comparing small-scale to demonstration-scale performance.

We cooperate closely with other ESP-CP tasks and the TFA to ultimately transfer the technologies being developed to the end user.

Benefit to DOE/EM

Technologies evaluated in this task are expected to apply to remediation of tank waste supernatants at most DOE sites, particularly highly alkaline supernatants that contain high concentrations of salts. Separating and concentrating the soluble radionuclides, particularly cesium, would result in a much smaller amount of radioactive waste for disposal or long-term storage. Removing 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.

We provide the TFA's CsRD at ORNL with sorbent selection information based on the evaluation and testing of proposed sorbents, and operational experience and characteristics using the sorbent and supernatant selected for use in the demonstration. We provide a test bed using actual supernatant for investigating other new technologies that become available during the program. Engineering-scale equipment can be used for testing because of the ready availability of supernatant.

Technical Approach

A 60-L supernatant sample was retrieved from the Melton Valley Storage Tank (MVST) W-27 in April 1995 and characterized. The sample has many similarities to supernatants in tanks at other DOE sites and provides a common basis to test different sorbents for their ability to remove

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[1] Oak Ridge National Laboratory is managed by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under Contract DE-AC05-96OR22464.

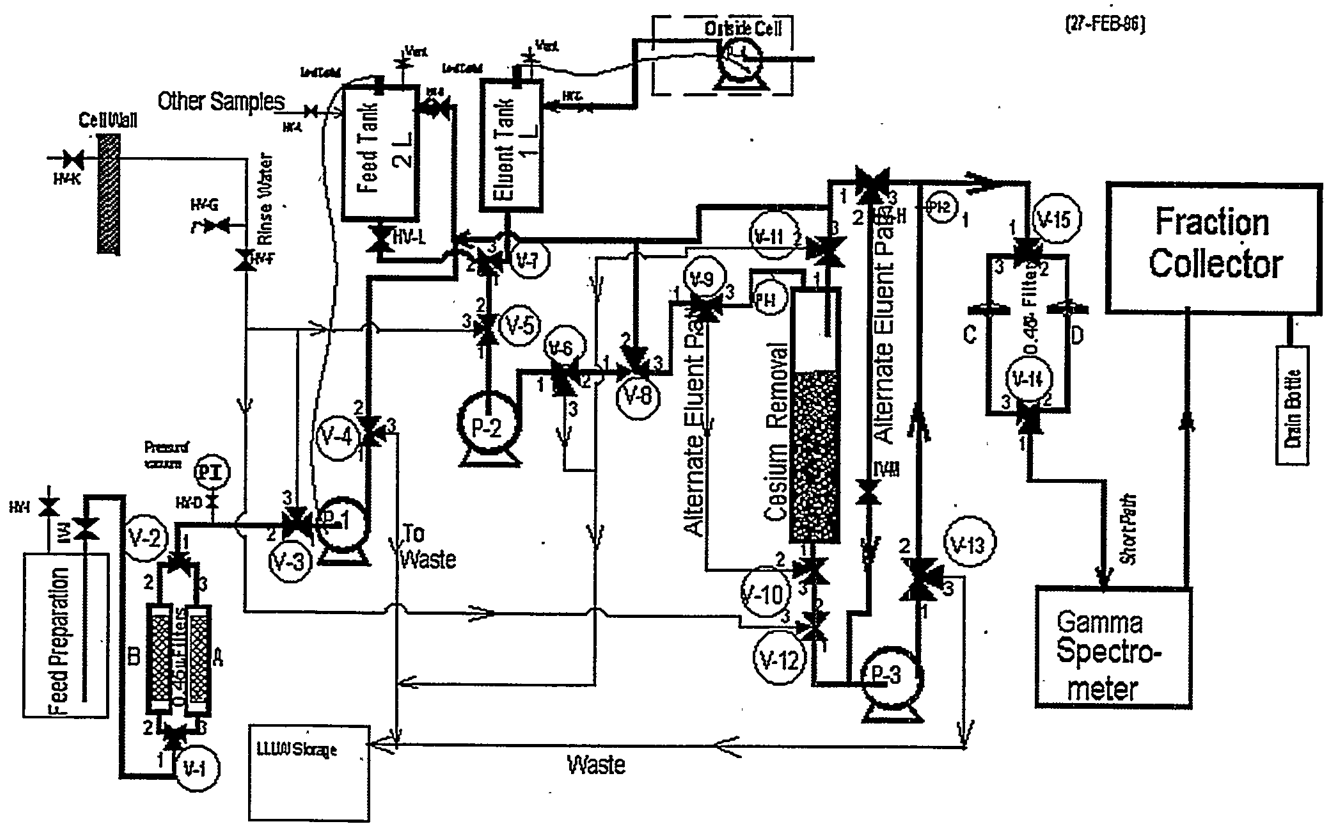

Figure 1. ORNL cesium removal system flow diagram

cesium from actual radioactive storage tank supernatant. The sorbents are tested using a 1.5- x 15-cm column containing about 10 to 12 cm^3 of sorbent at flow rates of 3 to 9 column volumes (CV) per hour. Other sorbent-containing apparatus such as 3M WEB and AEA Technology's EIX rig can also be connected easily into the system. Cesium breakthrough from the sorbent is followed by an online gamma-spectrometer; the effluent is also fractionated for chemical and radiological analyses. Sorbents that can be eluted and regenerated are cycled in place through loading, elution, and regeneration. Sorbents can also be analyzed by removal from the cell and counting on another gamma-spectrometer to determine the total loading and/or the efficiency of elution.

The MVST W-27 supernatant used for the cesium absorber tests was originally at pH 7.4, but was adjusted back to the pH levels in other tanks (about pH 12.5 to 13.3) by adding sodium hydroxide pellets. For tests to simulate some conditions at other DOE sites, the pH was increased to 14, and additional cold Cs nitrate was added to give a total Cs concentration seven to ten times the original concentration. The supernatant chosen for the CsRD was prepared by adding 50% caustic solution to tank W-27, settling for 2 weeks, and then pumping approximately 83,000 L to tank W-29 to mix with the supernatant heel still present after previous operations with W-29. The mixed W-29 was settled for 1 month, and then sampled for the CsRD qualification tests.

The supernatant pH was adjusted to 13.3, and settled and filtered. It contained about 3.2 x 10^5 Bq ^{137}Cs/mL, 7.1 x 10^{-6} *M* total Cs, about 0.26 *M* potassium, 4.7 *M* sodium, and 5.2 *M* nitrate. When adjusted to 1 *N* hydroxide (pH 14) it contained 3.4 x 10^5 Bq ^{137}Cs/mL, 1.0 x 10^{-5} *M* total Cs, 0.31 *M* potassium, and 5.52 *M* sodium, and with the Cs added had 7.5 x 10^{-5} *M* total Cs. The W-29 supernatant contained 4.15 *M* sodium, 0.38 *M* potassium, 4.6 x 10^5 Bq ^{137}Cs/mL, 4.3 x 10^{-6} *M* total Cs, 4.0 *M* nitrate, 0.44 *M* nitrite, and a pH of 12.68. Measured compositions are given in Table 1. The ^{137}Cs in MVST supernatants is one to two

Table 1. Analyses of the MVST W-27 and W-29 supernatants

	MVST W-27 (pH 13.3)	MVST W-27 (pH 14.02)	MVST W-29 (pH 12.68)
Radiochemicals	**Bq/mL**	**Bq/mL**	**Bq/mL**
^{60}Co	680	330	500
^{137}Cs	320,000	340,000	460,000
^{134}Cs	1400	920	7600
^{90}Sr	65,000	31,000	4100
^{99}Tc	270		342
Gross Alpha	0.9	0.4	30
Gross Beta	525,000	430,000	550,000
Cations/Anions	**mg/L**	**mg/L**	**mg/L**
Al	0.847	<0.146	4.17
As	0.0089	<0.250	<2.5e-1
Ba	8.04	5.61	0.865
Ca	89.1	3.1	1.42
Cd	0.22	<0.11	0.24
Cr	2.96	3.49	3.44
Cs	0.935	9.95	0.58
Cu	<0.0319	0.15	0.07
Hg	0.09	0.117	0.258
K	10,300	12,000	14,700
Na	113,000	127,000	95,400
Ni	1.22	0.73	1.04
Pb	0.0092	<10	2.89
Rb	1.1	2.06	1.28
Si		29.3	44.1
Sr		26.3	1.65
U	<1.0	0.495	13.3
Zn	0.473	<0.148	1.35
Br	288	<50.0	
Cl	3180	2960	3050
NO_3		2720	20,400
NO_3	322,000	298,000	250,000
SO_4	1540	1380	15,506
TIC, mg/L		300	980
TOC, mg/L		390	500
Density	1.27	1.3	1.233
TDS, mg/L		79,000	81,000
TS, mg/L		580,000	390,000
TSS, mg/L		500,000	310,000
Na/Cs	701,451	12,764	164,483
K/Cs	37,446	1206	25,345
Total Anion *M*	5.3897	6.0063	4.4754
Total Cation *M*	5.1983	5.832	4.5256
Difference	0.1914	0.1743	-0.0503

orders of magnitude less than that contained in some Hanford tank supernatants. The Cs level with cold Cs added approximates the values for Hanford tanks 101-SY and 103-SY (7 x 10^{-5} *M*) and also to the double-shell slurry feed simulant. The high Cs feed has an Na to Cs molar ratio of about 7.4 x 10^4 and a Na to K ratio of 18.

Accomplishments

Installation of the experimental equipment in the hot cell, development of the procedures used, and several sorbent tests were completed in FY 1995 and FY 1996. Six different sorbents and resins were recommended by the ESP-CP based on previous screening tests at Hanford, Sandia, Los Alamos, Savannah River, and Oak Ridge. Each was tested in continuous loading tests using W-27 supernatant at pH 13.3 and 7 x 10^{-6} *M* Cs and/or pH 14.0 and 7.5 x 10^{-5} *M* Cs. Included were 1) two different lots of resorcinol-formaldehyde (R-F) resin made by Boulder Scientific; 2) IBC Advanced Technologies' SuperLig®644C, batch 3695-GM1121; 3) Rohm & Haas CS-100 resin; 4) 3M SLIG WWL 644 WEB with SuperLig®644C imbedded; 5) granular CSTs developed by Sandia National Laboratories/Texas A&M University and supplied by UOP as IONSIV® IE-911 (Lots 07398-38B, 999096810001, and 99909610003); and 6) Eichrom Industries' granular potassium cobalt hexacyanoferrate (KCoFeC). A set of tests was completed using AEA Technology's EIX process for electrochemical elution using R-F resin and W-27 supernatant.

We provided direct input to the CsRD project for sorbent selection. The CSTs were recommended for the project based on the best CV at 50% breakthrough, best test-to-test consistency, and the fewest operational difficulties using the MVST W-27 supernatant. We also helped select the supernatant for the CsRD, provided the qualification tests for the supernatant and sorbent, and provided ^{137}Cs-loaded CST sorbent for waste acceptance criteria testing and for waste form development testing.

Experimental Results

3M SLIG WWL 644 WEB. 3M's SLIG WWL 644 WEB with SuperLig®644-imbedded material was contained in a Gelman 25-mm inline stainless-steel filter holder with filter volume (FV) of 1.29 mL. The apparatus was loaded at 1 mL/min (49.78 FV/h) in an upflow through one loading/elution/regeneration cycle. Brown color left the WEB filter for several FV after the supernatant feed began. Loading was 65 FV to 50% breakthrough. The filter was eluted with 0.5 *N* HNO_3 and regenerated with caustic solution.

Eichrom KCoFeC. Eichrom Industries' KCoFeC granular sorbent was 7.272 g of lot number JW-40-021 loaded at 9 CV/h using W-27 supernatant at pH 13.32. Normal column operation with low Cs breakthrough continued for over 250 CV, but then the sorbent began to disintegrate and the Cs level in the effluent rose rapidly and could not be filtered out using 0.2-mm filters.

SuperLig®644C. IBC's SuperLig®644C was run at 6 CV/h using 3.779 g of dry resin (11.2-mL volume) using W-27 supernatant at both pH 13.3 (Figure 2). A considerable amount of color was left with the initial few CV of feed through the column. After the breakthrough had reached 50% at about 100 CV, the loaded Cs was eluted with 0.5 *N* HNO_3 at 3 CV/h. Colored liquid also accompanied the first few CV of acid. The elution curve was very sharp and was 95% complete in 6 CV. The resin has a very low density and could be compressed easily (30% or greater), so calculations were adjusted for the smaller CV due to compression, giving a revised 50% breakthrough of about 138 CV.

SuperLig®644C was loaded with pH 14.0 MVST W-27 supernatant using a special weighted bed follower, developed by J. L. Collins at ORNL, to compact the bed (Figure 3). Loading was at 3.5 CV/h, elution used 0.5 *N* HNO_3, and regeneration used 2 *N* NaOH. The first cycle had a total Cs concentration of 1.1 x 10^{-5} *M* in the feed, and the following three had 7.5 x 10^{-5} *M* Cs. The bed volume changed by 40% to 50% when switching from feed to deionized water to acid and then caustic and feed. The first loading had 50% breakthrough at about 167 CV. Elution was complete in about 6 CV of 0.5 *N* HNO_3. The next three loadings (high Cs) and 50% breakthroughs occurred at 77, 65, and 50 CV respectively, while initial breakthrough of the cesium was less than 10 CV for all three. Two of the loading curves were approximately parallel to the first curve, while the fourth was completely different. Color was seen at the start of each loading and at each regeneration.

R-F Resin. Boulder Scientific's R-F resin was prepared and used in three tests with W-27 supernatant at pH 13.3 (see Figure 2). At 7 CV/h 50% Cs breakthrough occurred at 45 CV. At 2.9 CV/h, the 50% breakthrough was at 36 CV,

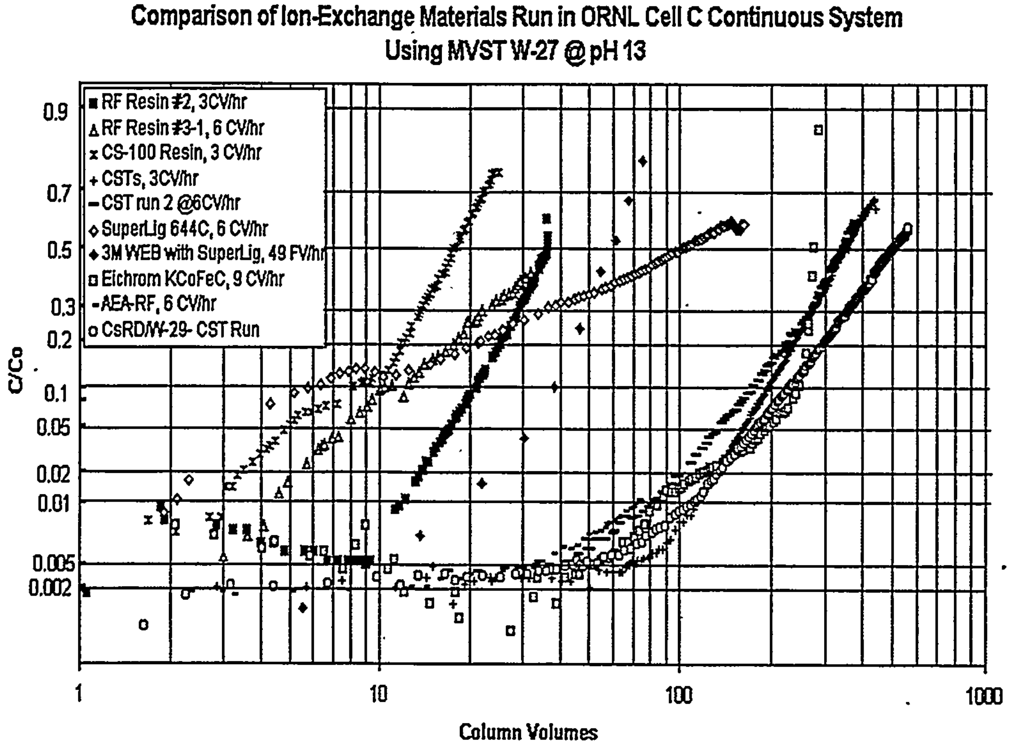

Figure 2. Loading curves for ORNL-tested cesium sorbents at pH 13.3 using MVST W-27

and the shape of the curve was similar to but steeper than that in the 7 CV/h R-F run. In the third test, R-F resin was loaded, eluted, regenerated, and then rinsed five times at 6.0 CV/h. For the first 3 to 4 CV of feed or regenerant through the bed, brown liquid exited the bed. The 50% breakthroughs were consistent at about 45 to 50 CV, but some operational problems began to develop during the last two loadings. Elution was completed with 0.5 *M* HNO_3 at about 3 CV/h, and the resin volume shrank from about 10 cm^3 to about 5.5 cm^3. Approximately 9 to 12 CV were required for Cs elution to be essentially complete.

Additional R-F resin was obtained from the ORNL Radiochemical Engineering and Development Center and loaded with pH 14.0 W-27 supernatant feed containing 1×10^{-5} *M* Cs at 3.5 CV/h to 70% breakthrough (see Figure 3). A weighted bed follower was also used. Cesium initially broke through at 7 CV, and then the curve was very steep to 50% at about 18 CV. The elution was with 0.5 *N* HNO_3.

A third R-F resin obtained from AEA Technologies (BSC 187) was used with the pH 13.3 W-27 supernatant at a feed rate of 6 CV/h (see Figure 2). The loading was continued through 75 CV with the breakthrough only reaching about 1.1 to 1.2%. The loading curve shows that the initial breakthrough did not occur until 15 CV, and then the curve was very shallow to 1% at about 65 CV. The brown color was also seen.

Crystalline Silicotitanates. CSTs from UOP, IONSIV® IE-911 Lot 07398-38B, were first tested at 3 CV/h in downflow using pH 13.3 W-27 supernatant for a total of more than 435 CV (see Figure 2) . No problems that could be attributed to the ion exchanger occurred during the continuous run of more than 6 days (24 h/day). The 1% breakthrough came after 100 CV, 10% breakthrough at about 190 CV, and 50% breakthrough at 350 CV. At 6 CV/h feed rate, the 50% Cs breakthrough was very close to that obtained at 3 CV/h at 340 CV. No difficulties with the system were observed during either loading.

CST-38B was next loaded at 6 CV/h with W-27 supernatant at pH 14.0 and a Cs concentration of 7.48×10^{-5} *M* to greater than 55% breakthrough (see Figure 3). The loading curve was parallel to the previous 6 CV/h curve, as expected, with the 50% breakthrough occurring at 272 CV (about 79% of the breakthrough for feed with lower Cs and hydroxide), the 10% breakthrough at 122 CV, and the

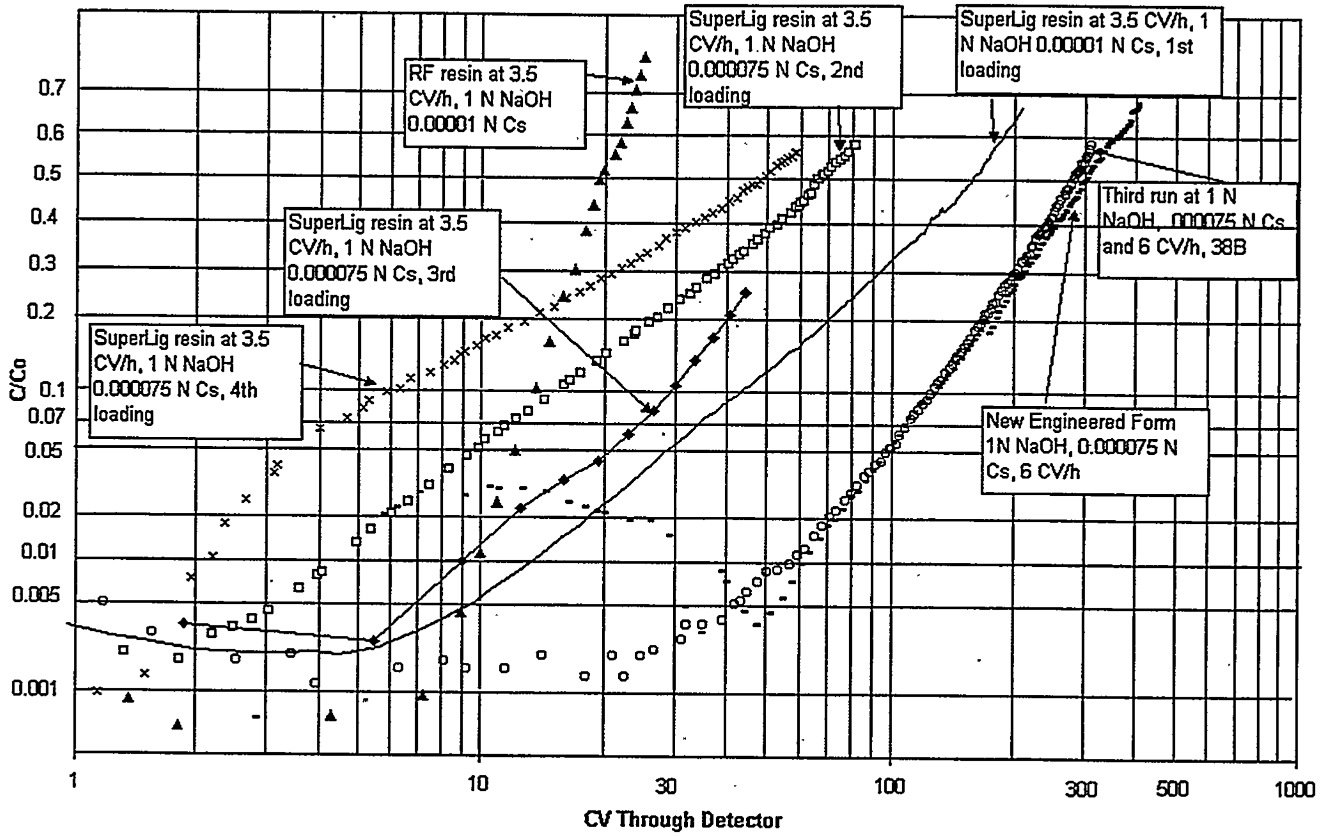

Figure 3. Loading curves using MVST W-27 feed adjusted to pH 14

1% breakthrough at 55 CV. Again, no difficulties were observed during operation.

UOP IONSIV®IE-911 (Lot 999096810001). IONSIV® IE-911 (Lot 999096810001), the production engineered form of the CSTs, was loaded in a repeat of the previous run using the pH 14 high-Cs feed at 6 CV/h (see Figure 3); however, lower Cs concentration feed was used in the last 150 CV. The sorbent was treated to remove fines, because the CST was fairly dusty, and the water was milky after first contact. Initial flow stabilization problems caused an erratic startup, but once flow was stabilized, the breakthrough curve returned to the level of background before starting the normal increase. The 50% breakthrough was 294 CV, the 10% breakthrough was 127 CV, and the 1% breakthrough was about 61 CV. This was about 3% to 10% better than the -38 B at the above breakthrough points. Because this CST is about 10% less dense than the -38 B material, the performance per mass of sorbent is roughly 10 to 20% better. No difficulties with the system were observed during operation, but the pH of the supernatant was reduced by the CST as it passed through the column for the first 100 CV. This is important to note if the supernatant contains any soluble aluminum that could precipitate in and on the bed if the pH drops even slightly.

IONSIV® IE-911, Lot 99909681003, and MVST W-29 Supernatant. For the CsRD qualification of IONSIV® IE-911, Lot 99909681003, and MVST W-29 supernatant, the CST was pretreated to pH 12.6 with caustic and then fluidized to remove fines using a simulant containing 4.5 *M* $NaNO_3$ and 0.1 *N* NaOH. The W-29 supernatant was sampled from the tank and then placed in the cell. The loading continued at 6 CV/h for 560 CV with a minor upset after 50 CV, but was completed uneventfully during the next 500 CV. Data for the different cesium analyses give 50% breakthroughs of 503.7 CV to 546.2 CV for ^{137}Cs analyses. The analyses showed that the CST loaded Ba, Ca, Cs, gross alpha and beta, ^{90}Sr, U, and Zn, but not Hg, Cd, ^{99}Tc, Cr, ^{106}Ru, Rb, Ni, Na, K, and Al. The increase in CV to 50% for the comparable CST runs with W-27 and W-29 was about 345 to 505 CV or a 45% increase, as a result of lower total Cs, lower nitrate, and lower pH in the W-29. The apparent breakthroughs for the U, ^{90}Sr, and Pb were 433 CV, 1164 CV, and 3327 CV, respectively. Sorbent from the loaded column was subjected to a modified TCLP procedure and showed no unacceptable values.

Results

Comparison of the column data for all sorbents with the W-27 feed to data obtained using simulant and actual supernatants at other sites showed good agreement and predictability from batch equilibrium to column testing, except for R-F resin, which varied greatly batch to batch. Further comparisons must take into account not only Cs concentrations, but the pH, the other anions and cations in the supernatant, and the ratios of other cations to the cesium concentration.

These comparative evaluations helped provide critical data for the selection of the sorbent for the CsRD, as well as data applicable to other DOE sites.

In addition to the Cs removal capacity of the materials tested, the operational characteristics during continuous loading experiments were monitored. The organic sorbents R-F, SuperLig®, and the 3M SLIG 644 WWL WEB materials all produced colored products when the feed was first introduced or during regeneration after elution. They also exhibited volume changes during various stages of the preparation, loading, elution, and regeneration. The high pH of the feed supernatant to the Eichrom KCoFeC resulted in its chemical breakdown and loss in the column effluent. No operational problems were noted for the CSTs.

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

Timothy L. Hubler, Pacific Northwest National Laboratory[1]

EM Focus Area: high-level waste tank remediation

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 by a relatively low-cost method. This particular tank pretreatment need may be met using the appropriate ion-exchange technology and materials.

Task Description

The goal of this task is to develop modified resorcinol-formaldehyde (R-F) resin to improve the chemical/oxidative stability of the resin. R-F resin is a regenerable organic ion-exchange resin that is selective for cesium ion in highly alkaline, high ionic-strength solutions. R-F resin tends to undergo chemical degradation, reducing its ability to remove cesium ion from waste solutions; the mechanistic details of these decomposition reactions are currently unknown. The approach used for this task is chemical modification of the resin structure, particularly the resorcinol ring unit of the polymer resin. This approach is based on prior characterization studies conducted at Pacific Northwest National Laboratory (PNNL) that indicated the facile chemical degradation of the resin is oxidation of the resorcinol ring to the *para*-quinone structure, with subsequent loss of ion-exchange sites for cesium ion. R-F resin represents an important alternative to current radiocesium remediation technology for tank wastes at both the Hanford and Savannah River sites, particularly if regenerable resins are needed.

Benefits to DOE/EM

This work will aid in development of 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.

Organic ion-exchange materials may have a significant impact on environmental remediation efforts at DOE sites because 1) they are regenerable materials, and thus reduce 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 Technology Center
Boulder Scientific Company
University of Idaho

Scientific Background

Phenolic condensation resins have been used effectively for selective ion-exchange separations of alkali metal ions for decades. Two such resins, Duolite™ CS-100 and R-F resin, have been considered for use in removal of radioactive cesium from tank wastes at Hanford. In comparisons of the two resins, R-F resin had significantly better performance for cesium removal compared to CS-100, as determined through column testing and batch distribution coefficients (K_ds).[1,2] However, R-F resin was subject to chemical oxidation that resulted in significant decline in cesium ion-exchange performance, while CS-100 had low but fairly consistent performance during an equivalent number of loading/eluting cycles. The contrasting characteristics of the two chemically and structurally similar materials presented the possibility to solve the chemical stability problems of R-F resin through an understanding of structure and function for the two resins.

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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.

Structure/function studies for R-F resin were initiated at PNNL under the Advanced Processing Technology Initiative in FY 1994. These studies undertook 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. Solid-state ^{13}C 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. 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. 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.

The effects of oxidation on R-F resins were elucidated by correlation of ^{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, and the number of ring hydroxyl groups (the sites at which ion-exchange occurs) decreases.

Preparation and characterization of modified condensation polymers using either phenol or resorcinol provided additional clues to the observed performance and chemical stabilities of both R-F and phenol-formaldehyde (P-F, or CS-100 type) resin. The polymer resins were modified by incorporation of fluorophenols and hydroxybenzoic acids into the polymer matrix. The results led to an understanding of the observed structure/performance characteristics of P-F resin in relation to R-F resin. Both the R-F and P-F polymer resins were found to be structurally similar with crosslinks in the 2- and 4- positions of the aromatic ring.

NMR spectroscopic studies correlated with K_ds indicated that R-F resin undergoes facile oxidation to form *p*-quinone structures (Figure 1). The K_ds obtained for the P-F resins were of much smaller magnitude than theoretical estimates because many of the ring hydroxyl groups were found to be etherified during resin preparation, thus rendering those ion-exchange sites nonfunctional (Figure 2). Therefore, the R-F resin has higher performance compared to P-F resin because it has a much higher capacity, assuming the mode of cesium ion selectivity for the two resins is the same. This is a reasonable assumption based on the similarity of the materials. The R-F resin does not undergo significant etherification of the ring hydroxy groups during resin synthesis because of differences in the electronic characteristics of resorcinol in comparison to phenol (i.e., resorcinol has greater electron density delocalized in the ring structure compared to phenol). However, the greater electron density of the resorcinol ring has the unwanted effect of making the resin more susceptible to oxidation, thus creating eventual loss of R-F resin's initially high performance for cesium sorption.

Technical Approach

The more facile chemical oxidation of the aromatic ring in R-F polymer resins occurs as a result of greater ring activation, which is related to the substituents on the aromatic ring. Hence modification of the aromatic ring in the appropriate positions is the approach used in this study to enhance the chemical/oxidative stability of the R-F resin. The technical approach included 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. Two substituents,

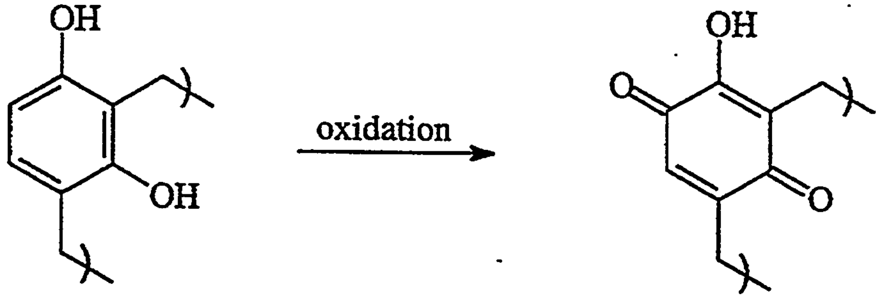

Figure 1. Oxidation of R-F resin gives p-quinones and loss of ion-exchange groups

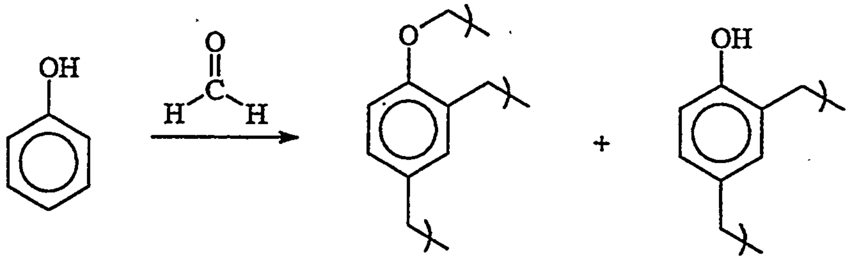

Figure 2. P-F resin undergoes extensive etherification and loss of ion-exchange sites during synthesis

methyl and fluorine, have been the focus of study during FY 1996. The most simple alkyl group, and the one least likely to have unwanted steric effects, is the methyl group. The fluorine group was chosen for study because of its high electronegativity and the potential of the strong carbon fluorine bond as a guard against ring oxidation.

Accomplishments

The starting materials for the polymer resins were prepared according to literature procedures. The 4-methylresorcinol was prepared by a hydrolysis reaction of 2,4-diaminotoluene with ammonium bisulfate[3] in a 2-gal inconel autoclave, which was equipped with a glass liner, Teflon-lined thermowell, and thermocouple. Literature routes for preparation of 4-fluororesorcinol involve use of highly reactive electrophilic fluorinating agents such as fluoroxytrifluoromethane (CF_3OF)[4] and cesium fluoroxysulfate ($CsSO_4F$).[5] We collaborated with fluorine researchers at the University of Idaho to examine alternative routes to 4-fluororesorcinol and to aid in the synthesis should it be necessary to use the literature routes. The major goal of their work was to find reagents that could be safely and easily handled using standard benchtop procedures rather than the specialized equipment required for fluorine syntheses. This research found alternative routes to 4-fluororesorcinol using a new electrophilic fluorinating agent, Selectfluor™, which is sold and distributed by Air Products and Chemicals, Inc. (Allentown, PA). The reaction (Figure 3) is run at 5°C in a benchtop procedure and the reagent is easily weighed and handled in the air. Separation of the two products from the reaction continues to be challenging, but can probably be solved with preparative HPLC technology.

Resins were prepared from reaction of formaldehyde with 4-methylresorcinol. The polymer strands appear to be less highly crosslinked as underivatized R-F resin. The methyl group may be sterically hindering the polymerization of the compound, as NMR evidence suggests formation of the methylol groups in the ring positions expected. Currently, a suitable sample for K_d analysis has not been obtained with 4-methylresorcinol.

A resin prepared from 4-fluororesorcinol/phenol (85%/15%) with formaldehyde appeared to be very stable to 2 *M* NaOH. The phenol was added to boost the crosslinking in the polymer at a modest potential cost to capacity. This material does not yet have the performance (K_d is 85 mL/g) to make it a viable alternative to R-F resin. Further analysis suggests that 80% of the fluorine on the resorcinol ring is displaced as fluoride ion during synthesis under alkaline conditions. Refinement of the synthetic approaches used for preparation of the derivatized resins will likely be needed to obtain the more robust resins. Other potential approaches may include an entirely new synthetic scheme using the same starting materials or preparation of resins using crosslinking agents such as phenol to aid crosslinking and chemical stability.

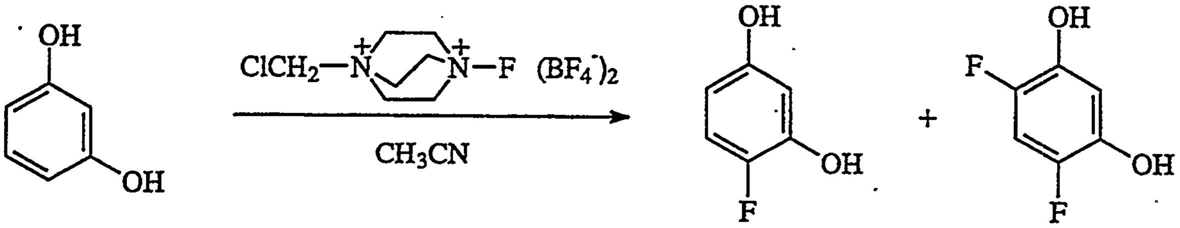

Figure 3. Facile preparation of 4-fluororesorcinol using Selectfluor™

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TTP Number RL36C343

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

Calvin H. Delegard, Pacific Northwest National Laboratory

EM Focus Area: high-level waste tank remediation

Technology Need

Isolating the transuranium elements (TRUs) and technetium (and other radionuclides) to a low-volume, high-level waste (HLW) fraction is a primary goal of Hanford Site tank waste processing (pretreatment). To perform the required separations of TRUs and technetium, fundamental understanding of their chemistries in alkaline media is required. Few predictive data on their behaviors and distributions (to the solid or solution phases) under existing Hanford Site tank conditions were available before the work of the Institute of Physical Chemistry of the Russian Academy of Sciences (IPC/RAS).

In addition, process methods must be developed to direct the TRUs and technetium to the HLW fraction in future waste processing operations. Data also are required on the distribution of plutonium in tank waste sludge for criticality safety in waste storage and processing.

Technology Description

DOE has engaged the IPC/RAS to study the fundamental and applied chemistry of the transuranium actinide elements (primarily neptunium, plutonium, and americium) and technetium in alkaline media. This work is supported by DOE because the alkaline radioactive wastes stored in underground tanks at DOE sites (Hanford, Savannah River, and Oak Ridge) contain TRUs and technetium, and these radioelements must be partitioned to the HLW fraction in planned waste processing operations. The chemistries of the TRUs and technetium are not well developed in this system.

Previous studies at the IPC/RAS centered on the fundamental chemistry of the TRUs and technetium in alkaline media, and on their coprecipitation reactions. During FY 1996, further studies of fundamental and candidate process chemistries were pursued with continuing effort on coprecipitation.

The technical liaison was established at Westinghouse Hanford Company to provide information to the IPC/RAS on the Hanford Site waste system, define and refine the work scope, publish IPC/RAS reports in open literature documents and presentations, provide essential materials and equipment to the IPC/RAS, compare IPC/RAS results with results from other sources, and test chemical reactions or processes proposed by the IPC/RAS with actual Hanford Site tank waste. The liaison task was transferred to the Pacific Northwest National Laboratory (PNNL) in October 1996.

Benefit to DOE/EM

Fundamental knowledge of the chemical behavior of the actinides and technetium in alkaline media is essential to the successful design and operation of the pretreatment processes used to segregate the low activity and high-level fractions of the 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 studies.

Results to date from the IPC/RAS show the solubilities of the actinides and technetium are strongly dependent on oxidation state and can be successfully altered by various common chemical oxidants and reductants. Oxidation states can also be changed by radiation-chemical reactions and are affected further by the presence of waste components in the radiation field. Solution decontamination by coprecipitation using the method of reappearing reagents (MAR) for both plutonium and neptunium has shown promising results.

Technology Transfer/Collaborations

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

Scientific Background

Neptunium, plutonium, americium, and technetium are elements having multiple oxidation states available in aqueous solution. In general, the lower oxidation states of these elements [(III) or (IV)] form oxides or hydrous oxides of low solubility in alkaline solution, while the higher oxidation states [(V), (VI), or (VII) for the TRUs and (VII) for technetium] give oxyanion salts of appreciable solubility, especially in highly alkaline solution.

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

Technical Approach

Laboratory studies at the IPC/RAS initially focused on the solubility, redox reactions, radiolysis effects, and coprecipitation of the TRUs and technetium in highly alkaline media. Subsequent studies continued the investigation of coprecipitation and other methods to remove these radioelements from alkaline waste. Studies are planned to expand this original work as well as investigate the behavior of plutonium in tank waste sludge.

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 are verified by comparison with published data as well as tests with genuine wastes available at the Hanford Site. Results from the IPC/RAS and Hanford Site studies are disseminated in technical publications and presentations.

Accomplishments

During FY 1994, the IPC/RAS prepared a technical literature review of the chemistry of the TRUs and technetium in alkaline media. This review was edited and published by the liaison as a Westinghouse Hanford Company document in FY 1995.

Four areas in the chemistries of the TRUs and technetium were investigated by the IPC/RAS in FY 1995:

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

Technical reports on the four tasks were written by the IPC/RAS scientists and published as Westinghouse Hanford Company documents in FY 1996. Brief summaries of the principal results follow.

Solubility

Knowledge of compound solubility is essential to predict the distribution of the TRUs and technetium to solid and solution phases in radioactive tank wastes. Initial divisions of the low activity and HLW fractions in tank waste treatment will be made using simple solid-liquid separation techniques (settling, centrifugation, filtration). However, if the solubility of a given radioelement is above the regulatory limit and enough radioelement is available, the solution phase will remain high level despite separation. The regulatory limit for the TRUs is 100 nCi/g of waste (the TRU limit). Because of the different half-lives of the significant isotopes of neptunium, plutonium, and americium, the respective TRU limits are about 7×10^{-4} *M*, 7×10^{-6} *M*, and 1.7×10^{-7} *M*.

The solubilities of neptunium, plutonium, and americium hydrous oxides and salts in sodium hydroxide (NaOH) solution as functions of NaOH concentration and element oxidation state were determined in studies at the IPC/RAS and at the Hanford Site.[1] The results are shown in Figure 1 with respect to the relevant TRU limits for these three radioelements.

Within a given element, solubility increases with increasing oxidation state. Solubilities of the three elements are comparable for a given oxidation state and sodium

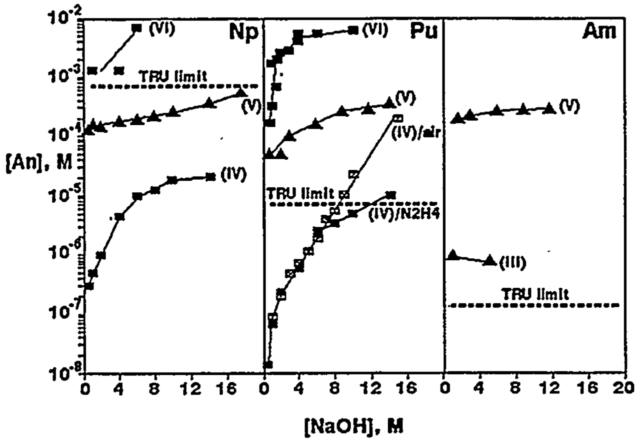

Figure 1. Solubilities of actinide compounds precipitating in sodium hydroxide solutions as functions of oxidation states and sodium hydroxide concentrations

hydroxide concentration. Neptunium exceeds the TRU limit in the (VI) state, approaches the limit in the (V) state, and is well below the TRU limit in the (IV) state. Plutonium solubilities remain near or below the TRU limit in the (IV) state, provided hydrazine (N_2H_4) holding reductant is present. In aerated solution, and above about 8 *M* NaOH, the Pu(IV) compound solubility exceeds the TRU limit because of oxidation of the dissolved plutonium to the (V) state. The TRU limit is exceeded for plutonium in the (V) and (VI) states at all NaOH concentrations studied. Americium exceeds the TRU limit about five-fold in the (III) state but exceeds the limit a thousand-fold in the (V) state.

Technetium(IV) and (V) solubility measurements are very sensitive to air oxidation. Solubilities measured in the presence of hydrazine range from $10^{-5.3}$ to $10^{-3.3}$ *M*. However, the solubility can be decreased significantly by other methods; electrodeposited Tc(IV) hydrated oxide has a solubility of $10^{-6.2}$ *M* in 4 *M* NaOH.

Oxidation/Reduction

As shown, oxidation state is very influential in establishing the solubilities of selected radioelements. Chemically reducing conditions strongly decrease the solubilities and thus favor partition of these elements to the solid (high-level) phase. On the other hand, if solubilization is desired, oxidizing conditions are required.

Oxidation/reduction reaction studies at the IPC/RAS elucidated the effects of likely process oxidants and reductants on TRU and technetium oxidation state. The strength of the reducing conditions required to produce tetravalent TRUs and pentavalent technetium increased in the order americium < plutonium < neptunium < technetium. Only the strongest reductant tested, hydrazine, reduced Tc(VII) to (V) whereas hydrazine or dithionite reduced Np(V) and Pu(V) to their (IV) states and Am(V) to the (III) state. Other reductants were less effective.

Because atmospheric oxygen is ubiquitous, oxidations of neptunium, plutonium, and technetium solids in the (IV) and (V) oxidation states were studied for this oxidant. With air, negligible oxidation of Pu(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. Persulfate and ozone were the most effective oxidants studied.

Radiation-Chemical Reactions

The solubility and oxidation-reduction reactions studies showed that certain oxidants and reductants can stabilize selected actinide and technetium oxidation states and thus influence solubility. Ionizing radiation-chemical processes occurring in the tank waste also can affect oxidation state distribution by generating oxidants and reductants directly from water

$$H_2O \rightarrow e_{aq}, H, OH, H_2O_2, H_2, H^+, OH^-$$

or by secondary reactions of the water radiolysis products with waste solutes.

The radioactive tank waste at the Hanford Site contains about 1 Ci combined beta and gamma activity per liter of waste; the energy of the radioactive decay deposits almost entirely in the waste to yield radiolytic dose rates of about 60,000 Gray per year. Radiation-chemical studies performed at the IPC/RAS used gamma irradiation up to 58,000 Gray in aerated alkaline solution to investigate the behaviors of Np(V) and (VI), Pu(VI), and Tc(IV), (V), and (VI).

In general, reducing conditions were imposed by radiation treatment of alkaline solution. The reducing conditions were enhanced in the presence of nitrite or organic waste components. Alkaline solution with nitrate alone yielded oxidizing conditions, however. Radiation-chemical reduction of neptunium to produce the poorly soluble (IV) state was observed under selected conditions. Similarly, reduction of Tc(VII) by radiolysis occurred provided organic constituents (chelators, alcohols) were present.

Coprecipitation

Despite the low chemical solubilities of the actinides in alkaline solutions, radiologically significant concentrations can exist in the as-stored waste or in solutions generated during waste processing for disposal. Therefore, additional decontamination of waste solutions from actinides may be required. Of the possible actinide removal techniques available in alkaline solution (solvent extraction, sorption or ion exchange, electrolysis, precipitation), coprecipitation may be the simplest to implement because equipment and operations requirements are relatively modest.

Coprecipitation by the MAR was studied for neptunium and plutonium in the (V) and (VI) states. The MAR uses precipitating agents that initially are soluble in alkaline solution. Reductive or thermal decomposition of the soluble agent to form the precipitating solid then takes place. Homogeneous precipitation of the carrier occurs throughout the solution, capturing the trace radionuclides. 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 less successful (DFs of 5 to 20).

Tests to remove solubilized neptunium by sodium uranate were more promising. The soluble precursor, uranyl peroxide, decomposes by catalysis to form the sodium uranate carrier. Neptunium DFs were about 150, whereas plutonium DFs were about 500.

Current Investigations

Four tasks authorized in FY 1996 to investigate the chemistry of the TRUs and technetium are being completed:

- stability of Pu(V) in sodium hydroxide solution
- further investigation of coprecipitation including the effects of waste components
- oxidation of organic waste components and reduction of Np(V) mediated by catalysis
- fission product and technetium removal from alkaline media.

Reports on these tasks are being prepared by the IPC/RAS. Early results show:

- Pu(V) stability to disproportionation increases sharply as hydroxide concentration increases from 4 to 8 *M*.
- coprecipitation of Np(V) with Cr(III) hydroxide is enhanced significantly by use of V(IV) reductant
- catalytic oxidation of organic waste components has been demonstrated with the relatively mild hydroperoxide oxidant
- Tc(VII) removals from solution by reduction followed by sodium uranate coprecipitation are poor.

Reference

1. Delegard CH. 1987. “Solubility of $PuO_2 \cdot xH_2O$ in alkaline Hanford high-level waste solution.” *Radiochimica Acta* 41, 11-21.

Publications

Publications describing the IPC/RAS studies and liaison activities are listed at the end of this document. The primary IPC/RAS reports are also available directly on the Internet at www.hanford.gov/twrs/tech/treat.htm.

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TTP Number RL37C334

Advanced Separations at Savannah River Site

Major C. Thompson, Savannah River Technology Center

EM Focus Areas: high-level waste tank remediation; subsurface contaminants

Technology Need

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 (Cs, Sr, tritium, actinides) and hazardous components (polychlorinated biphenyls [PCBs], cyanide, metal ions).

Technology Description

This task provides testbeds for ESP-developed materials and technology using actual SRS waste streams. The work includes different SRS waste streams: high-level waste (HLW) solutions currently stored in underground tanks onsite, water recycled from the waste vitrification plant, groundwater and other aqueous streams contaminated with metal ions and radionuclides, and reactor basin water in excess facilities. Another part of this task is to provide a report on materials for Cs removal from aqueous solutions for use as a reference.

High-Level Waste

In FY 1996, SRS started up facilities to process HLW solutions and sludges. The solutions are treated to remove ^{137}Cs, ^{90}Sr, and the actinides to levels below Nuclear Regulatory Commission Class A low-level waste (LLW). The treated solutions are then grouted for near-surface storage onsite. The separated radionuclides are transferred for mixing with the sludge and vitrification in the Defense Waste Processing Facility (DWPF).

The current process for Cs removal from solution is precipitation with tetraphenyl borate (TPB). However, difficulties have been encountered with decomposition of excess TPB during processing, which has stopped processing of supernatant. Crystalline silicotitanate (CST) is being evaluated as a possible alternative/second-generation technology for Cs removal from supernatant. Strontium and the actinides are separated in the current process by adsorption on monosodium titanate (MST) powder. The MST powder from the existing vendor is made by hydrolysis of titanium isopropoxide, which leaves a residual amount of flammable isopropanol in the MST. The current vendor has been unable to meet all the specifications for particle size, which led to low filtration rates during solid/liquid separation. The vendor was also having problems meeting the decontamination factor specifications for Sr. Thus, an alternative material and vendor was needed to ensure process operability.

Liquid recycled from the vitrification plant also requires Cs separation. Cesium is in the recycle stream because some Cs 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 the HLW evaporators and return the concentrated solutions to the existing process for Cs removal. The CST material is a good candidate for removing the Cs and allowing the solutions to be evaporated in LLW evaporators or be sent for onsite disposal as LLW along with the decontaminated supernatant solutions resulting in lower costs and more efficient operation of the HLW facilities.

Technology Transfer/Collaboration

AlliedSignal, Inc., Des Plaines, Illinois
AquaEss, San Jose, California
Lawrence Berkeley National Laboratory
Berkeley, California
3M, St. Paul, Minnesota
UOP Molecular Sieves, Mt. Laurel, New Jersey

Technical Approach

Sodium titanate (NaTi) developed by AlliedSignal Company under ESP funding has been tested for Sr and actinide removal in the SRS process. AlliedSignal makes NaTi by a process that leaves no flammable compounds in the product. Several different NaTi samples (dry solids and slurries) were made by AlliedSignal and tested with simulant and actual waste solutions. The material for Sr removal must meet several specifications and constraints to be compatible with the SRS process: Sr decontamination factor (DF) ≥ 150; <1 wt% material <1 μm; <1 wt% >35.5 μm; removal of enough transuranics (TRU) to allow the waste to meet Waste Acceptance Criteria for onsite disposal as Saltstone; U and Pu loading low enough to avoid nuclear criticality concerns, and rapid solubility in 2 wt% oxalic acid so that the cross-flow filters can be chemically cleaned when the pores become plugged with solids. Five samples of NaTi were tested with simulant solutions. The last sample met all requirements except that 1.5 wt% material was <1 μm. The material gave a Sr DF of 260; TRU decontamination comparable to monosodium titanate, U loading higher than monosodium titanate with Pu loading the same, and rapid dissolution in oxalic acid.

Tests with two tank waste solutions (tanks 43H and 46H) resulted in low Sr DFs due to cross contamination of the treated solutions in the hot cells. The initial samples were low in Sr, so high DFs were not anticipated. The samples were reused and showed a DF of 39 ± 1 for Sr from Tank 43 H supernatant with significant interference from ^{106}Ru. Simulant tests using ^{85}Sr tracer gave DFs of 39 ± 8 for Tank 43H and 54 ± 12 for Tank 46H. The measured DFs for Th, U, Np, Pu, Am, and Cm are shown in Table 1.

Cross-flow filter tests with simulant solution showed that the filtration rate with AlliedSignal NaTi was 35% lower than the monosodium titanate from the current vendor. The lower rate was attributed to a lower average particle size of 3.10 μm for the AlliedSignal NaTi versus 17.2 μm for the monosodium titanate. Thus, increasing the particle size of NaTiO should produce a material that provides better overall performance than the currently available monosodium titanate.

Table 1. Actinide decontamination factors for sodium titanate with actual waste

Radionuclide	DF Tank 43H	DF Tank 46H
^{230}Th	nd	>11
^{235}U	1.4	0.6
^{237}Np	2.8	>20
^{239}Pu	3.6	1.6
^{243}Am	nd	>11
^{245}Cm	>36	nd

nd = none detected

Crystalline silicotitanate has the advantage of removing Cs, Sr, and TRUs on a single adsorbent. Batch application of CST powder could resolve the present problems; however, there is a limit to the amount of titanium dioxide soluble in the SRS glass. Tests with CST powder during FY 1995 showed that Cs would have to be removed in columns rather than in batch extractions, so an engineered form was required to attain adequate flow. Tests of Cs separation from SRS waste supernatant have been started with the engineered form of crystalline silicotitanate, IONSIV®IE-911 manufactured by UOP. The material tested was from experimental batch 38-B, a noncommercial material. Tests involved measurement of the batch K_d for Cs from simulant and actual waste solutions. The Cs K_d with simulant solution containing a total Na concentration of 5.6 *M* averaged 1500 ± 171 mL/g compared to 1100 ± 55 mL/g with SRS Tank 43H waste supernatant. Capacity measurements made with simulants give a capacity of 29 mg Cs per g of CST for average SRS waste supernatant solution. Potassium concentration has little effect on the Cs K_d or capacity. Calculations of waste processing rates and CST capacity for Cs indicate that the TiO_2 limit for SRS glass would not be exceeded. Column studies are needed to ensure that adequate Cs DF can be attained at practical processing rates.

Work started on determining a simulant composition and obtaining samples of actual DWPF recycle solution. The recycle stream is complex and highly variable because the solution contains not only the scrub and wash solutions from the offgas system in DWPF, but also waste solutions from the DWPF analytical laboratory. Work will start with K_d measurements on simulants followed by tests with actual waste solution. Ion exchange column tests are planned for mid-FY 1997.

Reactor Basin Water

Savannah River Site has five closed reactors with cooling basins containing about 3 million gallons of Cs-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 can also be contaminated with radionuclides and hazardous metals from agricultural application before plant construction. The R Reactor basin water contains PCBs, cyanide, Cs, and Sr 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- (RCRA-) 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 started to demonstrate an integrated system for water treatment at the R Reactor basin with cartridge filters made using 3M membrane technology. Samples of R basin water were sent to SRTC for analyses and laboratory tests of the activated carbon filters and the anion exchange resin for cyanide removal. Analyses showed that there was no cyanide present.The original analyses did not recognize possible interferences from other anions such as nitrate. Thus, a false indication was given for cyanide. Multiple attempts to analyze for cyanide by the EPA method and other methods failed to detect any cyanide.

Difficulties were encountered in PCB analyses at Savannah River Technology Center (SRTC), resulting in inconclusive results from the laboratory tests for PCB removal. Plant personnel have also reported variability in the concentration of PCBs from sample to sample. The initially reported values corresponded to the solubility of specific PCBs in water. Additional samples are being analyzed to determine the reason for sample variability which may be attributable to the presence or absence of PCB-bearing solids in the samples.

Plans are complete for an onsite test of a single activated carbon filter cartridge to determine its capacity for PCBs. The test will be done when problems with sample analysis variability are resolved.

The PADU used for removal of Cs and Sr at Hanford's N-Springs was transferred to SRTC for demonstration of the integrated system. The unit is being modified so the first two filtration modules are used for removal of PCBs with activated carbon filters followed by removal of Cs. The demonstration will be done at a flow rate of 5 gallons per minute, which will be the highest rate demonstrated thus far with the cartridge filters.

Contaminated Groundwater

The polymer pendant ligand ion exchange resins, PS-CATS and PS-SED, from the ESP-funded work of Richard Fish at Lawrence Berkeley National Laboratory, were tested by AquaEss Inc. with simulants of two RCRA metal-contaminated groundwaters at SRS.

Analyses of the two waters are shown in Table 2.

Table 2. SRS groundwater contaminated with RCRA metals

Metal Ion	Drinking Water (mg/L)	D-Area Water (mg/L)	DCB-4A (mg/L)
Al	None	806	48.3
Ca	None	251	94.9
Co	None	3.81	0.285
Cr	0.05*	0.89	0.025
Cu	1.3**	1.1	0.194
Fe	0.3*	2920	0.062
Mg	None	238	55.3
Mn	0.05*	63.3	4.08
Ni	0.50**	7.29	0.580
Pb	0.05*	2.27	0.162
Sr	None	1.43	0.589
Zn	5.0*	17.8	1.05
pH	6.5-8.5*	2.01	3.9

*40 CFR 141.11
**40 CFR 141.51

The D-Area water is a severe test for selectivity where Cr(III) removal without removal of significant Fe(III) or Al(III) is desired for environmental remediation. Resins have already been identified for most of the other metal ions such as lead and copper. The tests were made with 150 mL of resin in 1-in.-diameter columns at a flow rate of 37.5 column volumes (CV)/h.

The tests with D-Area groundwater resulted in almost immediate breakthrough of most metal ions with both resins. For PS-CATS resin, 50% breakthrough was reached within 3 CV for all metals except Pb and Sr. For PS-SED resin, 50% breakthrough was also reached within 5 CV for all metals except lead and copper. No copper breakthrough at all was seen until after 5 CV.

Selective removal of nickel was desired for the other groundwater, DCB-4A. The resins performed better with this water, however, neither resin was selective for nickel over the other metal ions. Both resins gave the same results with 50% breakthrough for all metals except aluminum within 37 CV and 50% breakthrough for aluminum in less than 100 CV.

The columns were eluted with 2% sulfuric acid. Elution volume was minimized by recirculation of acid through the column before rinsing with a small quantity of fresh acid. The columns were loaded and eluted three times with indications that the elution was not always complete.

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TTP Number SR16C342

Electrochemical Treatment of Liquid Wastes

David T. Hobbs, Savannah River Technology Center

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

Technology Need

A significant quantity of waste at Hanford and Savannah River (SR) sites contains nitrates, nitrites, organic compounds, radionuclides (e.g., ^{99}Tc and ^{106}Ru), and Resource Conservation and Recovery Act (RCRA) metals (e.g., chromium, cadmium, and mercury). Complexing agents in Hanford waste prevent the efficient separation of radionuclides. Organic compounds in both Hanford and SR site waste are highly flammable, making waste storage and evaporation risky.

Technology Description

Under this task, 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 technology targets the 1) destruction of nitrates, nitrites and organic compounds; 2) removal of radionuclides; and 3) removal of RCRA metals.

The development program consists of five major tasks: 1) evaluation of 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 reactor, and 5) analysis and evaluation of test data.

The development program team is comprised of individuals from national laboratories, academic institutions, and private industry. Possible benefits of this technology include: 1) improved radionuclide separation as a result of the removal of organic complexants, 2) reduction in the concentrations of hazardous and radioactive species in the waste (e.g., removal of nitrate, nitrite, mercury, chromium, cadmium, ^{99}Tc, and ^{106}Ru), 3) reduction in the size of the offgas handling equipment for the vitrification of low-level waste (LLW) by reducing the source of NO_x emissions, 4) recovery of chemicals of value (e.g., sodium hydroxide), and 5) reduction in the volume of waste requiring disposal.

Benefit to DOE/EM

Much of Hanford's waste 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. Destroying organic compounds in both Hanford and SR wastes also reduces flammability risks associated with waste storage and evaporation.

Nitrate and nitrite are two of the major hazardous species present in Hanford and SR HLW. After removing the bulk of radioactivity, the decontaminated salt solution will be disposed in a cement waste form referred to as Saltstone at the SR and in a borosilicate glass waste form at Hanford. Destruction of the nitrate and nitrite before disposing the decontaminated salt solution in Saltstone eliminates possible groundwater contamination from the 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 (NaOH) is the major liquid-phase product of the process. If the NaOH could be recovered and recycled, significant reduction in the quantity of waste requiring disposal would be realized. Onsite use of the recovered NaOH would include neutralization of fresh waste and as a corrosion inhibitor in the waste storage and evaporation facilities. Thus, the quantity of NaOH available for recovery and recycle would increase by converting the sodium nitrate and nitrite into NaOH.

Modern electrochemical reactor designs make it relatively simple to scale the treatment facility to the size of the waste stream by adding modular reactor units. Aqueous electrochemical processes operate at low temperature (≤90°C) and near atmospheric pressure in contrast to high-temperature and pressure processes that are 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 by the process.

Electrochemical removal of radionuclides and RCRA metals from the wastes would also be beneficial. For example, removal of ^{99}Tc from the SR 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 LLW forms into groundwater.

Technology Transfer/Collaborations

Electrochemical processes are used to produce a variety of industrial chemicals and to treat waste streams and wastewater before disposal and release to the environment. Thus, there is a extensive data base 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 occur in collaboration with private industry through Cooperative Research and Development Agreements or licensing agreements. In addition to the specific waste components evaluated, the technology developed in this program should also prove 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.

The task is managed by staff at Westinghouse Savannah River Company, with collaborations by researchers at the University of South Carolina, Pacific Northwest National Laboratory, and The Electrosynthesis Company, Inc.

Technical Approach

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 liquid phase.

Depending on the characteristics, the modified species may no longer be a hazardous substance or may easily separate from the liquid phase (e.g., gas or solid). For example, previous work showed that nitrate and nitrite 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 also demonstrated that organic compounds (e.g., ethylenediaminetetraacetic acid, citrate, acetate, formate, and oxalate) oxidized to carbon dioxide and water at the anode.

Accomplishments

- Demonstrated the destruction of nitrate and nitrite in radioactive SRS wastes with a bench-scale flow reactor (Figures 1 and 2).
- Demonstrated the destruction of organic compounds and nitrates/nitrites in radioactive Hanford wastes with a bench-scale flow reactor.
- Demonstrated the destruction of organic compounds and nitrates/nitrites in Hanford and SRS waste simulants with a commercial-scale electrochemical flow 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 SRS 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.

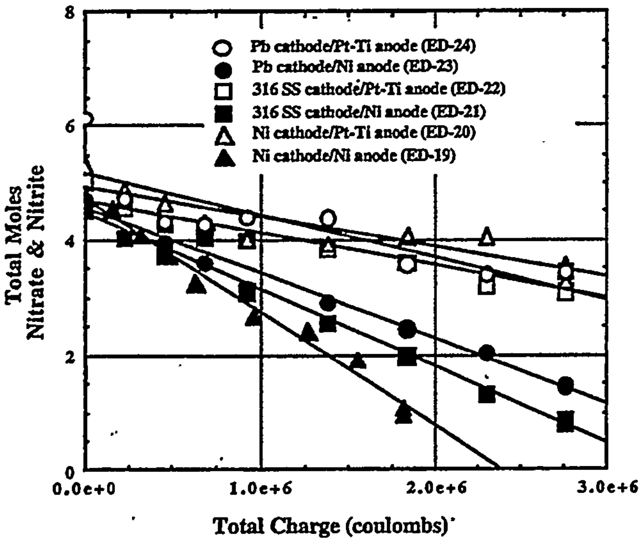

Figure 1. Change in the total moles of nitrate and nitrite in radioactive Savannah River waste with charge passed (batch test - undivided bench-scale electrochemical reactor with different cathode/anode combinations)

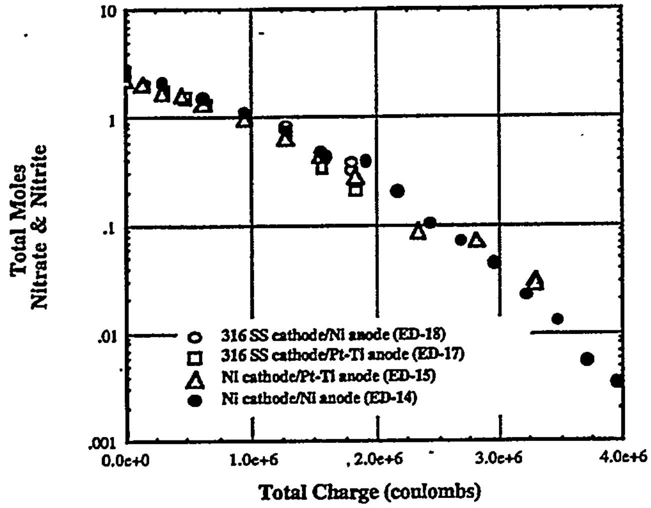

Figure 2. Change in the total moles of nitrate and nitrite in radioactive Savannah River waste with charge passed (batch test - divided bench-scale electrochemical reactor with different cathode/ anode combinations)

- Installed a pilot-scale testing facility at SR for non-radioactive simulant testing to support scale-up and design activities.
- Completed a preliminary conceptual design for an Electrochemical Denitration and Caustic Recovery (EDCR) facility for treating SR decontaminated salt solution (see Figure 3).

FY 1997 Work

During FY 1997, the following activities will occur: 1) complete cost evaluations for treating the SR decontaminated salt solution waste, 2) determine if SR High-Level Waste Division wishes to proceed with implementation of the technology, 3) resolve process control strategy and any problems with the evolution of ammonia/hydrogen, 4) review other work performed at Los Alamos National Laboratory and Lawrence Livermore National Laboratory, 5) conduct an independent review of nitrate destruction technologies, 6) determine feasibility of using porous electrode technology for chromate removal, and 7) determine feasibility of using electrochemical technology for the removal of technetium, other RCRA metals, and actinides from waste solutions.

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TTP Number SR16C341

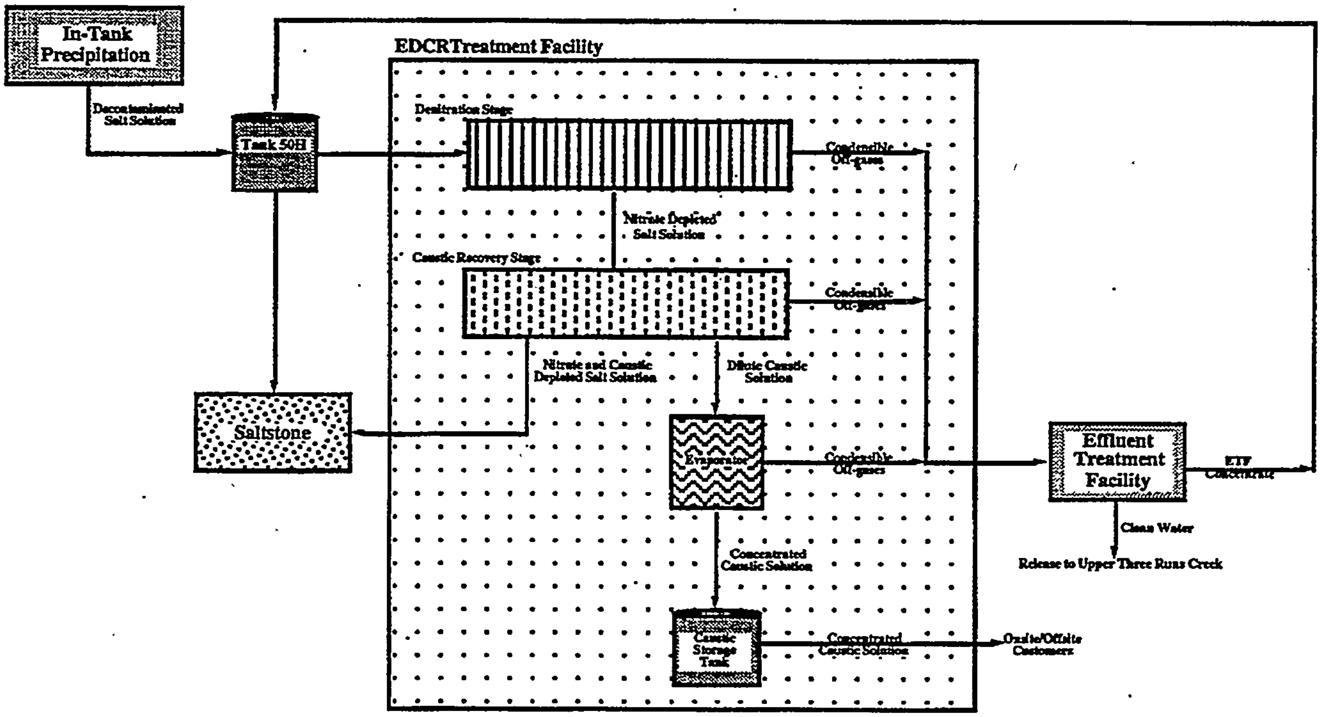

Figure 3. Schematic flow diagram for the electrochemical denitration and caustic recovery facility at SRS for treating decontaminated salt solution

Salt Splitting Using Ceramic Membranes

Dean E. Kurath, Pacific Northwest National Laboratory[1]

EM Focus Area: high-level waste tank remediation

Technology Need

Many radioactive aqueous wastes in the DOE complex have high concentrations of sodium that can negatively affect waste treatment and disposal operations. Sodium can decrease the durability of waste forms such as glass and is the primary contributor to large disposal volumes. Waste treatment processes such as cesium ion exchange, sludge washing, and calcination are made less efficient and more expensive because of the high sodium concentrations.

Some disposal strategies call for adding more sodium to the wastes as they are prepared for conversion to final waste forms. Separating and recycling sodium from the radioactive wastes can potentially reduce the costs by reducing waste disposal volumes, improving the efficiency of waste treatment processes, and avoiding the procurement of additional chemicals.

Technology Description

Pacific Northwest National Laboratory (PNNL) and Ceramatec Inc. (Salt Lake City UT) are developing an electrochemical salt splitting process based on inorganic ceramic sodium (Na), super-ionic conductor (NaSICON) membranes (Figure 1) that shows promise for mitigating the impact of sodium. In this process, the waste is added to the anode compartment, and an electrical potential is applied to the cell. This drives sodium ions through the membrane, but the membrane rejects most other cations (e.g., Sr^{+2}, Cs^{+}). The charge balance in the anode compartment is maintained by generating H^{+} from the electrolysis of water. The charge balance in the cathode is maintained by generating OH^{-}, either from the electrolysis of water or from oxygen and water using an oxygen cathode.

The normal gaseous products of the electrolysis of water are oxygen at the anode and hydrogen at the cathode. Potentially flammable gas mixtures can be prevented by providing adequate volumes of a sweep gas, using an alternative reductant or destruction of the hydrogen as it is generated. As H^{+} is generated in the anode compartment, the pH drops. The process may be operated with either an alkaline (pH >12) or an acidic anolyte (pH <1). Operation at the intermediate pH values is precluded by aluminum in the waste, which would precipitate as $Al(OH)_3$. Production of OH^{-} in the cathode compartment results in a rise in pH as the sodium hydroxide (NaOH) product is recovered.

Benefit to DOE/EM

The benefits of salt splitting using ceramic membranes are 1) waste volume reduction and reduced chemical procurement costs by recycling of NaOH; and 2) direct reduction of sodium in process streams, which enhances subsequent operations such as cesium ion exchange, calcination, and vitrification.

The greatest potential for beneficial application of a salt-splitting process based on NaSICON membranes occurs at the Hanford and Savannah River sites because of the large quantity of sodium in the tank wastes. The Hanford tanks contain an estimated 68,000 metric tons (MT) of soluble sodium, and proposed waste pretreatment activities would add another 11,000 MT. It is estimated that the decontaminated low-level waste (LLW) feed stream at the Savannah River Site (SRS) will contain a total of approximately 48,000 MT of sodium. Tank wastes at the Idaho Chemical Processing Plant (ICPP) contain approximately 165 MT of sodium. The quantity of sodium is much smaller because acidic high-level waste was not neutralized with NaOH.

The most immediate application of the salt-splitting process is at the SRS, where ongoing operations require 2.25 million L of 50 wt% NaOH per year. Salt splitting

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

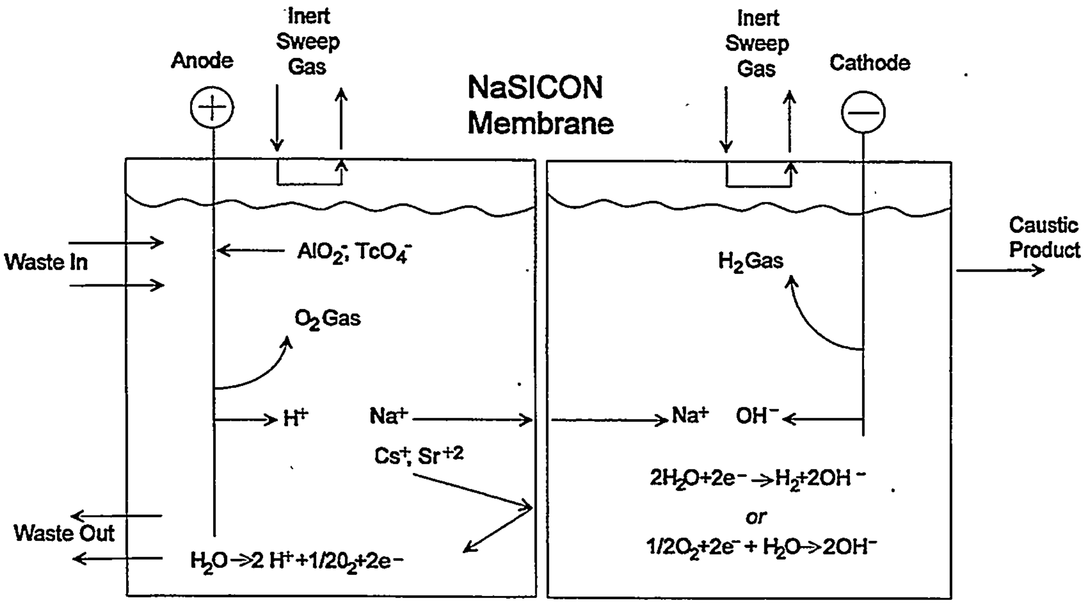


Figure 1. Salt splitting process using ceramic membranes

has been identified as a potential technology for reducing the volume and cost of salt stone and site personnel are actively evaluating the technology. The NaSICON membranes are scheduled to be tested and evaluated along with organic based membranes in FY 1997 as part of a demonstration sponsored by the Tanks Focus Area (TFA). It is anticipated that the primary use for the recovered caustic will be for onsite operations. Up to 80% of the sodium can, in principle, be recovered from the waste while maintaining an alkaline product stream if salt splitting is coupled with an electrochemical nitrate destruction process.

At Hanford, a need for approximately 16% of the sodium in the tanks has been identified, primarily by proposed tank waste pretreatment activities during Phase II of the privatization effort. Sodium hydroxide concentrations of 3 to 6 *M* are required for leaching of tank sludges and increasing the waste pH to protect against line plugging resulting from gelation and precipitation during waste transfer. Another 16% of the sodium could be readily removed from the waste without the need to drop the waste pH below 12. The potential savings associated with this have been estimated at $120 million minus the cost of building and operating a salt-splitting process.

By operating the electrochemical cells with an acidic sodium-depleted process stream it is estimated that 63% of the sodium could be removed before the LLW vitrification process would be limited by another component besides sodium; in this case, phosphate. The potential savings associated with this have been estimated at $550 million minus the cost of building and operating a salt-splitting process. In theory, up to 99% of the sodium could be removed from the waste using a salt-splitting process coupled with an electrochemical nitrate/nitrite destruction process. A beneficial impact on a cesium ion exchange process using crystalline silicotitanates appears possible but would also require some electrochemical destruction of nitrates.

The salt-splitting process has the potential to reduce the difficulties in calcining the sodium-bearing waste at the ICPP, although ongoing calcining operations are reducing the volume of waste. This application would require the use of an acid-resistant membrane similar to those being developed by Ceramatec Inc. for the salt splitting of sodium sulfate waste from paper mills. Salt-splitting technology may be applied in a waste immobilization facility that is to be constructed for radionuclide removal from dissolved calcine.

Technology Transfer/Collaborations

In the past 2 years, a separate DOE program has funded Ceramatec Inc. to develop acid-resistant sodium-selective membranes.[1,2] The goal of this program is to provide technology that would permit the salt splitting of a Na_2SO_4

waste stream into a NaOH stream and a 10% sulfuric acid product at pulp/paper mills. The NaOH would be recycled into the plant and the sulfuric acid sold as a product. The primary milestone in this program is the development of a NaSICON-type product that would be compatible with strong acids and NaOH solutions.

PNNL is adapting the salt-splitting process using the NaSICON materials to a radioactive environment. Ceramatec Inc. is developing membrane compositions and refining the manufacturing process to produce RE-NaSICON membranes with improved sodium transport properties. Bench- and pilot-scale test units are being developed for evaluation in a TFA-sponsored demonstration of the salt-splitting process at SRS.

Scientific Background

The ceramic membranes are from a family of materials known in the electrical battery industry as NaSICONs. The NaSICON ceramics are unique in that they possess channels within the crystal structure for sodium ion conduction (Figure 2). 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 compositions that have been investigated are based on the rare earth (RE) ions (i.e., $Na_5RESi_4O_{12}$) dysprosium (Dy) and neodymium (Nd). The channel size is determined by the size of the RE ion.

These materials act as ion-selective membranes using a combination of steric and electronic effects. The only other ions found to have a significant conductivity relative to that of sodium are hydronium, other protonated ions, potassium, and silver. Most other monovalent cations are excluded by size while multivalent ions are excluded from the crystal lattice due to electroneutrality constraints.

Technical Approach

The overall project objective is to supply a salt-splitting process unit based on ceramic membranes that impacts the waste treatment and disposal flowsheets and meets user requirements. The potential flowsheet impacts include improving the efficiency of the waste-pretreatment processes, reducing volume, and increasing the quality of the final waste disposal forms. Meeting user requirements implies developing the technology to the point where it is available as standard equipment with predictable and reliable performance.

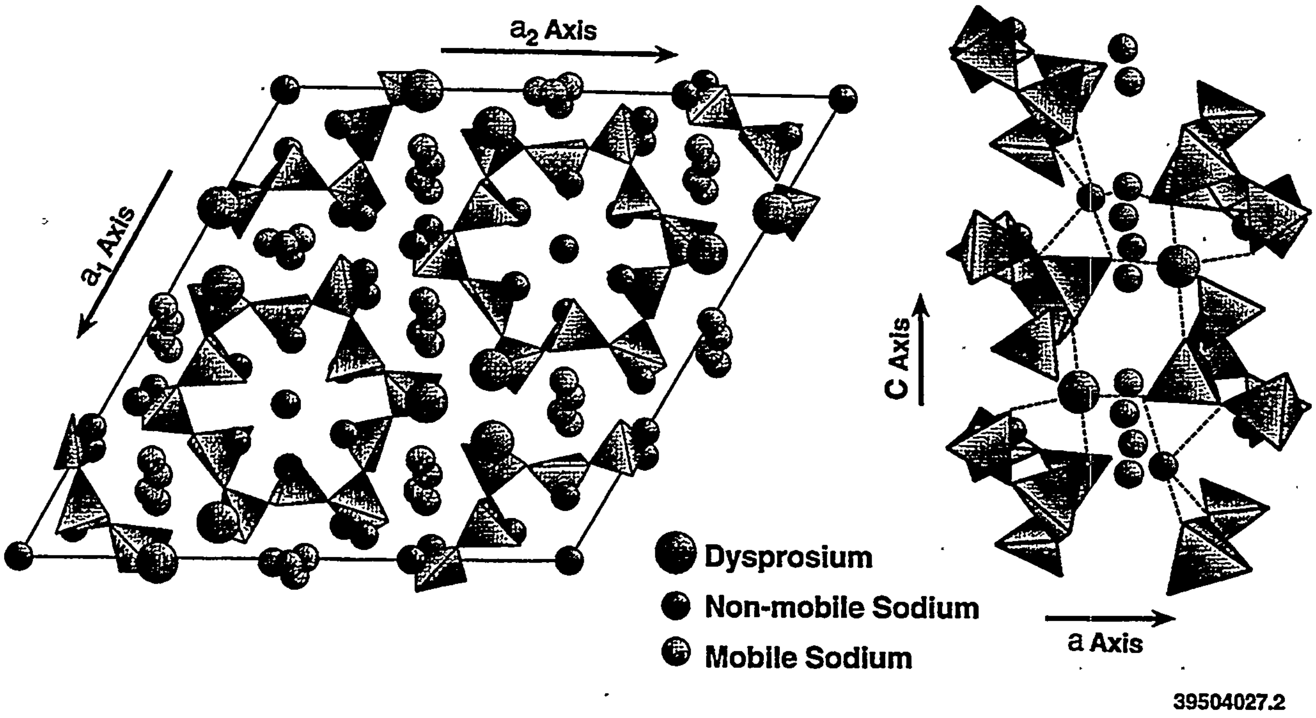


Figure 2. The RE-NaSICON unit cell structure[3]

A phased approach to the implementation of this technology is being used. Phase I involves applications requiring the separation of limited amounts of sodium for onsite recycle as NaOH. These applications present limited but significant technical challenges that involve processing only alkaline waste solutions (i.e., pH >12) after radionuclide decontamination (low radiation) and containing low quantities of suspended solids. Phase II involves applications that present an expanded set of technical challenges including processing acidic and alkaline solutions before radionuclide decontamination (high radiation) and slurries containing a high concentration of solids while producing a nonradioactive caustic product.

A large number of electrochemical cell designs have been developed for a host of applications, and extensive use of this body of knowledge has been made. Industries especially relevant to this project include 1) the chlor-alkali industry, where caustic is produced in a divided electrochemical cell; 2) the nuclear industry, where heavy water and tritium-containing water are electrolyzed; and 3) multiple industries using chromium, where divided flow-through concentric cylindrical cells may be used in electrodialysis for combined Cr(III) oxidation and cation removal for treatment of liquors containing dissolved chromium.

Accomplishments

Scoping experiments in FY 1995 confirmed the high selectivity of Dy-NaSICON for sodium ions relative to hydronium, cesium, aluminum, and strontium ions in alkaline waste solutions and slightly acidic solutions.[1,4] Scoping experiments on irradiation damage by ^{60}Co gamma rays indicated that the Dy-NaSICON material is resistant to exposures up to 10^9 R. Adequate current densities were achieved using Dy-NaSICON. Excellent compatibility with basic or even slightly acidic solutions was observed with Dy-NaSICON; however, mass loss and surface cracks were observed in strong acids.

Development and testing of RE-NaSICON membranes continued in FY 1996 with long-term testing (>1000 h) of Dy-NaSICON membranes and the development of an Nd-NaSICON material. A prototypical design was developed for incorporation of the RE-NaSICON membranes into scaffolds for implementation in commercially available plate and frame electrochemical cells.[5] Several bench-scale units (Figure 3) have been designed and fabricated based on two different membrane sizes (2.54 cm and 3.9 cm). The electrochemical cell used to test the membranes is an Electro MP cell (Electrocell AB), which is a scaled-down version of the production-scale Electro Prod cell. Testing with simple and complex Hanford waste simulants has been initiated.

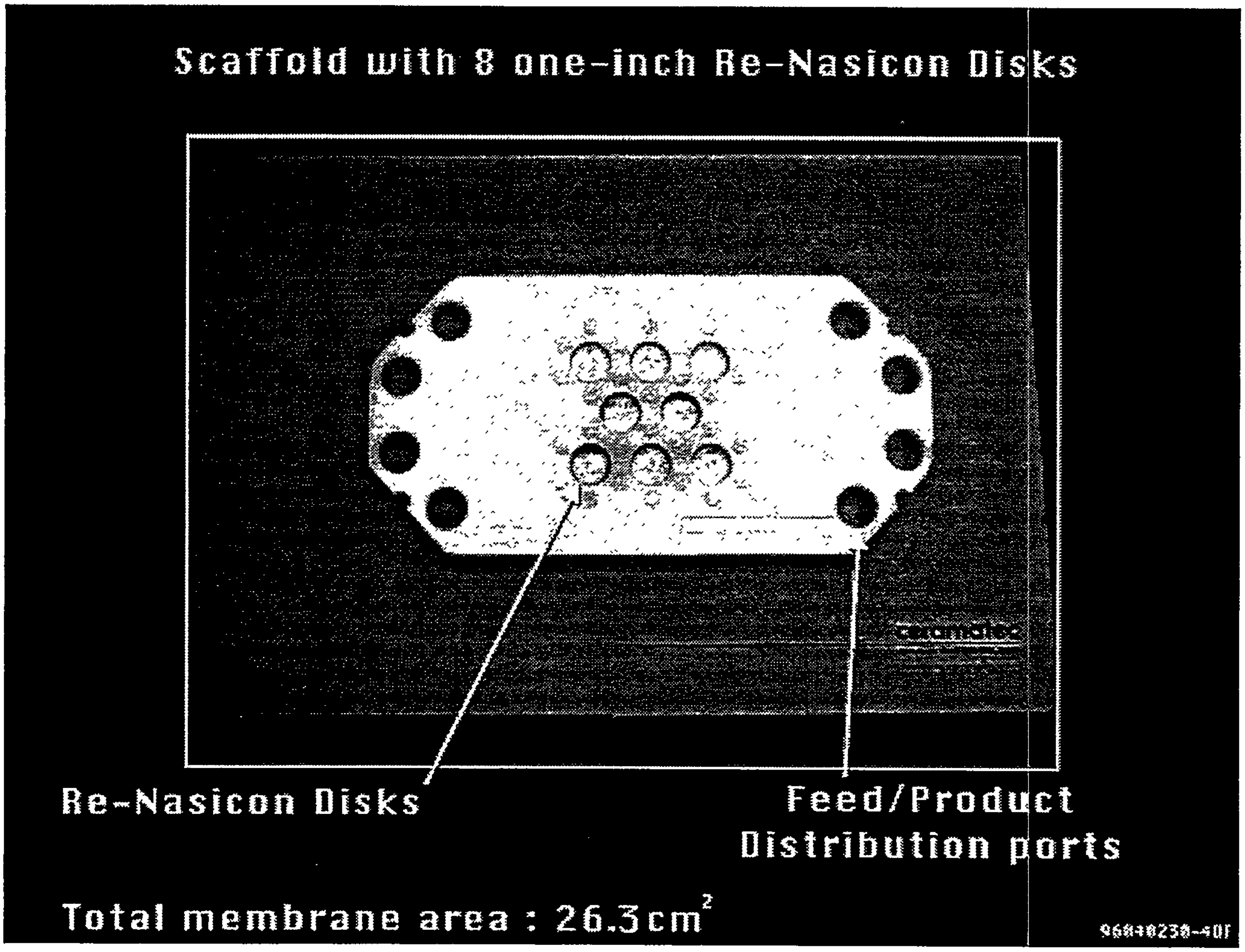
The bench-scale electrochemical cell has been installed in a walk-in fume hood for testing with tank waste simulants. The system is operated in a batch recycle mode with periodic samples withdrawn for analysis using inductively coupled plasma (ICP). Tank waste simulants tested to date include a simple three-component solution, a more complex simulant representing the Hanford Tank waste, neutralized current acid waste (NCAW), and a Savannah River simulant.

A single Dy-NaSICON disk was operated for a total of 1160 h with various anolyte solutions. The initial (first 100 h) sodium transport efficiency was in excess of 90%, but fell to 30 to 40% after 200 h of operation. Increasing the anolyte sodium concentration from 1 to 4 *M* increased the sodium transport efficiency to about 50%.

A set of four Nd-NaSICON membranes (3.9 cm OD) has been tested for 650 hours at an applied potential of 5 V. The current density ranged from an initial value of about 20 mA/cm^2 to 110 mA/cm^2 after 350 h (Figure 4). The average sodium transport efficiency was about 20%. A caustic product with a NaOH concentration of 3.73 *M* was produced from NCAW simulant, meeting the caustic concentration specification at the Hanford Site.

Recently, Ceramatec has discovered a new membrane material composition that conducts sodium at a rate 2 to 3 times greater than previous membrane materials. Testing with a single disk for 1000 h indicates a sodium transport efficiency in excess of 90%.

Membrane fouling has not been observed in any of the tests even though the pH dropped to the point at which large amounts of $Al(OH)_3$ precipitated. Fouling would be indicated by a drop in ionic conductivity, but the opposite has been observed with the membranes generally becoming more conductive as the experiment proceeds.



Scaffold with 8 one-inch Re-Nasicon Disks

Total membrane area : 26.3cm^2

Figure 3. Scaffold containing RE-NaSICON membranes

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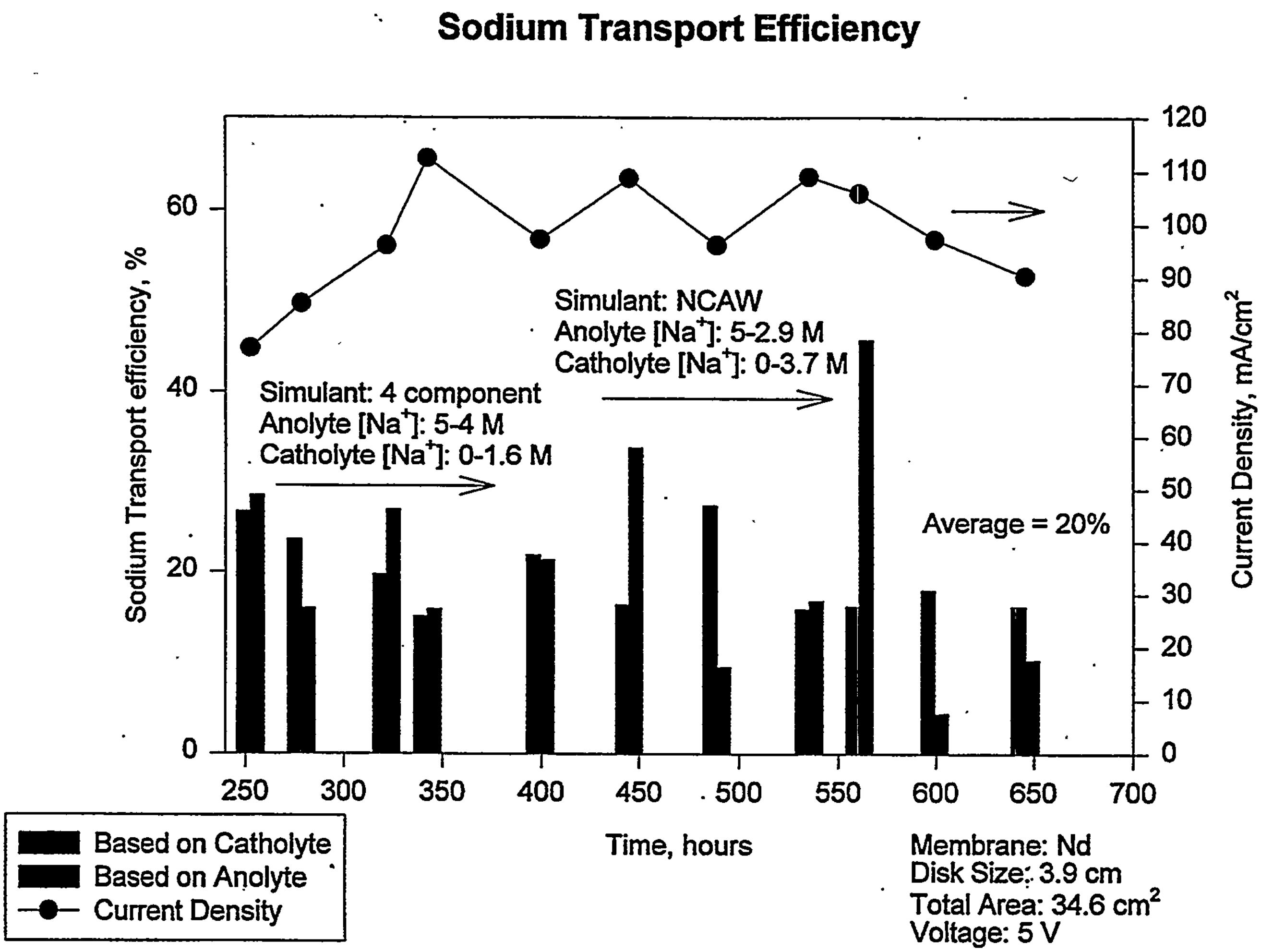

Figure 4. Performance of Nd-NaSICON

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TTP Number RL36C341

4. Wednesday Presentations—Second Half-Day

- ☐ Ligand Modeling and Design
- ☐ Solvent Extraction of Radionuclides from Aqueous Tank Waste
- ☐ Advanced Integrated Solvent Extraction Systems
- ☐ Separation Technologies for the Treatment of Idaho National Engineering Laboratory Wastes
- ☐ Magnetic-Seeding Filtration
- ☐ Advanced Nuclear Precleaner
- ☐ Template-Mediated Synthesis of Periodic Membranes for Improved Liquid-Phase Separations

Ligand Modeling and Design

Benjamin P. Hay, Pacific Northwest National Laboratory

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

Technology Need

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. Ion exchange and solvent extraction processes are under development at a number of sites. Many of these processes require metal-ion-selective organic ligands.

The successful performance of such separation methods depends largely on the properties of the organic ligand (e.g., selectivity, binding affinities, binding kinetics, and solubility). Therefore, much effort is spent synthesizing, characterizing, and testing a large number of 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.

Technology Description

The purpose of this work is to develop and implement a molecular design basis for selecting organic ligands that would be used in 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 the development of 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 with the aid of 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 through collaboration with other DOE national laboratories and private 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.

Benefit to DOE/EM

This new technology, the design criteria coupled with the computer-based molecular model, will provide a means 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 regulations regarding the safe handling and disposal of chemical reagents. Therefore, this capability will save significant costs in ligand identification, evaluation, and deployment.

This technology will allow the development of ligands with 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.

Problems concerning the stability of metal complexes and selectivity of complex formation are of fundamental importance. This technology has potential application to the wide variety of ligand types and associated metal complexes that are being addressed by other DOE programs involving environmental cleanup, fate and transport of environmental contaminants, development of sensors, and nuclear medicine. Private sector application of this technology in the chemical industry, medicine and pharmacology, hydrometallurgy, and geochemistry is also possible.

Technology Transfer/Collaborations

University of Georgia - We are working with Professor Norman Allinger (author of the molecular mechanics modeling software, MM3) to add a methodology for treating high-coordinate metal complexes to the next scheduled release of the software, MM3(96).

Argonne National Laboratory - We are performing calculations for Dr. E. Philip Horwitz and co-workers to optimize the performance of the SREX and CSEX ligands.

Oak Ridge National Laboratory - We are performing calculations for Dr. Bruce Moyer and co-workers to identify structural factors that control reactivity in benzocrowns and improve the Cs/Na selectivity that can be obtained with ligand-bearing benzoether groups.

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 C, H, N, P, O, S, F, Cl, Br, and I atoms. All commercial molecular mechanics software packages come with sets of parameters for organic compounds, but most do not contain parameters for treatment of metal-ligand complexes. This is due in part to the past focus on pure organic systems and in part to 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 (Li, Na, K, Rb, Cs) and alkaline earth (Mg, Ca, Sr, Ba, Ra) metal ions with ligands that contain aliphatic ether donor atoms (e.g., the strontium-extraction (SREX) reagent, di-*t*-butyl-dicyclohexano-18-crown-6). This parameter set was completed and validated. Recently, the MM3 parameter set was extended to include metal complexes of the alkali and alkaline earth metal ions with ligands bearing benzoether donor atoms. This extension allows molecular mechanics calculations to be performed 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.

The generation of 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.

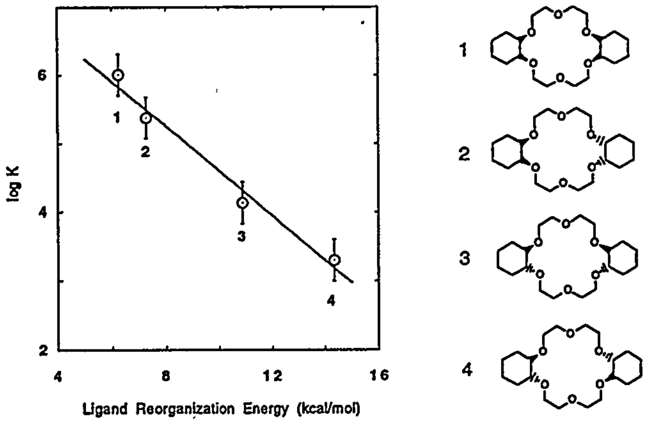

Figure 1. Plot of experimental complex stability (log K in methanol at 25°C) versus calculated ligand reorganization energy for potassium complexation by four diastereomers of dicyclohexano-18-crown-6

Ligand design criteria (i.e., "rules-of-thumb") that can readily be applied by synthetic chemists are an important by-product of this work. For example, the elucidation of 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 allow a synthetic chemist to predict how the addition of alkyl groups to crown ethers will alter the complex stability.

Accomplishments

An inexpensive, off-the-shelf molecular model (MM3) has been configured to handle aliphatic and aromatic crown ether ligands and their complexes with the alkali and alkaline earth metal ions. The model has been demonstrated to accurately predict 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 ether ligands have been developed. Design criteria for aromatic ether ligands (e.g., benzocrown ethers, calixarenes, and spherands) are under development.

This model is currently being applied to the design and screening of multidentate ether ligands for the separation of Cs, Sr, and Ra. The benefit of such application was demonstrated in FY 1996. In a collaborative effort with Argonne National Laboratory, we used the extended MM3 model to identify the optimum stereisomer out of 40 possible diastereoisomers of the SREX reagent. This stereoisomer has been isolated, tested, and found to yield significantly better strontium extraction than any of the commercially available compositions of the SREX reagent. With the modeling approach, we were able to screen 40 structures and identify the correct path to the desired result in the time that would have been required to prepare and test one structure. The alternative trial-and-error experimental approach would have required synthesis and testing of all 40 stereoisomers, a task of 10 to 20 man-years, to achieve the same result.

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Solvent Extraction of Radionuclides from Aqueous Tank Waste*

Bruce A. Moyer*, Peter V. Bonnesen, and Richard A. Sachleben, Oak Ridge National Laboratory; Ralph A. Leonard, Argonne National Laboratory; Gregg J. Lumetta, Pacific Northwest National Laboratory

EM Focus Area: high-level waste tank remediation

Technology Needs

Disposal of the large volumes of highly radioactive wastes stored in underground tanks at Hanford, Oak Ridge, Savannah River, and Idaho Falls is one of DOE's largest problems. Acceptable disposal costs can be achieved only by reducing the volume of waste that must be committed to a geologic repository and minimizing secondary waste streams. Toward this end, priority needs of the ESP-CP, the Tanks Focus Area (TFA), and the Tank Waste Remediation System (TWRS) programs include efficient processes for the separation of Tc, Sr, and Cs from the tank wastes. These programs have sponsored tasks that have, in fact, led to an array of promising new technologies. The new technologies would presumably be employed in series and would each entail specific process requirements, consumption of materials, effluent streams, stripping (if applicable), and impacts on vitrification.

Although implementing these new technologies would likely produce cost savings compared to baseline processes, in no case does it appear that significant problems and uncertainties have all been eliminated or that further significant economies could not be gained. For example, some proposed technologies require adjustment of the waste stream. Others mix the separated fission products with chemicals or materials that adversely impact vitrification. Further, high concentrations of competing ions in the waste reduce separation efficiency, limiting effective capacity to a fraction of that theoretically obtainable; this increases the quantity of chemicals and materials consumed per unit volume of waste. Finally, it may be possible to achieve large cost savings by reducing the size of the process equipment needed, because the major cost of a new high-level facility derives directly from the mass of concrete used in construction. These facts well justify development of improved or alternative technologies.

Technology Description

This task aims toward development of efficient solvent-extraction processes for the removal of the fission products ^{99}Tc, ^{90}Sr, and ^{137}Cs from alkaline tank wastes. Processes already developed or proposed entail direct treatment of the waste solution with the solvent and subsequent stripping of the extracted contaminants from the solvent into a dilute aqueous solution. Working processes to remove Tc (and Sr) separately and Cs separately have been developed; the feasibility of a combined process is under investigation. The SRTALK process[1,2] uses a crown ether in a modified kerosene to remove Tc in the form of pertechnetate from alkaline waste; Sr is co-extracted from certain wastes, such as Oak Ridge Melton Valley Storage Tank (MVST) waste.

Figure 1 depicts SRTALK configured as a Tc extraction system, wherein the stripping water is passed through an anion-exchange resin to concentrate the Tc more than 40 times more efficiently than direct treatment of the waste by the anion-exchange resin. If a conventional strong-base resin is used, the eluant consisting of ethylenediamine and stannous chloride recommended by N. C. Schroeder[3] at Los Alamos National Laboratory may be used. Because the strip solution is slightly acidic, however, a weak-base resin may be used, potentially allowing elution with alternative aqueous solutions. The SRTALK system shown in Figure 1 thus represents a significant value added to anion-exchange technology applied to Tc removal from alkaline waste.

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* This research was sponsored by the Efficient Separations and Processing Crosscutting Program, Office of Science and Technology, Office of Environmental Management, U.S. Department of Energy, under contract number DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

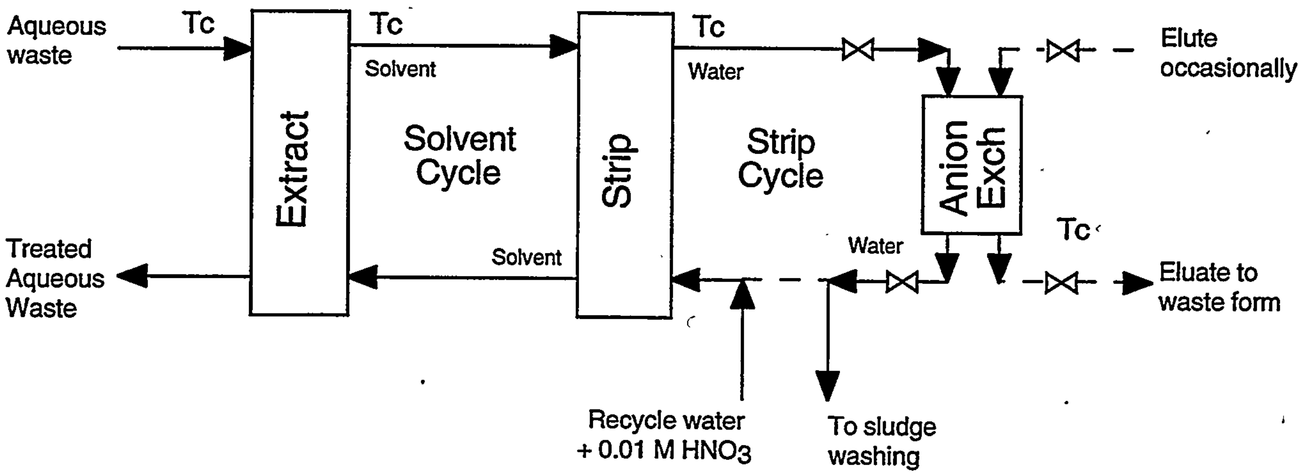

Figure 1. The SRTALK process for removal of pertechnetate from alkaline tank supernatant waste solutions is shown as a simplified configured system involving concentration of the separated Tc onto an anion-exchange resin. In practice, the solvent extraction would be conducted in continuous countercurrent multistage centrifugal contactors, and at least two anion-exchange columns would be employed to permit simultaneous loading and stripping of the resin. The solvent is completely recycled in the process. The strip solution is partly recycled.

Similarly, an alkaline Cs solvent-extraction process has been developed. Although the process has not yet undergone testing on actual tank waste, it may also be configured in tandem with a follow-on sorption technology in much the same manner shown in Figure 1 for SRTALK. The low concentration of competing sodium and potassium ions in the strip solution greatly enhances uptake efficiency by certain sorbents. Thus, one may choose, for example, inexpensive zeolite materials that are highly compatible with subsequent vitrification. Again, solvent extraction adds value to sorption technology and to the pretreatment system overall.

Because Tc, Sr, and Cs will be vitrified together in the high-level fraction, however, a process that could separate Tc, Sr, and Cs *simultaneously*, as opposed to sequentially, potentially offers the greatest impact. Figure 2 presents a simplified diagram of a proposed solvent-extraction cycle followed by three possible treatments for the stripping solution. Some degree of recycle of the stripping solution (option a) is expected. Simple evaporation (option c) is possible before vitrification; this offers the greatest possible volume reduction with simple operation and no consumption of chemicals, but it is energy intensive. If the contaminants are concentrated (option b) by fixed-bed technology, the energy penalty of evaporation can be avoided and vitrification facilitated without any additional secondary waste being produced.

Benefit to DOE/EM

Although the solvent-extraction approach may be viewed as an alternative technology, we prefer to suggest it as enhancing or adding value to solid-phase extraction technology. Because the solvent-extraction process effectively transfers the contaminants to a low-salt solution, the reduced concentration of competing ions means that solid-phase extractants, such as sodium titanate (Sr), zeolites (Sr, Cs), crystalline silicotitanates (Sr, Cs), resorcinol-formaldehyde resin (Cs), resin anion exchange (Tc), or iron metal (Tc), will be able to remove the contaminants with markedly greater efficiency than is possible by treating the waste directly with the solid materials. Increased uptake efficiency means that a smaller mass of solid materials will be required, and decontamination factors can be increased. The adverse impact of the sorbent materials on vitrification could thereby be reduced or even made favorable.

Overall, the proposed technologies offer the following major advantages: 1) direct treatability of the waste; 2) safe, economical, and efficient stripping using only water or dilute acid solution; 3) the use of diluents with high flash point, low toxicity, and low water solubility; 4) large volume reduction; 5) back-end concentration options; and 6) excellent compatibility with vitrification. Compared with other extractants, the most important advantage of crown ethers lies in the ease of stripping. Water suffices to strip

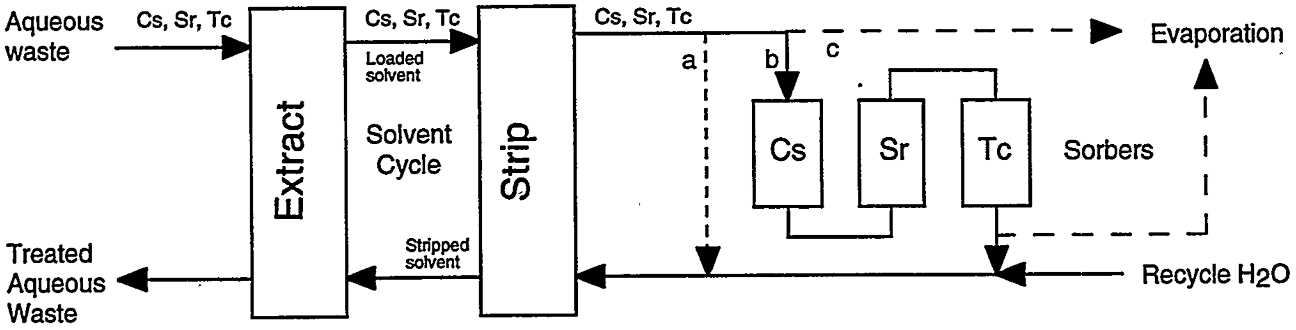

Figure 2. Proposed combined solvent-extraction process for the separation of Cs, Sr, and Tc from alkaline supernatant tank waste. A new solvent under development is used to remove the fission products simultaneously from the aqueous feed, and the loaded solvent is then stripped with a dilute aqueous solution, allowing the solvent to be recycled. Three options are available for treatment of the stripping solution: a) recycle, b) solid-phase extraction, and c) evaporation.

the solvent, though dilute (0.01 *M*) nitric acid is preferred for optimum phase-contacting performance, leading to minimal secondary waste production.

Compared to a sequence of three separation technologies, a combined Cs, Sr, and Tc extraction process promises the most compelling benefits. The most important of these is the reduction in space requirements, leading to a proportionate decrease in capital investments to build processing facilities. In addition, the overall operation can be potentially simplified and made safer, and a number of separate waste streams can be eliminated.

Technology Transfer/Collaborations

During FY 1997, engineering scale-up of the SRTALK process will be carried out at Argonne National Laboratory (ANL) by R. A. Leonard. The ANL effort will entail testing SRTALK solvent on Hanford waste simulant in centrifugal contactors and determining the parameters required to optimize countercurrent operation. Centrifugal contactors are preferred, indeed required, to minimize the inventory of expensive solvent by maximizing throughput. In addition, radiation damage to the solvent is minimized, and space requirements are minor by comparison to pulse columns or mixer-settlers. Facilities at ANL include a bank of 2-cm centrifugal contactors.

Testing of Tc solvent extraction (SRTALK) and Cs solvent extraction on actual Hanford supernatant tank waste is being conducted at Pacific Northwest National Laboratory (PNNL) by G. J. Lumetta. These batch tests will validate the simulant tests carried out at ORNL on selected wastes, especially those identified for Phase I of the privatization of the Hanford tank cleanup. Hot cell facilities and quantities of the waste for testing are available at PNNL, and analytical protocols have been established.

Collaboration with B.P. Hay at PNNL benefits this task through design of improved extractants. Molecular mechanics and quantum calculations point to specific structures which optimize metal ion binding efficiency and selectivity. Improved performance has already been realized in the SRTALK process, which employs the commercial crown ether bis-(*t*-butylcyclohexano)-18-crown-6. Hay's calculations have identified the most effective isomer of this crown ether, enabling Eichrome Industries, Inc., to improve the effectiveness of their product. Currently, calculations are being performed to improve the effectiveness of our cesium extractant.

Technology transfer begins with publications and reports together with invention disclosures leading to licensable patents. In this regard, a patent has been granted for the SRTALK process.[4] An invention disclosure for the alkaline cesium extraction process is being drafted. A patent application on pertechnetate separation from nitrate media by supported liquid membranes (SLM) has been filed. Ultimately, the end users whose interest is most important here are the consortia carrying out Phase I of the privatization of the Hanford cleanup. Accordingly, our literature and progress reports are available to these industries for their evaluation. Other technology transfer will involve an industry to manufacture and commercialize our new extractants. Eichrom Industries has expressed interest in new extractants developed under this task. Negotiations with Commodore Membrane Technologies for a license to the SLM technology are in progress.

The TFA and TWRS programs will receive the primary benefit from this ESP-CP program. Support in FY 1998 will be sought for demonstrating the SRTALK process on actual Hanford waste in centrifugal contactors and for engineering development of the alkaline cesium extraction process.

Scientific Background

The SRTALK Tc extraction process operates by extraction of an alkali metal pertechnetate ion pair, where the crown ether binds a sodium or potassium cation to form a large, hydrophobic cation.[1,2,5] The preferred counter-anion generally corresponds to the one having the lowest hydration energy. Among the abundant anions in the waste, the pertechnetate anion possesses the lowest hydration energy and thus is selected. Typical TcO_4^-/NO_3^- selectivities obtained are on the order of 500 to 1000. Of the commercial crown ethers, bis-(*t*-butylcyclohexano)-18-crown-6 performs most effectively. Concentrations in the range 0.01 to 0.05 *M* in the solvent generally suffice to yield Tc distribution coefficients in the useful range 1 to 10. Under these conditions, essentially complete stripping occurs in two to three contacts with water or, for best phase disengagement, 5 to 10 m*M* nitric acid. The types of diluent and modifier employed strongly control the efficiency of extraction and stripping. An aliphatic kerosene, Isopar® L, modified with tributylphosphate (TBP) at ratios of 1:1 to 1:2 (Isopar® L:TBP) performs effectively.

It should be pointed out that the process described depends on the extraction of Tc in the heptavalent state (i.e., pertechnetate). Ordinarily, the standard reduction potentials favor this state in alkaline solutions exposed to air. However, certain conditions can change this expectation; for example, recent results of N.C. Schroeder (LANL)[6] and D.L. Blanchard (PNNL)[7] have shown that the Hanford complexant concentrate (CC) waste contains a significant fraction of Tc in a form not extractable as pertechnetate anion. Even a double-shell slurry feed tank waste (AW-101) involves a low, but real, fraction of nonextractable Tc. Further investigation of the state of Tc in other Hanford tanks is needed. In FY 1997, the ability of the SRTALK process to remove non-pertechnetate Tc will be examined in batch tests.

The chemical literature provides many examples of solvent extraction of alkali and alkaline-earth metal ions by crown ethers. In particular, systems selective for Cs and Sr have been reported,[8] though their applicability for decontamination of alkaline tank waste has not yet been demonstrated. Our efforts toward a combined solvent-extraction system will in part be based on such reported extractants and on more effective compounds designed and synthesized under this program.

Technical Approach

Whereas it has been commonly thought that separation methods applicable to complex matrices must be made extremely selective, this work addresses the question of whether a *group* selection for Tc, Sr, and Cs can be made practical. 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 reveal that crown ethers may well offer this ability.

Owing to its high selectivity, good mass-transfer properties, and versatility, solvent extraction offers a potentially attractive vehicle for the combined Tc, Sr, and Cs 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. Use of centrifugal contactors should provide for efficient recycle of the solvent, minimizing inventory requirements, entrainment losses, and radiation degradation. Solvent extraction has proven to be effective in many nuclear separations, establishing a good foundation for further application.

In FY 1997, efforts will be dedicated to finding appropriate extractants, diluents, and modifiers for the combined extraction of Tc, Sr, and Cs. Key issues involve achieving sufficiently high extraction and stripping ratios for all of these contaminants, as some factors which enhance Cs extraction might prove deleterious for Tc or Sr. As mentioned above, the SRTALK process will undergo engineering scale-up to centrifugal contactors at ANL. An alkaline cesium extraction process will be further developed and tested on actual waste. Specific extractants for strontium will be identified, and the possibility of nonpertechnetate Tc extraction will be investigated.

Accomplishments

SRTALK Process Demonstrated in Mixer-Settler Test of Pertechnetate Extraction

A mixer-settler test of the SRTALK crown-ether process was completed, successfully demonstrating continuous extraction and stripping cycles in the solvent extraction of pertechnetate from tank-waste simulant. The test specifically demonstrated practically complete extraction from a simulant of Hanford double-shell slurry feed (DSSF-7) containing 97.0 mCi/L $^{99}TcO_4^-$ and subsequent transfer of 95% of the pertechnetate to a dilute solution of nitric acid. Previous tests have shown that this separation could be performed batchwise on the scale of a few milliliters in laboratory vials. Good batch results had been obtained for various simulated and actual supernatant tank wastes; actual waste samples tested included Hanford double-shell slurry feed from tank AW-101 (test done by G. J. Lumetta and co-workers at PNNL) and Oak Ridge MVST W-29. However, the present mixer-settler results demonstrate the viability of the process in continuous countercurrent equipment and thereby mark the passage of SRTALK process development into the engineering domain.

The solvent used in the mixer-settler experiment consisted of 0.02 *M* bis-(*t*-butylcyclohexano)-18-crown-6) in a kerosene process diluent (Isopar® L) containing TBP modifier at 1:1 vol/vol concentration. Completed in August 1996, the first half of the test demonstrated a continuous three-stage extraction cycle. Excellent phase disengagement was observed over the course of the 4-h run, which consumed approximately 4 L of each phase at equal flow rates of approximately 15 mL/min. Stage-to-stage efficiency was good, with an average steady-state decontamination factor of 6.7 ± 1.2 per stage, resulting in an overall removal of more than 99.6% of the Tc from the waste simulant. The resulting solvent containing the extracted Tc was stripped in a subsequent three-stage continuous mixer-settler test conducted in September. The solvent was stripped with 10 m*M* nitric acid using the same laboratory mixer-settler equipment used in the extraction cycle, under the same flow conditions. Phase coalescence was again excellent, and 95% of the Tc contained in the solvent was removed following the three-stage contact with the strip solution.

Measurements of the other components in the strip solution revealed that the process has a high selectivity for pertechnetate, increasing the ratio of pertechnetate to nitrate (the chief competing anion) more than five hundred-fold in the strip solution relative to the aqueous feed. It must be recognized that the process does not concentrate the Tc, however, but rather separates it from the high concentration of electrolytes in the waste. Concentration is then effected in the follow-on anion exchange step.

The pertechnetate contained in the mixer-settler strip solution was concentrated with very high efficiency on an anion-exchange resin. Table 1 illustrates the comparative performance for anion exchange from our strip solution from the mixer-settler experiment and from a DSSF-7 simulant[3]. The resins used include a variety of commercially available resins, as well as resins prepared by S. D. Alexandratos (University of Tennessee, Knoxville) under another ESP-CP-supported task.[9] It can be seen that using solvent extraction to remove pertechnetate from the waste, followed by stripping and anion-exchange, allows pertechnetate to be concentrated from a large volume of waste into a small volume of resin. The efficiency by which the resin is used in this manner obviously far surpasses the efficiency of the resin when contacted directly with the waste.

Extraction and Stripping of Cesium from Alkaline and Acidic Waste Simulants

We have developed a new solvent for the extraction of cesium from alkaline and acidic tank waste. The best solvent composition so far tested can deliver Cs distribution ratios of 1.8 from a Hanford tank AW-101 waste simulant and 5.4 from a tank AP-106 waste simulant with only 0.02 *M* extractant. Stripping performance is good; following extraction from the AW-101 simulant, 97% of the Cs contained in the organic solution can be removed following two aqueous stripping contacts (1:1 phase ratio). Cesium can also be extracted from an acidic waste simulant (1 *M* sodium nitrate, 1 *M* nitric acid, 1 m*M* cesium nitrate) using this solvent at only 0.01 *M* extractant; a Cs distribution ratio of 1.6 was obtained, and >99% of the extracted Cs was stripped in two contacts. An invention disclosure on the Cs extraction and stripping process is being drafted.

We are in the process of screening extractants and modifiers to be used in a solvent for the extraction of strontium from alkaline waste. To date, we can obtain strontium distribution ratios of near unity from both mildly alkaline waste simulants such as that approximating tank AP-106 (free hydroxide concentration = 0.08 *M*), and simulants where the free hydroxide concentration is 1.0 *M*. Work

Table 1. Batch-equilibrium sorption results for pertechnetate from aqueous stripping solution from SRTALK mixer-settler experiment for selected synthetic and commercial anion exchange resins. Uncertainties in K'd values are ± 5%. Results for sorption of pertechnetate directly from DSSF-7 simulant are provided for comparison.[a]

Resin	1 h K'_d Strip Solution (mL/g)	4 h K'_d Strip Solution (mL/g)	2 h K'_d DSSF-7 (mL/g)[a]	6 h K'_d DSSF-7 (mL/g)[a]
Reillex™-HPQ	12000	13300	293	332
Purolite® A-520E	20400	31800	392	527
Sybron Ionac® SR-6	17900	40000	105	188
VP02-152 (laboratory)	27100	42400	Not determined	Not determined
VP02-217 (laboratory)	33800	62200	Not determined	Not determined

[a] Data for sorption of Tc from DSSF-7 reported by N. C. Schroeder.[3]

is in progress to further investigate strontium extraction and to obtain higher distribution ratios before formulating a solvent for the combined extraction of cesium, strontium, and pertechnetate.

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TTP Number OR16C341

Advanced Integrated Solvent Extraction Systems

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EM Focus Area: high-level waste tank remediation

Technology Need and Description

Advanced integrated solvent extraction systems are a series of novel solvent extraction (SX) processes that will remove and recover all of the major radioisotopes from acidic-dissolved sludge or other acidic high-level wastes. The major focus of our effort during the last 2 years has been the development of a combined cesium-strontium extraction/recovery process, the Combined CSEX-SREX Process.

The Combined CSEX-SREX Process relies on a mixture of a strontium-selective macrocyclic polyether and a novel cesium-selective extractant based on dibenzo 18-crown-6. The process offers several potential advantages over possible alternatives in a chemical processing scheme for high-level waste treatment. First, if the process is applied as the first step in chemical pretreatment (Figure 1), the radiation level for all subsequent processing steps (e.g., transuranic extraction/recovery, or TRUEX) will be significantly reduced. Thus, less costly shielding would be required. The second advantage of the Combined CSEX-SREX Process is that the recovered Cs-Sr fraction is non-transuranic, and therefore will decay to low-level waste after only a few hundred years. Finally, combining individual processes into a single process will reduce the amount of equipment required to pretreat the waste and therefore reduce the size and cost of the waste processing facility.

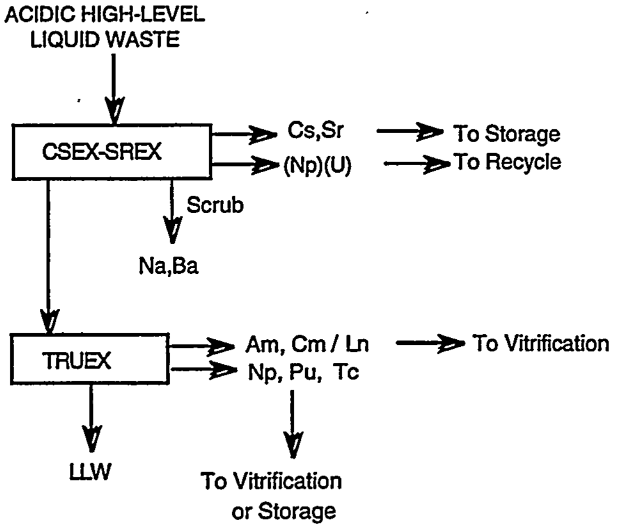


Figure 1. Treatment of acidic high-level liquid wastes using a front-end Combined CSEX-SREX Process

Technology Transfer/Collaborations

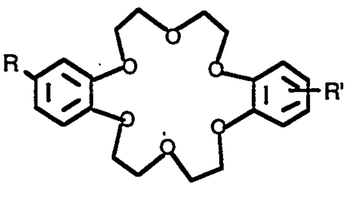
In an ongoing collaboration with Lockheed Martin Idaho Technology Company (LMITCO), we have successfully tested various segments of the Advanced Integrated Solvent Extraction Systems. Eichrom Industries, Inc. (Darien, IL) synthesizes and markets the Sr extractant and can supply the Cs extractant on a limited basis. Plans are under way to perform a test of the Combined CSEX-SREX Process with real waste at LMITCO in the near future.

Scientific Background/Technical Approach

During the last 2 years, we have made significant advances in the development of extractants for use in acid-side SX systems for the extraction/recovery of Cs and Sr. The combination of a large ionic radius and low charge makes the selective extraction of Cs and Sr from highly acidic nitrate media difficult. Nevertheless, by exploiting the principles of molecular recognition and solvation effects, we have developed Cs and Sr extractants that can be combined in a plutonium-uranium extraction-like system that can selectively extract Cs and Sr from highly acidic nitrate media. Both Cs and Sr are readily recovered using dilute nitric acid. Figures 2 and 3 show the structures and extraction equilibria involved. Figure 4 depicts the nitric acid dependency of Cs and Sr extraction by the Combined CSEX-SREX Process solvent. The Combined CSEX-SREX system was tested in a batch countercurrent mode in FY 1995 using acidic waste simulant from LMITCO. The results were very favorable.

Cs Extractant:

bis-4,4'(5')[(2-hydroxy-alkyl)benzo]-18-crown-6



Extraction Equilibrium

$$Cs^{1+} + NO_3^- + \overline{CE} \rightleftharpoons \overline{Cs(CE)NO_3}$$

where CE = Crown Ether

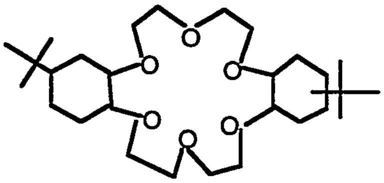
Phase Modifier / Diluent:

1.2 M TBP - 5% (v/v) lauryl nitrile - Isopar™-L

Figure 2. Cesium extractant and extraction equilibrium

Sr Extractant:

bis-4,4'(5')[(tert-butyl)cyclohexano]-18-crown-6



Extraction Equilibrium:

$$Sr^{2+} + 2NO_3^- + \overline{CE} \rightleftharpoons Sr(CE)(NO_3)_2$$

where CE = Crown Ether

Phase Modifier / Diluent:

1.2 M TBP - 5% (n/n) lauryl nitrile - Isopar™-L

Figure 3. Strontium extractant and extraction equilibrium

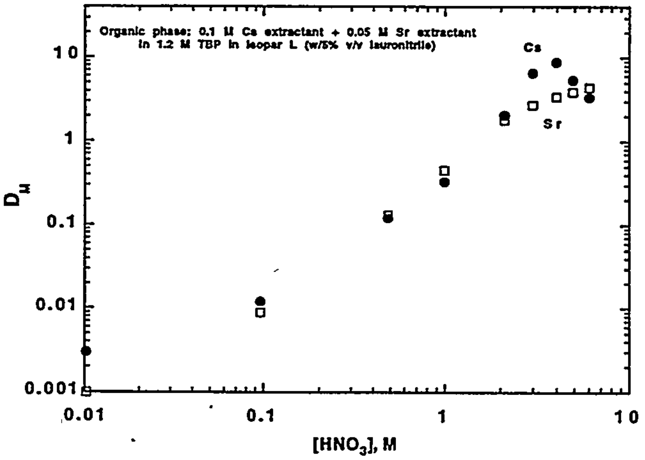


Figure 4. Nitric acid dependency of Cs and Sr extraction by Combined CSEX-SREX Process solvent

Accomplishments

The Combined CSEX-SREX Process was hot-tested in a continuous countercurrent mode using a 24-stage mini-centrifugal contactor. The flowsheet and flow rates of each solution are shown in Figure 5. Table 1 shows the composition of the feed solution obtained from LMITCO, and Table 2 shows the concentrations of radioisotopes after spiking the feed solution before the test run. The steady-state concentrations of Cs and Sr in the aqueous raffinate (DW) were 5.0×10^{-9} *M* and $<9 \times 10^{-9}$ *M*, respectively. Essentially all (> 99.99%) of the Cs and Sr was recovered in the strip effluent (EW). As expected, ^{241}Am remained entirely in the aqueous raffinate; the ^{241}Am concentration in EW was $<1 \times 10^{-9}$ *M*.

The distribution of Tc throughout the flowsheet is more difficult to describe because Tc never appeared to reach steady state. The results do indicate, however, that the Combined CSEX-SREX Process will not effectively remove and recover Tc from the feed solution. Technetium removal and recovery will have to be left to the TRUEX process as shown in Figure 1.

Overall, the hot test continuous countercurrent run was highly successful. The decontamination of the aqueous raffinate with respect to Cs and Sr was 4.5×10^5 and $>2.6 \times 10^5$, respectively. Both Cs and Sr are effectively stripped from the organic phase. No detectable Am was found in the Cs-Sr product. Phase disengagement was excellent throughout the test run. Only minimum entrainment of process solvent in the aqueous raffinate was observed.

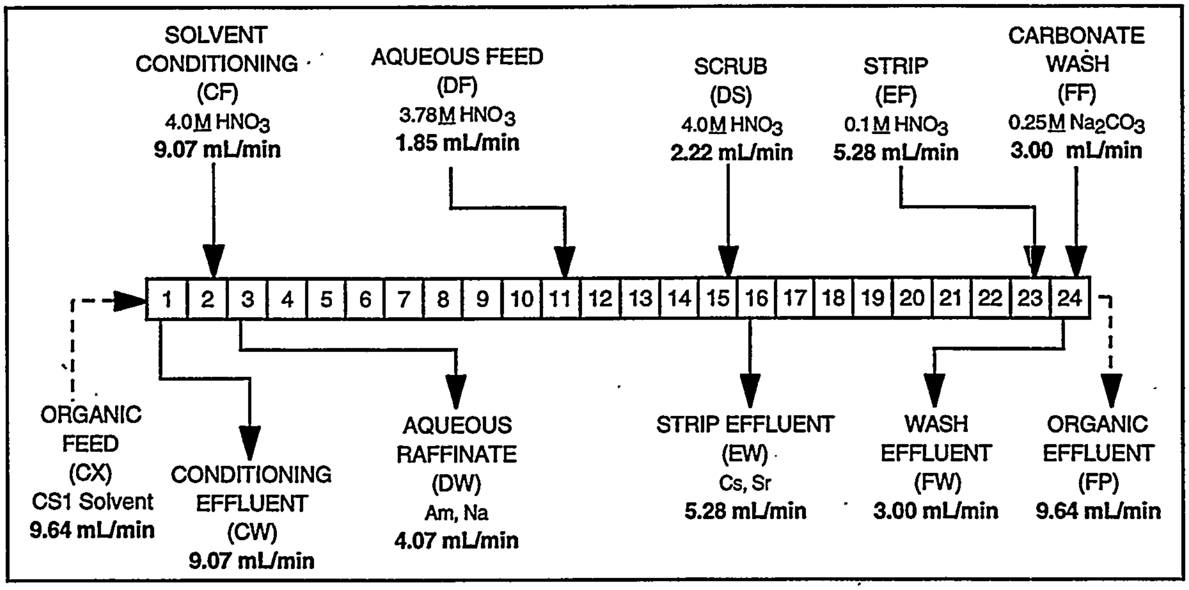


Figure 5. Flowsheet for test CS1 of the Combined CSEX-SREX Process

Table 1. Composition of zirconia calcined waste simulant from Lockheed Martin Idaho Technology Company

Component	Concentration (*M*)
H^+	3.78
Al^{3+}	0.486
B^{3+}	0.086
Ca^{2+}	0.778
CrO_4^{2-}	0.00585
Cs^+	0.005
F^-	1.24
Fe^{3+}	0.0149
NO_3^-	6.39
Na^+	0.015
Sr^{2+}	0.0039
ZrO^{2+}	0.225

Table 2. Concentration of radioactive isotopes in the aqueous feed (DF)

Isotope	Concentration (mCi/L)
^{85}Sr	1.34
^{99m}Tc	135
^{137}Cs	0.19
^{241}Am	10.7

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TTP Number CH26C321

Separation Technologies for the Treatment of Idaho National Engineering Laboratory Wastes

Terry A. Todd, Idaho National Engineering Laboratory

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

Technology Needs

The Idaho National Engineering Laboratory (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 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 dispositioning of accumulated radioactive wastes.

Currently about 6.8 million L of acidic, radioactive liquid waste that is not amenable to calcination, and about 3800 m^3 of calcine exist at the ICPP. Legal drivers (court orders) and agreements between the state of Idaho, the U.S. Navy, and DOE exist that obligate INEL to develop, demonstrate, and implement technologies for treatment and interim storage of the radioactive liquid and calcine wastes. Per these agreements, all tank waste must be removed from the underground liquid storage tanks by the year 2012, and high-level radioactive waste must be treated and removed from INEL by 2035.

Separation of the radionuclides from the wastes, followed by immobilization of the high-activity and low-activity fractions in glass and grout, respectively, is the approach preferred by INEL. Technologies to remove actinides (U, Np, Pu, and Am), Cs, Sr, and possibly Tc from highly acidic solutions are required to process INEL wastes. Decontamination of the wastes to NRC Class A low-level waste (LLW) is planned. Separation and isolation of Resource Conservation and Recovery Act (RCRA) metals (Hg, Pb, Cd, and Cr) from the highly radioactive waste streams may also be required. A process flowsheet for the treatment of INEL highly radioactive wastes is shown in Figure 1.

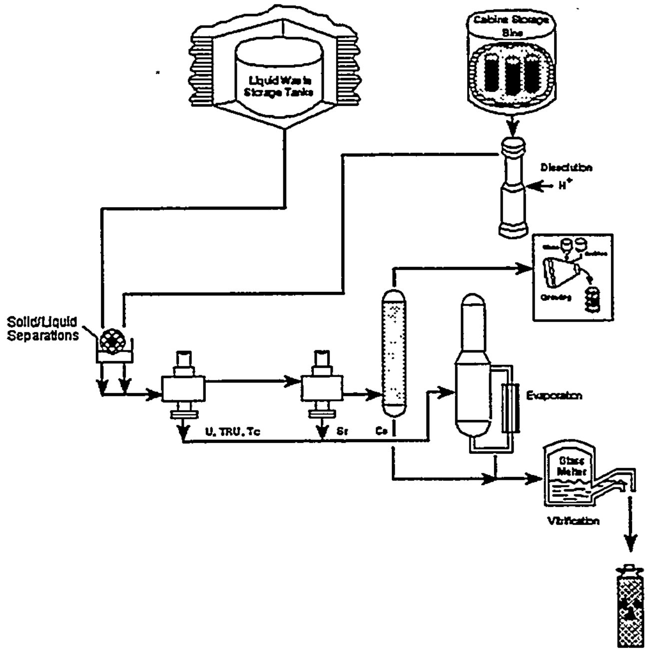

Figure 1. ICPP waste processing flowsheet

Remediation efforts will begin in FY 1997 to remove volatile organic compounds (VOCs) and radionuclides (Cs and Sr) from groundwater located at the Test Area North (TAN) facility at INEL. A plume of VOCs and radionuclides has spread from the former TSF-05 injection well, and a Comprehensive Environmental Response, Conservation, and Liability Act (CERCLA) remediation action is under way. A Record of Decision was signed in August 1995 that commits INEL to remediate the plume from TSF-05. Removal of Sr and Cs 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 Cs and Sr, respectively. CERCLA remediation efforts of contaminated groundwater at other INEL facilities will be under way for the next several years. Cesium and Sr are the major contaminants that must be removed from the groundwater.

Technology Description

The INEL is collaborating with several DOE and international organizations to

- Develop and evaluate technologies to treat acidic high-level radioactive wastes. The focus is on the removal of Cs, Sr, and actinides from wastes typically 1 to 3 *M* in nitric acid.
- Develop and evaluate technologies to treat groundwater contaminated with radionuclides and/or toxic metals.

Specific technologies under evaluation are described here.

Cobalt Dicarbollide

A collaborative program between the Khlopin Radium Institute (KRI) of St. Petersburg, Russia, and INEL has resulted in testing of a chlorinated cobalt dicarbollide based solvent for the removal of Sr and Cs from ICPP wastes. Recent work at KRI has produced a non-aromatic solvent that would be acceptable for use in the U.S. This process was tested successfully in centrifugal contactors with simulated waste in 1995 and with actual waste in 1996. Current efforts are focused on developing a combined solvent for the simultaneous removal of actinides, Cs, and Sr. The combined solvent will be tested in batch contacts using actual INEL tank waste in FY 1997.

Copper Potassium Hexacyanoferrate

A collaborative program between the Institute of Physical Chemistry-Russian Academy of Sciences (IPC-RAS), Moscow, Russia, and INEL has resulted in column testing of a copper potassium hexacyanoferrate sorbent for removing Cs from ICPP tank wastes. Small-scale column tests were performed with simulated and actual tank wastes, and the commercially produced cyanoferrate sorbent. Continued testing and evaluation of this sorbent in larger-scale columns is planned.

Crystalline Silicotitanate

Small-scale column tests were performed with simulated and actual tank wastes and crystalline silicotitanate sorbent (IONSIV® IE-911). The IONSIV® IE-911 sorbent is effective at removing Cs from acidic (1 to 1.5 *M*) solutions.

Polyacrylonitrile-Based Sorbents

A hexacyanoferrate/polyacrylonitrile composite sorbent was developed and tested with simulated INEL tank waste at the Czech Technical University in Prague, Czech Republic. A collaborative program to test this sorbent for removing Cs from actual tank waste at INEL has been established.

Combined Cs/Sr Solvent

Dr. E. Philip Horwitz and coworkers at ANL have developed a crown ether extractant for the selective removal of Cs from acidic solutions. A countercurrent flowsheet test was recently performed at ANL using simulated INEL dissolved calcine with a solvent containing the crown ether extractant for the SREX process and the newly developed crown ether for Cs extraction. The test demonstrated excellent decontamination factors ($>10^4$) for Cs and Sr from INEL dissolved pilot-plant calcine. Testing of this combined process in a 24-stage centrifugal contactor pilot plant with actual waste will be performed at INEL in FY 1997.

Ion-Exchange Technologies for Decontaminating Groundwater

Evaluations of numerous sorbents for the removal of Sr and Cs from contaminated groundwater are in progress. Sorbents tested to date include IONSIV® IE-911, CsTreat (potassium cobalt hexacyanoferrate), Pellx-137 zeolite, Ionac® C-250, sodium titanate (AlliedSignal), and a Russian-manufactured manganese hydroxide sorbent. Sorbents have been tested in columns and in 3M web cartridge systems.

Benefits

The radionuclide content of INEL wastes is much less than 1 wt% with the remainder comprised of inert materials. With the proper selection/combination of technologies, it is possible to decontaminate INEL wastes sufficiently to achieve NRC Class A LLW for the bulk constituents. The high-level waste (HLW) 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 LLW stream and the much lower throughput HLW stream. It would also save considerable costs for interim storage and final geologic disposal of the HLW fraction. A comparison of waste volumes for the treatment of liquid tank waste is shown in Figure 2.

An economically viable technology for the removal of Cs and Sr from contaminated groundwater has not been implemented to date. The testing performed with the novel sorbents at the TAN facility demonstrated a simple and effective alternative for removal of these radionuclides.

Technology Transfer/Collaboration

Khlopin Radium Institute, St. Petersburg, Russia
Institute of Chemical Technology-Russian Academy of Sciences, Moscow, Russia
Czech Technical University
Argonne National Laboratory
Eichrom Industries, Inc.
UOP
AlliedSignal Inc.
3M
Parsons Environmental Services
MSE Inc.

Technical Background and Approach

In FY 1993 a joint development program was established within the ESP-CP to evaluate technologies currently under development in the Former Soviet Union for the treatment of high-level radioactive waste. This joint program, between the KRI 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 the removal of actinides and Tc and a cobalt dicarbollide derivative process for the simultaneous removal of Cs and Sr from acidic waste. Modifications have been made to both Russian process flowsheets to enhance extraction performance and to improve the safety characteristics of the processes. Batch contact tests and centrifugal contactor flowsheet tests have been performed at both KRI and INEL. A bank of 26 stages of 3.3-cm contactors is under fabrication in Russia and will be shipped to INEL for testing in FY 1997. The focus of testing is with actual waste solutions for both the laboratory and flowsheet tests.

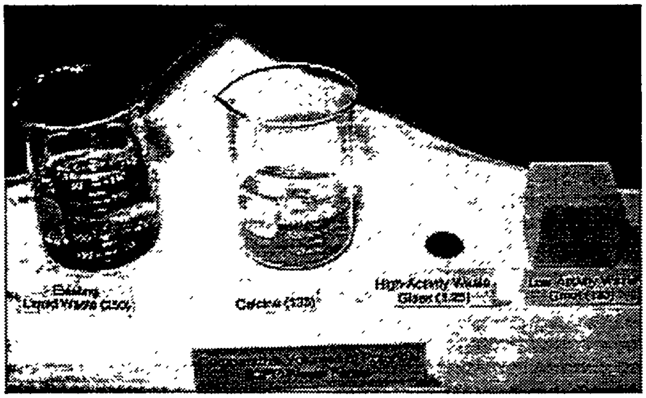

Figure 2. Representative waste volumes from processing INEL liquid tank waste

Removal of Cs from acidic waste streams is less developed than for alkaline wastes. Several ion-exchange technologies have been recently developed within the ESP program that are applicable to acid-side Cs removal. Recently, several ion-exchange materials became available on engineered supports including crystalline silicotitanate (CST), nickel hexacyanoferrate/polyacrylonitrile (NiFC-PAN), and a copper hexacyanoferrate/silica composite (CuFC). Testing of these technologies using simulated INEL waste is in progress. Testing of the engineered form of these technologies with actual waste was performed in FY 1996 and will be continued in FY 1997. Testing will be performed in conjunction with the producers of these materials, namely UOP for the CST, the Czech Technical University for the PAN composite, and IPC-RAS for the CuFC/silica composite.

Removal of the fission products Cs and Sr from contaminated groundwater is feasible using a number of sorbents in either packed columns or in 3M web systems. Cesium removal has been effectively demonstrated using a number of sorbents such as CST, hexacyanoferrates, and natural zeolites. These sorbents all have a high selectivity and capacity for Cs. Removal of Sr from groundwater is more challenging because of the competition for ion-exchange sites by Mg and Ca, both present in groundwater at concentrations higher than Sr. The presence of these ions reduce the capacity of the sorbent for Sr and lead to earlier breakthrough than experienced with Cs sorbents. Novel sorbents with increased selectivity for Sr over Ca and Mg are being developed and tested.

Accomplishments

Testing of the modified cobalt dicarbollide process, which incorporated a non-aromatic diluent in centrifugal contactors using actual INEL acidic liquid waste was completed. The testing was conducted jointly with KRI scientists at INEL. Cesium and Sr removal efficiencies of 99.4% and 96.3%, respectively, were achieved using 24 stages of centrifugal contactors. The removal efficiencies for both Cs and Sr were less than expected due to incomplete washing of the solvent before recycle to the extraction section. With minor flowsheet adjustments, it is expected that removal efficiencies of >99.9% can be achieved for both Cs and Sr.

A second test was performed with the cobalt dicarbollide process using the non-aromatic diluent without the presence of polyethylene glycol (PEG) in the solvent. The PEG is normally added to the solvent to facilitate Sr extraction. This test was performed to determine the effectiveness of the cobalt dicarbollide process as a Cs-only separation process. The test was performed with actual tank waste, in the 24 stage centrifugal contactor pilot plant, located in a shielded hot cell facility. Greater than 99.998% of the Cs was removed from the waste in this test, which corresponds to a low-level waste activity of only 0.0027 Ci/m^3 (the NRC Class A LLW Criteria is 1 Ci/m^3).

A test was completed using 20% iso-amyldialkylphospine oxide in dodecane to remove actinides and Tc from actual tank waste using 24 stages of centrifugal contactors. Operational problems were experienced with the centrifugal contactors during the test. The rotors in two of the contactor stages (both in the strip sections) were found to be inoperable. The problem was not discovered until after the test was completed. The extraction section removed about 99% of the gross alpha activity in the waste feed.

Tests using the Russian-manufactured potassium copper hexacyanoferrate/silica composite sorbent were performed at IPC-RAS and INEL with small-scale columns using both simulated and actual tank waste. Tests performed with simulated waste indicate that 50% breakthrough of Cs occurred at 1500 to 2000 bed volumes (BV) of waste processed, at a feed rate of 6 to 7 BV/h. These tests also demonstrated that nearly 100% of the Cs loaded on the sorbent can be eluted with 10 BV of 8 *M* nitric acid. The test performed at INEL with actual tank waste resulted in 50% Cs breakthrough in 300 BV of waste processed. This is believed to be due to a very inconsistent flow rate to the 1 cm^3 column. Additional testing of the sorbent with actual waste is planned in FY 1997.

A 1 cm^3 column test using CST (IONSIV® IE-911) and actual waste was performed. This test was performed with a positive displacement metering pump that resulted in a constant flow to the column of 6 BV/h. About 800 mLs of actual waste were treated with 50% Cs breakthrough occurring at 660 BV. No attempt was made to elute Cs from the CST sorbent.

Laboratory experiments were performed to determine the effectiveness of the TRUEX and SREX processes for removing and recovering Hg and Pb from acidic mixed-waste solutions. A flowsheet to selectively partition Sr and Pb from simulated INEL tank waste was developed and tested in centrifugal contactors. Both Sr and Pb are quantitatively extracted in the flowsheet and selectively stripped using dilute nitric acid (for Sr) and ammonium citrate (for Pb). This flowsheet will be tested on actual INEL tank waste in FY 1997 with the support of the Tanks Focus Area.

Testing of novel ion-exchange sorbents for Cs and Sr removal from contaminated groundwater is in progress. Results will be available at a later date.

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TTP Number ID76C311

Magnetic-Seeding Filtration

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EM Focus Areas: high-level waste tank remediation; subsurface contaminants

Technology Need

This project is focused on technology needs for two major target problems with liquid waste streams: 1) removal of fine particulates and 2) removal of dissolved contaminants. Solid-liquid separation has been identified as a major need for several DOE Focus Areas. For instance, particulates pose operational problems in processes such as ion exchange that are used to treat tank wastes, process wastes, and groundwater. Particulates can cause clogging of mixed-waste incinerator injector nozzles. The removal of particulates associated with contaminants is also necessary in many cases to achieve required decontamination factors. DOE facilities at Hanford, Savannah River, and Oak Ridge, among others, need methods for removing colloids and fine particulates.

The removal of dissolved contaminants is a widespread need that is frequently met by precipitation and sorption processes. Precipitation processes depend on formation of solids containing target contaminants; therefore, implementation in practical processes requires efficient solid-liquid separation. This need is amplified in cases where radioactive contaminants are removed, because achievement of required decontamination factors will require the removal of colloidal precipitates. Newly devised sorbents have been developed for contaminant removal that are effectively 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. Proof-of-principle experiments have indicated the possibility of applying magnetic-seeding filtration as an efficient polishing step for both of these types of processes.

Technology Description

Magnetic-seeding filtration is a technology under development for the enhanced removal of magnetic and non-magnetic particulates from liquids. This process (Figure 1) involves the addition of a small amount of magnetic seed particles (such as naturally occurring iron oxide) to a waste suspension, followed by treatment with a magnetic filter. Non-magnetic and weakly magnetic particles are made to undergo nonhomogeneous flocculation with the seed particles, forming flocs of high magnetic susceptibility that are readily removed by a conventional high-gradient magnetic filter.

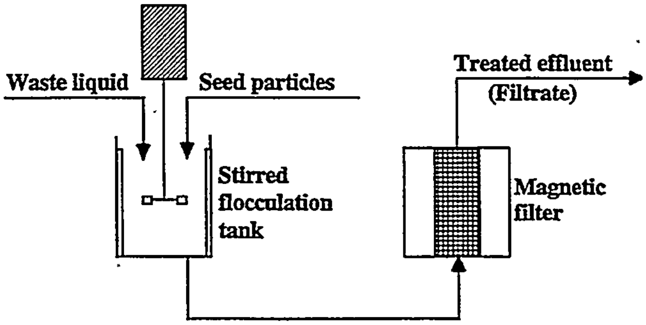

Figure 1. Schematic of magnetic-seeding filtration process

This technology is applicable to a wide range of liquid wastes, including groundwater, process waters, and tank supernatants. Magnetic-seeding filtration may 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. Waste stream characteristics for which the technology may be applicable include

1) particle sizes ranging from relatively coarse (several microns) to colloidal particles, 2) high or low radiation levels, 3) broad-ranging flow rates, 4) low to moderate solids concentration, 5) cases requiring high decontamination factors, and 6) aqueous or non-aqueous liquids. At this point, the technology is at the bench-scale stage of development; laboratory studies and fundamental modeling are currently being employed to determine the capabilities of the process.

Benefit to DOE/EM

Development of this technology is expected to provide benefit to all DOE sites and several Focus Areas where particulate and/or contaminant removal is an important issue. Examples of the benefits to be obtained include

- EM-30 operations throughout DOE will benefit from the development of magnetically enhanced solid/liquid separations for removing fine precipitate particulates to achieve sufficient decontamination factors.
- This technology may be highly valuable for contaminant removal from process wastewater, groundwater, and tank waste streams in enabling the use of newly devised sorbents that are effectively applied by fluidizing them in solution and then settling and/or filtering.
- Magnetic separations may provide an alternative or supplement to settling and cross-flow filtration in addressing solid/liquid separations as a major need area in the Tanks Focus Area (TFA) for the pretreatment of high-level tank wastes.
- This technology may be applied to other solid/liquid separations needs becoming evident in mixed waste and groundwater treatment processes.

This project provides benefit to DOE/EM by

- Evaluating the capabilities of magnetic-seeding filtration for solid/liquid separations.
- Providing data for the application of magnetic separations to precipitation processes.
- Providing useful information for application of magnetic seeding to processes such as treatment of tank supernatants and mixed waste.
- Evaluating the applicability of magnetic separations to specific DOE streams through laboratory testing and pilot testing.

Furthermore, this project, through mathematical modeling and experimental testing, will result in predictive tools for determining the applicability of magnetic-seeding filtration under various operating conditions.

Technology Transfer/Collaborations

The fundamental modeling work is performed at Oak Ridge National Laboratory (ORNL) in collaboration with the Georgia Institute of Technology. This interaction not only serves programmatic goals, but also provides educational training. Collaboration has been initiated with Argonne National Laboratory (ANL) to evaluate/optimize magnetic filtration for removal of magnetic sorbents. In addition, opportunities for teaming with industrial firms are being pursued.

Scientific Background

The technology under development, magnetic-seeding filtration, is based on the interparticle forces that exist in magnetic fields. Particles that have paramagnetic properties (examples are many iron- and cobalt-containing compounds) may be caused to flocculate by the application of a magnetic field;[1-7] in addition, paramagnetic particles and flocs are readily removed by a simple high-gradient magnetic filtration (HGMF) 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,[5,6,7] 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.

There are two keys to particle removal by a magnetic-seeding filtration approach: 1) aggregation of target particles with the seed particles, and 2) removal of the resultant flocs by a magnetic filter. The first process is governed by interparticle forces, including electrostatic, van der Waals, and inertial forces, while the second process involves magnetic susceptibility of particles (or flocs), collector geometry, magnetic field strength and geometry, flow rate, particle-collector interactive forces, etc. The design of an efficient particle removal process depends on the proper selection of operating parameters, including seed-particle type and size, pH, and ionic strength, such that the particles targeted for removal are flocculated with a sufficient number of seed particles to cause them to be removed under the given operating conditions of the magnetic filter, including magnetic field strength, flow rate, and filter geometry. This project aims to develop an understanding of the interplay between each of these process variables such that the magnetic-seeding filtration approach may be effectively applied to DOE waste streams.

Technical Approach

The technical approach taken consists of experimental and theoretical studies aimed at developing magnetic-seeding filtration from a promising, but unproven, technology at the bench scale to applications for treatment of DOE waste streams. Bench-scale testing has been initiated with idealized systems and waste surrogates. Bench-scale tests will progress to samples of actual waste, followed by pilot demonstrations.

Magnetically seeded solid-liquid separations have been investigated experimentally by combining magnetic seeding flocculation under turbulent-shear flow and high-gradient magnetic filtration. Experiments have been conducted with five types of particles: 1) well-characterized, uniform polystyrene microspheres; 2) sodium titanate particles, characteristic of powdered sorbents; 3) Melton Valley Storage Tank (MVST) sludge surrogate particles; 4) ORNL's Radiochemical Engineering and Development Center (REDC) low-level waste suspension surrogate; and 5) solids from precipitation processes developed for treatment of ORNL newly generated liquid low-level waste (NGLLLW). The polystyrene particles provide a model system for more controlled investigation of the effect of process variables and for verification of model development, while the other particles are representative of real systems. The effect of several parameters, such as solution pH and ionic strength, particle size, flow rate, magnetic-field strength, and agitation speed, on the particle removal efficiency were determined.

In parallel with experimental efforts, a theoretical analysis has been undertaken to develop fundamental models that may be used for process optimization and performance prediction. This analysis simulates the magnetic-seeding flocculation and filtration processes, including all known forces on particles under the influence of a magnetic field. A key part of this work will be verification of model predictions by comparison with results from the experimental portion of this work. The predictive model will then be used to design and optimize pilot- and large-scale treatment processes.

Accomplishments

The effect of several process variables on the performance of magnetic-seeding filtration were investigated using the model system of synthetic polystyrene and polystyrene/magnetite (40% by weight) particles.[6,7] Seed-particle concentration, solution pH, and ionic strength—parameters that determine the zeta-potential of particles and thus directly affect the efficiency of flocculation—were found to significantly affect the particle-removal performance. The separation efficiency increased as the size of the particles to be separated increased. Other factors, including flow rate, magnetic field strength, agitation rate, and agitation time had a secondary effect on removal efficiency. It was shown that magnetic-seeding filtration could successfully remove nonmagnetic polystyrene particles from liquid suspensions, resulting in removal efficiencies of greater than 99% at optimized conditions of pH and seed particle concentration.

Additional, and more practical, information regarding the capabilities of magnetic-seeding filtration for effective treatment of DOE waste streams was obtained by experiments conducted with surrogate wastes, particularly the MVST and REDC surrogates.[6,7] These two surrogates are similar in the fact that they consist of submicron particles (average diameters of 0.75 and 0.73 μm, respectively); however, the major difference lies in their magnetic susceptibilities—the MVST particles are diamagnetic (repelled by a magnetic field), and the REDC particles are paramagnetic (attracted by a magnetic field). Results obtained for these two systems are shown in Figures 2 and 3. These figures show the removal efficiency for each type of particle from suspensions containing 100 ppm of particles in simulated waste liquid (pH 13.5 and >5 *M* Na^+ for MVST and

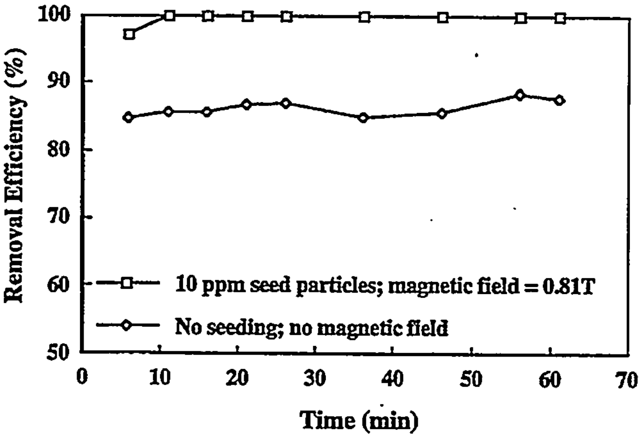

Figure 2. Results obtained in experiments with MVST waste surrogate suspension

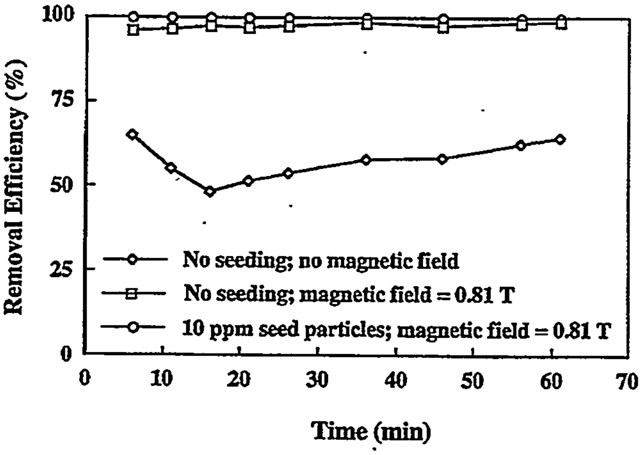

Figure 3. Results obtained in experiments with REDC waste surrogate suspension

pH 13 and ~0.2 *M* Na⁺ for REDC) using small amounts of commercially available black iron oxide as seed particles.

The MVST results (Figure 2) show that without the aid of seed particles and magnetic field, a significant portion of the particles (approximately 50% to 90%) are removed by conventional filtration. It was also found that there is no enhancement of particle removal by the addition of seed particles without an applied magnetic field. However, magnetic-seeding filtration (with 10-ppm seed particles and 0.8 Tesla field strength) removed nearly all (99.7% for the conditions shown) of the fine particles from the MVST suspension. Both addition of seed particles and application of a magnetic field are necessary for effective removal of the diamagnetic particles.

For the REDC suspension (Figure 3), as with the MVST particles, a significant fraction (50% to 75%) of particles are removed without seeding or magnetic field. However, because of the paramagnetic properties of the REDC surrogate particles, magnetic filtration without addition of seed particles, using an applied field of 0.8 Tesla, resulted in removal of 96% to 98% of the particles. Magnetic seeding filtration with the addition of 10-ppm seed particles and 0.8 Tesla magnetic field treated the REDC suspension to detection limits.

Ongoing experiments continue to yield important practical information. For instance, it was found that higher removal efficiencies are achieved using seed particles of smaller size, even with a lower seed-particle concentration. This has practical implications regarding the optimization of applications, both in terms of removal efficiency and in the mass of the final waste form. Experimentation with sodium titanate sorbent particles showed that these particles may also be effectively removed by magnetic seeding flocculation and filtration under the proper conditions, and experiments with ORNL NGLLLW precipitates and magnetic sorbent particles obtained from ANL are ongoing with preliminary positive results. Further experiments are under way using cryogenic magnets, exploring the capabilities for treatment of the surrogate wastes under higher magnetic field strengths (up to 6 Tesla).

Theoretical approaches have been developed to predict the performance of the two key processes in magnetic-seeding filtration.[5,6,7] A model to predict the evolution of particle size and magnetic susceptibility under turbulent-shear flocculation is under development. The collision frequency employed in the model is a function of the rate of turbulent energy dissipation, kinematic viscosity, and size of particles. In addition, a model to predict the performance of a magnetic filter is being developed. The interaction forces between a ferromagnetic wire and a small paramagnetic particle in a uniform magnetic field have been considered, and the force balance equation including gravitational, magnetic, hydrodynamic-drag, and inertial forces has been derived. A particle trajectory equation, suitable for high-gradient magnetic separation, has been obtained by neglecting the inertial force. This trajectory equation has been incorporated in a magnetic-seeding flocculation model. The solution of the trajectory equation provides the critical capture radius, which can then be used in the estimation of the filter performance based on a macroscopic equation.

The modeling results have shown that, as expected, flocculation occurs faster in a turbulent-shear regime than in a Brownian regime. For example, in one case, the percentage of the smallest size class of particles after 2 minutes of flocculation was found to be 83% under Brownian diffusion, while only 47% under turbulent-shear. It has also been shown that particle size plays a major role in particle-particle interactions and particle-collector interactions during filtration. In addition, it was determined that the orientation of the magnetic field plays a significant role in particle collision efficiency and frequency, with a vertical field orientation being optimum. The modeling results will be verified by comparison with the experiments. The product of this work will be a predictive model that can be used to design and optimize pilot- and large-scale treatment processes.

The results of the work conducted to date strongly suggest that this technology has the potential to enhance separations of colloidal particles from waste streams. Other potential applications will be investigated by work in the near future with surrogate suspensions from other systems and actual waste samples obtained from end-users.

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TTP Number OR16C343

Advanced Nuclear Precleaner

Steve R. Wright, InnovaTech, Inc.

EM Focus Area: decontamination and decommissioning

This Phase II Small Business Innovation Research (SBIR) program's goal is to develop a dynamic, self-cleaning air precleaner for high-efficiency particulate air (HEPA) filtration systems that would extend significantly the life of HEPA filter banks by reducing the particulate matter that causes filter fouling and increased pack pressure.

HEPA filters are widely used in DOE, Department of Defense, and a variety of commercial facilities. InnovaTech, Inc. (Formerly Micro Composite materials Corporation) has developed a proprietary dynamic mechanical separation device using a concept called Boundary Layer Momentum Transfer (BLMT) to extract particulate matter from fluid process streams. When used as a prefilter in the HVAC systems or downstream of waste vitrifiers in nuclear power plants, fuel processing facilities, and weapons decommissioning factories, the BLMT filter will dramatically extend the service life and increase the operation efficiency of existing HEPA filtration systems. The BLMT filter is self cleaning, so there will be no degraded flow or increased pressure drop. Because the BLMT filtration process is independent of temperature, it can be designed to work in ambient, medium, or high-temperature applications.

In the Phase I SBIR program, InnovaTech developed airflow theory for submicron exclusion and modified a two-dimensional computerized flow simulation model. We then researched applicable standards and government regulations concerning the application of filtration equipment in the nuclear industry, and demonstrated empirically a reduced-scale prototype filter that exceeded theoretical and analysis expectations. All technical objectives of the Phase I proposal were met.

During Phase II, we are continuing development of the computerized flow simulation model to include turbulence and incorporate expansion into a three-dimensional model that includes airflow behavior inside the filter housing before entering the active BLMT device. A full-scale (1000 ACFM) prototype filter is being designed to meet existing HEPA filter standards and will be fabricated for subsequent testing. Extensive in-house testing will be performed to determine a full range of performance characteristics. Final testing and evaluation of the prototype filter will be conducted at a DOE Quality Assurance Filter Test Station.

InnovaTech, Inc. has approximately 3600 ft^2 of R&D and manufacturing space in an office and laboratory building near Research Triangle Park, North Carolina. InnovaTech has basic and advanced materials and mechanical engineering lab equipment sufficient to meet any project objectives.

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Template-Mediated Synthesis of Periodic Membranes for Improved Liquid-Phase Separations

Howard Groger, American Research Corporation of Virginia

EM Focus Areas: subsurface contaminants

Technology Description

Solid/liquid separations of particulates in waste streams will benefit from design and development of ultrafiltration (UF) membranes with uniform, tailorable pore size and chemical, thermal, and mechanical stability. Such membranes will perform solid/liquid separations with high selectivity, permeance, lifetime, and low operating costs. Existing organic and inorganic membrane materials do not adequately meet all these requirements. An innovative solution to the need for improved inorganic membranes is the application of mesoporous ceramics with narrow pore-size distributions and tailorable pore size (1.5 to 10 nm) that have recently been shown to form with the use of organic surfactant molecules and surfactant assemblies as removable templates. This series of porous ceramics, designated MCM-41, consists of silica or aluminosilicates distinguished by periodic arrays of uniform channels.

In this Phase I Small Business Innovation Research program, American Research Corporation of Virginia will demonstrate the use of supported MCM-41 thin films, deposited by a proprietary technique, as UF membranes. Technical objectives include deposition in thin, defect-free periodic mesoporous MCM-41 membranes on porous supports; construction of a fully instrumented membrane test unit; measurement of membrane separation factors, permeance, and fouling; and measurement of membrane lifetime as part of an engineering and economic analysis.

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5. Thursday Presentations

☐ Inorganic Chemically Active Adsorbents (ICAAs)
☐ TUCS/Phosphate Mineralization of Actinides
☐ Mercury and Tritium Removal from DOE Waste Oils
☐ Metal-Binding Silica Materials for Wastewater Cleanup
☐ A Novel Fiber-Based Adsorbent Technology
☐ Self-Assembled Monolayers (SAMMS) on Mesoporous Supports for RCRA Metal Removal
☐ Simultaneous Treatment of Chlorinated Organics and Removal of Metals and Radionuclides with Bimetals and Complexing Acids—Application to Surfactant Solutions
☐ Recyclable Bio-Reagent for Rapid and Selective Extraction of Contaminants from Soil
☐ Innovative Methods to Stabilize Liquid Membranes for Removal of Radionuclides from Groundwater
☐ A New Separation and Treatment Method for Soil and Groundwater Restoration

Inorganic Chemically Active Adsorbents (ICAAs)

Moonis R. Ally, Oak Ridge National Laboratory; Larry Tavlarides, Syracuse University

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

Technology Needs

DOE is focusing attention on technologies to remediate its existing facilities because of public awareness of environmental issues and environmental regulations. This project responds directly to the ESP-CP needs statement for the Mixed Waste, Subcon, and D&D Focus Areas.

Technology Description

Oak Ridge National Laboratory (ORNL) researchers are developing a technology that combines metal chelation extraction technology and synthesis chemistry. We begin with a ceramic substrate such as alumina, titanium oxide or silica gel because they provide high surface area, high mechanical strength, and radiolytic stability. One preparation method involves silylation to hydrophobize the surface, followed by chemisorption of a suitable chelation agent using vapor deposition. Another route attaches newly designed chelating agents through covalent bonding by the use of coupling agents. These approaches provide stable and selective, inorganic chemically active adsorbents (ICAAs) tailored for removal of metals.

Benefits to DOE/EM

The technology has the following advantages over ion exchange:

- higher mechanical strength
- higher resistance to radiation fields
- higher selectivity for the desired metal ion
- no cation exchange
- reduced or no interference from accompanying anions
- faster kinetics
- easy and selective regeneration.

Target waste streams include metal-containing groundwater/ process wastewater at ORNL's Y-12 Plant (multiple metals), Savannah River Site (SRS), Rocky Flats (multiple metals), and Hanford; aqueous mixed wastes at Idaho National Engineering Laboratory (INEL); and scrubber water generated at SRS and INEL. Focus Areas that will benefit from this research include Mixed Waste, and Subsurface Contaminants.

Technology Transfer/Collaboration

Based on laboratory studies of other ICAAs for the removal of Pb, Cu, and Cd, 3M has expressed interest in manufacturing and commercial sales of these materials. The DOE-sponsored research will provide data on new materials that may lead to a commercial product within 5 years. No commercial partner is needed at this stage, but it is possible to leverage DOE resources with private sector funding in FY 1998 or FY 1999.

Technical Approach

The materials that we want to synthesize are discretely different from ion exchange materials. The latter operate by exchanging one type of ion for another. Inorganic chemically active materials uptake cations or anions via a reversible chelation reaction. Uptake of ions takes place in the forward reaction, and the ions are released when the reaction is made to reverse itself, thereby regenerating the material for the next cycle. Unique selective properties are engineered into these materials by considering the donor atoms within the molecular structure of the chelating agent, the nature of the metal ion species, and pore geometry of the ceramic substrate. The material is tailored to permit uptake of cations or anions from solution, and their subsequent recovery, over many cycles. The reversible chelation reactions and mass transfer processes that govern the uptake and release of cations or anions indicate greater capacity and faster kinetics than that for ion exchange materials.

Scientific Background

One strategy to achieve the specificity is to design and synthesize multidented ligands with mixed donor atoms with appropriate spatial arrangements on the support surfaces. Two methods of preparation are vapor deposition and covalent bonding. In the former approach, surface modification of the substrate by titanium coating and/or silyization with organo-functional silanes is followed by chemisorption of suitable chelating agents using vapor deposition. The latter approach attaches desired functional groups of chelating molecules to the supports through covalent bonding by using silane coupling agents.

Unique selective properties can be engineered into these materials by considering aspects of coordination chemistry such as donor atoms within the molecular structure of the chelating agent, metal-ligand complex geometry, and the nature of the metal ion species. These factors are integrated with the support properties of pore diameter, porosity, and silanol group (-OH) density to develop suitable ICAAs.

Two methods of covalent attachment will be considered:

1. Chelate-functional silanes will be prepared by reacting derivatives of a desired chelating agent with the appropriate silane coupling agents in a separate step. These chelate-functional silanes will be attached to the surface to achieve high surface coverage density of the chelating groups.
2. Silane coupling agents will be attached to the surface followed by coupling of the chelating agent.

Selection of one method over another will depend on the ability of the silane coupling agent, chelating agent and chelate-functional silanes to access the silanol groups within the substrate pores as a result of their molecular size and viscosity. Because siloxane bonds exhibit lower stability in highly alkaline solutions, organofunctional titanates can be employed to replace siloxane bonds (Si-O-Si-C) by Si-O-Ti-C or Si-O-Ti-Si-C to increase the stability. High coverage density composite materials will be synthesized, which will permit high uptake of ions from solution and their subsequent recovery over many cycles.

Characterization of ICAAs is performed with Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRFT-IR) and ^{29}Si Nuclear Magnetic Resonance (NMR) to provide structural information on successful covalent bonding of chelating agents on to the substrate. These studies will be performed primarily by Professor Larry Tavlarides' staff at Syracuse University. Further characterization of the ICAAs under conditions typically found in industry and for DOE applications will be done at ORNL, where facilities exist for adsorption column tests, wide range of analytical services, and automated equipment.

Accomplishments

This project is a new start. To date, four ligands have been selected, and four ICAAs materials have been synthesized for the removal of cobalt from waste solutions. These materials will undergo testing at ORNL within the coming months. Additional materials for the removal of chromium are also planned later in the fiscal year.

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TTP Number OR16C344

TUCS/Phosphate Mineralization of Actinides

Kenneth L. Nash, Argonne National Laboratory

EM Focus Area: subsurface contaminants

Technology Need

Most of the radionuclides in buried waste disposal trenches (or otherwise dispersed in the environment) are sorbed on surfaces. These surfaces may be metallic, organic (paper and plastic), or mineral in nature. The chemical form of the sorbed radionuclides is extremely variable, ranging from rather intransigent oxide films to potentially soluble metal nitrate residues. The principal vector for insertion of radionuclides into the biosphere is groundwater movement, which is an important concern for certain species.

An approach to isolating radionuclides from the hydrosphere that is receiving increasing attention is in situ immobilization. Rather than removing the actinides from contaminated soils, this strategy transforms the actinides into intrinsically insoluble mineral phases resistant to groundwater leaching. 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 challenges of this approach are to accomplish the immobilization without causing collateral damage to the environment and to verify system performance.

The mineralization concept represents 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 by other technologies. The process could be applied to waste disposal sites (used either before or after burial) like Hanford and Idaho, areas of accidental environmental contamination (Fernald, Rocky Flats), or even to stabilize heavy metals in commercial mill tailings piles.

Technology Description

This program has as its objective the development of a new technology that combines cation exchange and mineralization to reduce the concentration of heavy metals (in particular actinides) in groundwaters. The treatment regimen must be compatible with the groundwater and soil, potentially using groundwater/soil components to aid in the immobilization process. The delivery system (probably a water-soluble chelating agent) should first concentrate the radionuclides then release the precipitating anion, which forms thermodynamically stable mineral phases, either with the target metal ions alone or in combination with matrix cations. This approach should generate thermodynamically stable mineral phases resistant to weathering. The chelating agent should decompose spontaneously with time, release the mineralizing agent, and leave a residue that does not interfere with mineral formation. For the actinides, the ideal compound probably will release phosphate, as actinide phosphate mineral phases are among the least soluble species for these metals. 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 phosphate to foster formation of crystalline mineral phases.

Benefits to DOE/EM

Because it involves only the application of inexpensive reagents, the method of 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 increased 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 groundwaters 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.

Technology Transfer/Collaborations

We have an ongoing collaboration with Eichrom Industries, Inc., (Darien, IL), who have successfully marketed various separations technologies developed within our group. They have expressed an interest in providing reagents and treatment protocols for the eventual application of this technology, but do not presently have the personnel or expertise to perform any in situ demonstrations. We may need an additional partner to handle the eventual application.

We have made contact with the U.S. Department of Agriculture laboratory in Peoria, Illinois, regarding the potential availability of inexpensive supplies of phytic acid. Our collaboration with the Fernald Environmental Management Project allowed us to obtain a soil sample (currently scheduled for disposal at Fernald) on which we completed a fully successful demonstration of the efficacy of phytic acid cation exchange. Unfortunately, the technology will apparently not be applied at Fernald because of cost considerations. We are currently in contact with Idaho National Engineering Laboratory (INEL) for a second lab-scale test using samples from that site. Both soil and groundwater contaminated with transuranic elements are known to exist at INEL.

Scientific Background

Unplanned releases and direct discharges have contaminated soils and waters at many DOE sites. At some sites, planned disposal of materials contaminated with radionuclides into landfills or directly to soil 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 of groundwater through underlying geologic strata. This pathway represents a potential direct route for invasion of the biosphere by radioactive metal ions. The long-lived radionuclides typically considered to have the greatest potential for environmental mobility are ^{3}H, ^{99}Tc, $^{134-137}Cs$, ^{129}I, and the actinides in their upper oxidation states (V and VI). The current focus of this program is on the actinides.

The variety of oxidation states of the actinides impacts their potential for mobility in the environment. For Th through Pu (except for Pa, which is not considered in this program), the most common oxidation state in the solid state is the tetravalent, though there are known solid compounds of U(VI). The dominant solution phase species for U, Np, and Pu are the pentavalent or hexavalent oxidation states, which exist in aqueous solution as the dioxocations. Am and Cm exist exclusively in the trivalent state under environmentally relevant conditions. The trivalent, tetravalent, and hexavalent oxidation states are strongly complexed by several naturally occurring ligands (carbonates, humics, hydroxide) and man-made complexants (such as EDTA); moderately complexed by sulfate, fluoride, and phosphate; and weakly complexed by chloride. Carbonate complexes extend the solubility of hexavalent actinides to very high pH. Most free ions are moderately to strongly sorbed on mineral surfaces, but complexation by water-soluble chelating agents can interfere with this process. The pentavalent oxidation state, which is dominant under a wide range of conditions for Np and in near neutral pH for Pu, is neither strongly complexed nor readily precipitated and so has the greatest inherent potential for environmental mobility.

Under reducing conditions, actinide (III) or (IV) hydroxides, oxides, hydroxycarbonates, or carbonates are the most probable "naturally occurring" stable mineral phases (in near-surface waters). Phosphates, vanadates, and aluminosilicates mineral phases are common in the subsurface, but less common as matrices for freshly precipitated actinides. Under oxidizing conditions, U, Np, and Pu exist in the V and VI oxidation states, which typically exhibit higher solubility limits. Under environmental conditions of pH and E_h (redox potential), there is substantial evidence that the pentavalent oxidation state of Pu is the thermodynamically favored oxidation state for Pu in solution. Neptunium favors the pentavalent oxidation state under a wider variety of conditions. In the pentavalent oxidation state, the actinides are weakly complexed by common complexants, not strongly hydrolyzed, and poorly retained by mineral surfaces. Increasing the thermodynamic driving force for immobilizing these elements is therefore critical for minimizing the potential for their migration in the environment.

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, Th, and U 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 support the low solubility of *f* element phosphates (particularly in the III and VI valence state). Coupled with the relative ease of delivery of phosphate as an organophosphorus complexant, these observations led us to believe that phosphate mineralization was the best approach to in situ isolation of actinides.

Technical Approach

The task has as its objectives 1) identification of a hydrolytically unstable organophosphorus complexant and demonstration of its decomposition 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. Verifying reduced 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. Identifying potential complications in the process and limitations in its applicability is also a goal of this research.

As conceived initially, this program was to rely on the class of compounds we call Thermally Unstable Complexants (TUCS). These ligands, diphosphonic acid chelating agents designed to spontaneously decompose on demand, proved too robust for our purpose under environmental conditions. The organophosphate complexing agent phytic acid (myo-inositol (hexakisphosphoric acid)) was then identified as a potential substitute for the phosphonate chelating agents. Phytic acid, in fact, 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 a readily hydrolyzed releasing phosphate, and the organic residue (inositol) does not complex metal ions and hence will not interfere with the mineralization process. It also possesses good microbial nutrient properties and could conceivably be used in connection with a bioremediation strategy (though such an application is beyond the present scope of this program).

During the first year of this research program (FY 1995), we identified the natural product phytic acid as a species having the desired attributes and determined its rate of hydrolysis (in the absence of microbial action). Its hydrolytic lifetime was established at 100 to 150 years at 25°C and pH 5 to 6. This relatively long lifetime led us to consider in greater detail the possibility of using insoluble phytates as cation exchange media for actinides. We also identified (experimentally and by calculation) the most probable actinide phosphate mineral phases that control solubility and demonstrated the generation of phosphate minerals as a result of phytate decomposition. Using radiotracer techniques, we established phosphate control of Eu^{3+} and Am^{3+} solubility at the 10^{-9} to 10^{-10} *M* concentration range and uranyl solubility control at 10^{-7} to 10^{-8} *M*. The former result was consistent with thermodynamic calculations, the latter actually exceeded the predictions of thermodynamic data at high pH (i.e., uranyl concentrations were lower than predicted). The process was less effective for Np(V) control, achieving [Np(V)] about 10^{-6} *M* at pH 7 to 8 and 1 mM total phosphate but having relatively little effect at lower pH and phosphate concentrations.

Our programmatic objectives for FY 1996 included 1) examination of the cation exchange behavior of calcium phytate, 2) exploration of the effect of coprecipitation mechanisms for enhanced stability of the solid, and 3) completion of a test of the process for controlling uranium solubility in soil from the Fernald site (in the laboratory). The following text will demonstrate that the addition of calcium at 10^{-3} to 10^{-2} *M* reduces the solubility of Np(V) to below 10^{-6} *M* at pH <7, that $Ca_{4.5}H_3$(phytate) is an effective cation exchanger for U(VI) and Np(V) between pH 5 and 8, and that phytic acid is more effective on a per equivalents basis than freshly precipitated hydroxyapatite for reducing soluble uranium concentrations in contact with soil from the Fernald site.

Accomplishments

As a part of our FY 1996 research effort, calcium was added to the phosphate systems studied previously to examine the effect of this important groundwater cation. It was anticipated that calcium ion will facilitate the precipitation of actinides through either sorption or coprecipitation processes. In the absence of phosphate (work completed in FY 1995), uranyl concentration in the synthetic groundwater increases with pH from 5 to 8, probably a result of carbonate complexing. At both 10^{-4} and 10^{-3} *M* total phosphate, uranyl concentrations decline by about an order of magnitude. Changing pH has a relatively minor effect on uranyl concentrations. Addition of Ca^{2+} at 10^{-3} to 10^{-2} *M* further decreases the uranyl concentration, though the relationship appears to be somewhat complex. The data suggest a consistent correlation of minimum uranyl concentrations at pH 7 for all solutions. At higher pH, the uranyl concentrations rise slightly, perhaps due to carbonate complexation, but this effect may be related to two-phase equilibria of the solubility controlling species.

Neither calcium nor phosphate has much effect on Np(V) concentrations at pH 5 to 6 and most calcium/phosphate concentrations. At pH 6, 10 mM Ca^{2+}, 1.0 mM PO_4^{3-}, the highest concentrations of each, the Np(V) concentration is reduced by nearly a factor of 50 to about 10^{-6} *M*. At 0.1 mM phosphate and pH 7 to 8, an increase in the calcium concentration from 1.0 to 10 mM lowers [Np(V)] by about a factor of 2. At 1.0 mM total phosphate, the impact of an order of magnitude increase in $[Ca^{2+}]_t$ is much greater, leading to [Np(V)] at 10^{-7} *M* for pH 7, 1.0 mM PO_4^{3-}, 10.0 mM Ca^{2+}. We observed white solids in the samples at higher pH, which were identified by X-ray diffraction as calcium hydroxyapatite, but hydroxyapatite is known to readily incorporate foreign cations into its matrix. We therefore cannot say whether the reduced Np concentrations result from coprecipitation, double salt formation, or sorption phenomena.

Our tests of the cation exchange behavior of a calcium phytate was divided into three phases: characterizing solid calcium phytates, adding a mixture of soluble calcium and uranyl to a sodium phytate solution, and examining uranyl cation exchange onto the previously characterized calcium phytate. In the first stage of these experiments, the dominant calcium phytate solid species was identified as $(Ca_{4.6}Na_{0.20}H_{2.6}(CH(PO))_6 \cdot 6.5H_2O$, independent of the initial ratio of Ca:phytate. In the study of uranyl exchange for Ca on phytate, we determined that uranyl does substitute for Ca on phytic acid whether prepared from homogeneous aqueous solution or by the liquid-solid contact method. Substitution up to 96% of the theoretical maximum of 6 equivalents was observed without any indication of resolubilization of the uranyl phytate.

Our initial test of this process with actual soil samples involved addition of calcium phytate, sodium phytate, or hydroxyapatite to a Fernald soil sample in contact with synthetic groundwater containing radiotracer uranium. Equilibrium was apparently rapidly achieved in the laboratory in these two-phase experiments. Substitution of 4% (each) hydroxyapatite reduces uranyl concentrations by about a factor of 2, calcium phytate tenfold, and sodium phytate by $>10^3$. The relative effects of higher and lower weight percents of these three materials indicated (somewhat surprisingly) that hydroxyapatite has generally little impact on uranyl concentration even at 10% while calcium phytate and sodium phytate are 100 times more effective under most conditions (Figure 1). Experiments at the highest sodium phytate concentrations suggest that soluble phytate at high concentrations may slightly increase the concentration of uranyl in solution, though even under these conditions, the phytate isolation mechanism is clearly superior to hydroxyapatite.

The relative effectiveness of calcium phytate and hydroxyapatite is particularly striking and potentially important. Hydroxyapatite ($Ca_{10}(OH)_2(PO_4)_6$, formula weight 1004.8 g/mol) is under consideration at several DOE environmental restoration sites (including Fernald and Hanford) as a soil additive to reduce the environmental mobility of radionuclides, including actinides. Hydroxyapatite could function as a potential source of phosphate

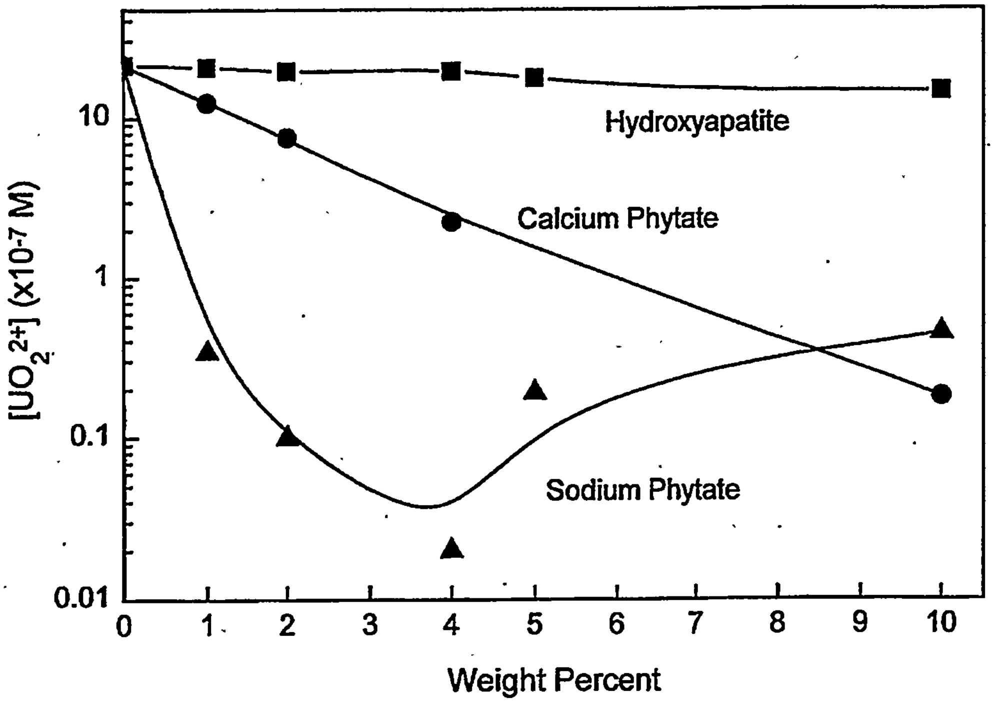

Figure 1. Effect of phytate and hydroxyapatite on uranyl concentrations in groundwater contacted with glacial till soil from Fernald

for direct actinide mineralization, but, the low solubility product of hydroxyapatite (log $K_{sp} = -58.33$ - $K_{sp} = [Ca^{2+}]_5[OH][PO_4^{3-}]_3$) probably maintains phosphate at too low a concentration for this mechanism to be very important. It is likely that the principal mechanism for actinide solubility control by hydroxyapatite is surface sorption. Our tests with Fernald soil in the laboratory indicate that this process is not very effective, at least under the conditions we examined. As the relative percentages of phosphate in hydroxyapatite and calcium phytate is similar (57% versus 60% by weight), the difference between the two media cannot be attributed to the amount of phosphate present. The phosphate in phytic acid clearly is in a more suitable form for metal ion sequestration, almost certainly reflecting the more favorable orientation of the phosphate groups in phytate as compared with hydroxyapatite. We can conclude that chelation/precipitation is a superior mechanism to surface sorption for uranium sequestration.

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TTP Number CH26C322

Mercury and Tritium Removal from DOE Waste Oils

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EM Focus Areas: mixed waste characterization, treatment, and disposal; subsurface contaminants

Technology Need

Tritium processing in the past at the Savannah River Site (SRS) has generated significant quantities of tritium-contaminated vacuum pump oil. Current operations generate 9000 L of oil each year; the backlog for treatment is 78,000 L. The SRS incinerator can process oils, but the annual limit for tritium is 1200 Ci, and the typical oil contains 20 Ci/L. A method for separating tritium (dissolved gas, tritiated water, or tritiated hydrocarbons) from these highly contaminated oils is needed to ensure their timely disposal. Mercury is also present in the vacuum, and Resource Conservation and Recovery Act levels for mercury (0.2 mg/L to 260 mg/L) have been exceeded; it is believed that mercury is present as elemental mercury in the oil. Successful removal of mercury from these oils would benefit the other sites, because the Mixed Waste Inventory Database lists 17,300 m^3 of waste oils contaminated with mercury being stored on DOE sites.

Technology Description

This work covers the investigation of vacuum extraction as a means to remove tritiated contamination as well as the removal via sorption of dissolved mercury from contaminated oils. The radiation damage in oils from tritium causes production of hydrogen, methane, and low-molecular-weight hydrocarbons.[1,2] When tritium gas is present in the oil, the tritium atom is incorporated into the formed hydrocarbons. The transformer industry measures gas content/composition of transformer oils as a diagnostic tool for the transformers' condition.

The analytical approach (ASTM D3612-90) used for these measurements is vacuum extraction of all gases (H_2, N_2, O_2, CO, CO_2, etc.) followed by analysis of the evolved gas mixture. This extraction method will be adapted to remove dissolved gases (including tritium) from the SRS vacuum pump oil. It may be necessary to heat (60°C to 70°C) the oil during vacuum extraction to remove tritiated water. A method described in the procedure is a stripper column extraction, in which a carrier gas (argon) is used to remove dissolved gases from oil that is dispersed on high surface area beads. This method appears promising for scale-up as a treatment process, and a modified process is also being used as a dewatering technique by SD Myers, Inc. (a transformer consulting company) for transformers in the field by a mobile unit.

The vacuum extraction process is being tested and the conditions optimized for removing dissolved gases and water from oil. To some extent, mercury will also be removed in the process. Removal efficiency will be determined by pre- and post-analyses. Mathematical correlations will be developed to allow large-scale design of the process.

Although some mercury may be removed during the vacuum extraction, the most common technique for removing mercury from oil is by using sulfur-impregnated activated carbon (SIAC). SIAC is currently being used by the petroleum industry to remove mercury from hydrocarbon mixtures, but the sorbent has not been previously tested on DOE vacuum oil waste. It is anticipated that a final process will be similar to technologies used by the petroleum industry and is comparable to ion exchange operations in large column-type reactors; the sorption process on SIAC proceeds by the formation of tight, covalent sulfur-mercury bonds on the surface of the material. Under ideal conditions, the mercury capacity of the sorbent may be as high as 25% by weight.

The fluid-flow properties of the DOE vacuum oil wastes are likely to be quite different from the low-molecular weight hydrocarbons being used in industrial applications. It is necessary to gather rate and mass transfer information from laboratory experiments to scale-up the process for demonstration or full-scale use. It is anticipated that overall performance of this process may be enhanced by controlling factors such as sorbent particle size, temperature, viscosity, etc. Additional cofactors, including an easily recoverable solvent, will enhance fluid flow as well.

Another technique recently explored in the petroleum industry has been the use of hydrogen sulfide as a "scrubbing gas" for removal of elemental mercury from liquid hydrocarbons. Although this procedure is relatively untested and experimental, this project will include a few laboratory studies using the procedure.

Benefit to DOE/EM

Successful demonstration of tritium removal would allow reduction of mixed-waste inventory and treatment of currently generated waste. Successful removal of mercury from oils from SRS would benefit the other DOE sites where mercury-contaminated waste oils are being stored.

Technology Transfer/Collaborations

None at this point. Collaborations may be initiated with SD Myers, Inc. for design of large-scale vapor extraction system.

Technical Approach

The work is divided into three elements:

- **Screening Experiments.** In these experiments the technologies (vacuum extraction and mercury sorption) will be tested. Tritium and mercury will be measured before and after treatment via direct counting and cold vapor atomic absorption, respectively. The experiments will be carried out on actual waste from SRS.
- **Bench-Scale Experiment.** In this task a small benchtop unit will be designed for testing at DOE sites. The experiments carried out will determine size and configuration of the equipment.
- **Field-Scale Testing.** A unit will be constructed and tested on actual waste. The data collected will be used to estimate feasibility and cost of a large-scale implementation.

Accomplishments

The waste has been sampled and was shipped in December 1996.

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TTP Number OR17C332

Metal-Binding Silica Materials for Wastewater Cleanup

Franklin O. Kroh, TPL, Inc.

EM Focus Areas: subsurface contaminants

Technology Description

In this Phase I Small Business Innovation Research program, TPL, Inc. is developing two series of high-efficiency covalently modified silica materials for removing heavy metal ions from wastewater. These materials have metal ion capacities greatly exceeding those of commercial ion exchange resins. One series, containing thiol groups, has high capacity for "soft" heavy metal ions such as Hg, Pb, Ag, and Cd; the other, containing quaternary ammonium groups, has high capacity for anionic metal ions such as pertechnetate, arsenate, selenite, and chromate. These materials have high selectivity for the contaminant metals and will function well in harsh systems that inactivate other systems.

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A Novel Fiber-Based Adsorbent Technology

Thomas A. Reynolds, Chemica Technologies, Inc.

EM Focus Areas: subsurface contaminants; mixed waste characterization, treatment, and disposal

Technology Description

In this Phase I Small Business Innovation Research program, Chemica Technologies, Inc. is developing an economical, robust, fiber-based adsorbent technology for removal of heavy metals from contaminated water. The key innovation is the development of regenerable adsorbent fibers and adsorbent fiber cloths that have high capacity and selectivity for heavy metals and are chemically robust. The process has the potential for widespread use at DOE facilities, mining operations, and the chemical process industry.

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Self-Assembled Monolayers on Mesoporous Supports (SAMMS) for RCRA Metal Removal

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EM Focus Area: mixed waste characterization, treatment, and disposal

Technology Needs

The Mixed Waste Focus Area has declared mercury removal and stabilization as the first and fourth priorities among 30 prioritized deficiencies.[1] Resource Conservation and Recovery Act (RCRA) metal and mercury removal has also been identified as a high priority at DOE sites such as Albuquerque, Idaho Falls, Oak Ridge, Hanford, Rocky Flats, and Savannah River.[2-4]

Existing technologies for RCRA metal and mercury removal from diluted wastewater include sulfur-impregnated carbon,[5] microemulsion liquid membranes,[6] ion exchange,[7] and colloid precipitate flotation.[8] In the sulfur-impregnated carbon process, metal is adsorbed to the carbon, not covalently bound to the matrix. The adsorbed metal needs secondary stabilization because the metal-laden carbon does not have the desired long-term chemical durability because of the weak bonding between metal and active carbons. In addition, a large portion of the pores in the active carbon is large enough for the entry of microbes to solubilize the mercury-sulfur compounds. The RCRA metal loading is not as high as that of mesoporous-based materials.

The microemulsion liquid membrane technique uses an oleic acid microemulsion liquid membrane containing sulfuric acid as the internal phase to reduce the wastewater mercury concentration from 460 ppm to 0.84 ppm.[6] However, it involves multiple steps of extraction, stripping, demulsification, and recovery of mercury by electrolysis with use of large volumes of organic solvents. The liquid membrane swelling has a negative impact on extraction efficiency. The slow kinetics of the RCRA metal-ion exchanger reaction requires long contacting time. This process also generates large volumes of organic secondary wastes.

The ion exchange process[7] uses Duolite™ GT-73 ion exchange organic resin to reduce the mercury level in wastewater from 2 ppm to be below 10 ppb, but oxidation of the resin results in substantially reduced resin life and an inability to reduce the Hg level to below the permitted level. Hg loading is also limited, and the Hg-laden organic resin does not have the ability to resist microbe attack, and Hg can be released into the environment if it is disposed of as a waste form.

The reported removal of RCRA metal from water by colloid precipitate flotation reduces mercury concentration from 160 ppb to about 1.6 ppb.[8] This process involves the addition of HCl to adjust the wastewater to pH 1, addition of Na_2S and oleic acid solutions to wastewater, and removal of colloids from the wastewater. In this process, the treated wastewater is potentially contaminated with the Na_2S, oleic acid, and HCl by treatment itself. The separated mercury needs further treatment to be stabilized as a permanent waste form for disposal.

No existing technologies have been developed for removing mercury from pump oil. Some preliminary laboratory study of a zinc powder/filtration process was carried out by the Pantex Plant with certain success, but the work was discontinued due to losses of key personnel.[3]

Technology Description

Under this task, a proprietary new technology, Self-Assembled Monolayers on Mesoporous Supports (SAMMS), for RCRA metal ion removal from aqueous wastewater and mercury removal from organic wastes such as vacuum pump oils is being developed at Pacific Northwest National Laboratory (PNNL).

The six key features of the SAMMS technology are 1) large surface area (>900 m^2/g) of the mesoporous oxides

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

(SiO_2, ZrO_2, TiO_2) ensures high capacity for metal loading (more than 1 g Hg/g SAMMS); 2) molecular recognition of the interfacial functional groups ensures the high affinity and selectivity for heavy metals without interference from other abundant cations (such as calcium and iron) in wastewater; 3) suitability for removal of mercury from both aqueous wastes and organic wastes; 4) the Hg-laden SAMMS not only pass TCLP tests, but also have good long-term durability as a waste form because the covalent binding between mercury and SAMMS has good resistance to ion exchange, oxidation, and hydrolysis; 5) the uniform and small pore size (2 to 40 nm) of the mesoporous silica prevents bacteria (>2000 nm) from solubilizing the bound mercury; and 6) SAMMS can also be used for RCRA metal removal from gaseous mercury waste, sludge, sediment, and soil.

Benefits to DOE/EM

The development of SAMMS technology benefits DOE/EM in providing opportunities for "breakthroughs" for RCRA metal and mercury removal/stabilization with significant cost and time reduction in the environmental restoration efforts. PNNL has been working with the Y-12 Mercury Reduction Program of Martin Marietta Energy Systems, Inc., in developing plans to demonstrate SAMMS technology for removal of mercury from the legacy wastewater slated for treatment at the Central Pollution Control Facility, and/or the shallow groundwater and base sump water at Y-12 plant at Oak Ridge. Oak Ridge also expressed interest in demonstrating SAMMS for the removal of Hg from gaseous waste streams in the thermal treatment of Oak Ridge Hg wastes and from inorganic solids before thermal treatment. Discussions are also under way with Westinghouse Savannah River Company regarding the removal of Hg from the tritiated pump oil at the Savannah River Site (SRS). A proposal was also submitted for removing Hg from the KI/I2 leachates and soils using SAMMS technology.

Scientific Background

The SAMMS materials are based on self-assembly of functionalized monolayers on mesoporous oxide surfaces. Figure 1 shows the TEM micrograph of the mesoporous silica and a schematic of the SAMMS material.

Self-Assembled Functional Groups on Oxide Surfaces

The self-assembled monolayer interface provides three important functions: 1) molecular recognition for metals, 2) covalent bonding to the support materials, and 3) high population density of the functional groups on the substrate surfaces.

Molecular self-assembly is a unique phenomenon in which functional molecules aggregate on an active surface, resulting in an organized assembly having both order and orientation.[9-11] In this approach, bifunctional molecules containing a hydrophilic head group and a hydrophobic tail group adsorb onto a substrate or an interface as closely packed monolayers. The driving forces for the self-assembly are the inter- and intra-molecular interactions between the functional molecules (such as van der Waals forces). The tail group and the head group can be chemically modified to contain certain functional groups to promote covalent bonding between the functional organic molecules and the

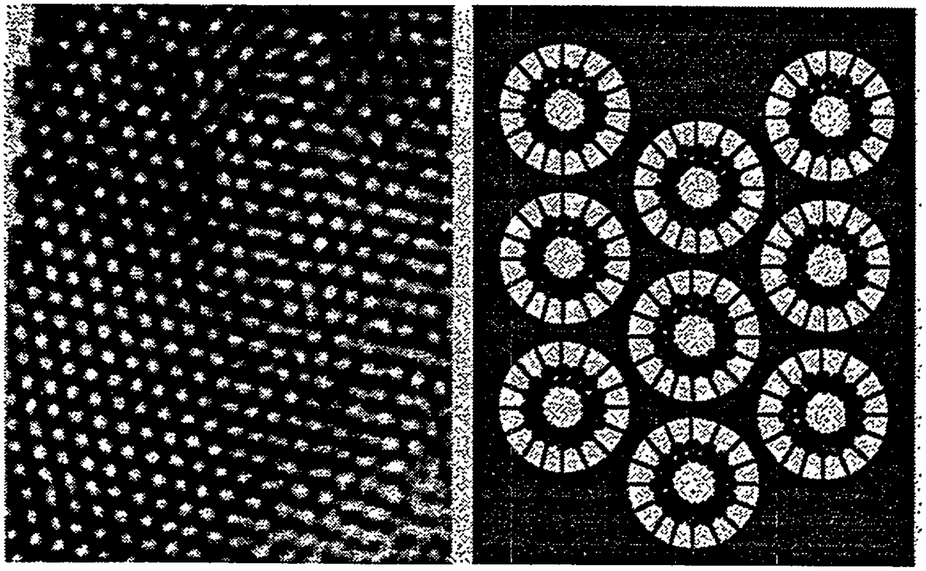

Figure 1. (Left) TEM micrograph of the mesoporous silica support, showing uniform and ordered porosity. (Right) Self-assembled monolayers on mesoporous silica, with mercury bonded by the functional groups.

substrate on one end, and molecular bonding between the organic molecules and the metals on the other.[9] By populating the outer interface with specific functional groups, an effective means for scavenging heavy metals is made available. The metal-loading capability is determined by the available surface area of the underlying inorganic support. A high surface area support allows for high RCRA metal loading.

High-Surface Mesoporous Supports

The unique mesoporous oxide supports provide high surface area (>900 m^2/g), thereby enhancing the metal loading capacity. They also provide an extremely narrow pore size distribution, which can be specifically tailored from 15 Å to 400 Å, thereby minimizing biodegradation from microbes and bacteria. Mesoporous structures can be disposed of as stable waste forms.

The porous supporting materials used in this research (SiO_2, ZrO_2, TiO_2) are synthesized through a co-assembly process using oxide precursors and surfactant molecules.[12-15] The material synthesis is accomplished by mixing surfactants and oxide precursors in a solvent and reacting the solution under mild hydrothermal conditions. The surfactant molecules form ordered liquid crystalline structures, such as hexagonally ordered rod-like micelles, and the oxide materials precipitate on the micellar surfaces to replicate the organic templates formed by the rod-like micelles. Subsequent calcination to 500°C removes the surfactant templates and leave a high surface area oxide skeleton. The pore size of the mesoporous materials is then determined by the rod-like micelles, which are extremely uniform. Using different chain length surfactants produces mesoporous materials with different pore sizes.

Separation Performance

The most important separation performance features of SAMMS are:

- **High RCRA Metal Loading.** The large surface area of the mesoporous oxides (>900 m^2/g) ensures high capacity for metal loading (more than 1 g mercury per gram of SAMMS)
- **High Selectivity.** Self-assembled functional groups provide the high affinity and selectivity for RCRA metals such as Hg, Ag, Pb, Cd, Ni, and Co without interference from other abundant cations (such as alkaline and alkaline earths) in wastewater and in soils.
- **High Flexibility.** SAMMS bind different forms of mercury, including metallic, inorganic, organic, charged, and neutral compounds; suitability for removal of mercury from both aqueous and organic wastes such as vacuum pump oils; applicability to clean up not only wastewater, but also gaseous wastes, sludge, sediment, and soil.
- **Stable Waste Form.** The mercury-loaded SAMMS not only pass TCLP tests, but also have good long-term durability as a waste form because 1) the covalent binding between mercury and SAMMS has good resistance in ion-exchange, oxidation, and hydrolysis over a wide pH range, and 2) the uniform and small pore size (2 to 40 nm) of the mesoporous silica prevents bacteria (at least 2000 nm in size) from solubilizing the bound mercury (microbes are mainly responsible for solubilizing the mercury compounds in the environment into the deadly methylmercury). The SAMMS technology is superior to many existing technologies because of the direct generation of a stable waste form that does not require secondary treatment.
- **Fabrication Versatility.** The SAMMS materials can be also fabricated into various engineering forms such as pellets, columns, or films. They have good mechanical strengths and are very durable and stable in air and in aqueous solution.

No secondary wastes will be generated during the application of SAMMS for clean up because no chemicals, washing solution, regeneration, and secondary treatment are involved. The RCRA metal-laden SAMMS can be disposed as nonhazardous solid wastes directly.

Cost Estimates

The life-cycle cost of the SAMMS technology is expected to be much lower than the current technology because it is simple to apply, no secondary wastes are generated, no secondary treatment is needed, and the RCRA metal-laden SAMMS can be disposed as nonhazardous solid wastes. The cost of SAMMS materials is expected to be in the same range as the commercial organic ion exchange resin, Duolite™ GT-73, but the SAMMS has a mercury loading almost 10 times as high as that of the commercial product.

Technical Approach

The objective of this task is to develop and demonstrate SAMMS as a technical- and cost-effective technology for RCRA metal removal from wastewater, and mercury removal from organic wastes such as vacuum pump oils.

The work scope includes:

- developing and optimizing simple and reliable methods for the synthesis of SAMMS material
- investigating the mercury binding characteristics of SAMMS in both aqueous and oil wastes in terms of selectivity, capacity, equilibrium constants, and kinetics
- evaluating the chemical durability, especially the oxidation resistance of SAMMS under field application conditions
- demonstrating the suitability of the metal-loaded SAMMS as a durable waste form by evaluating its durability with respect to pH, redox environments, salt types and concentration, temperature, lifetime, biological resistance, and disposal conditions
- preliminary cost estimates of materials and equipment
- bench-scale demonstration of SAMMS technology with actual wastes within 2 years.

Accomplishments

Procedures for self-assembly of a variety of functional molecules on oxide surfaces have been extensively investigated and established at PNNL.[9-11] Procedures for synthesizing mesoporous silica, zirconia, alumina, and titania supports have been developed at PNNL and by other groups as well.[11,14,15] The procedure for making SAMMS is currently being optimized. Several types of SAMMS materials have been recently synthesized. Surface characteristics of the mesoporous support plays a significant role in the anchoring of the functional groups on the surface.[16]

Preliminary trials of the mercury-binding abilities of SAMMS were conducted in simulated wastewater of SRS radioactive waste holding Tank L and simulated nonradioactive vacuum pump oil waste of the SRS Tritium Facilities. The analyzed compositions of wastewater at pH 3, 7, and 9 and the oil waste were shown in Table 1. These waste solutions were mixed with SAMMS powders at volume ratios of waste to SAMMS ranging from 20 to 100 (Table 2) at room temperature for 2 h. The remaining RCRA metals in solution were analyzed using cold vapor atomic absorption for Hg and ICP-AES for other metals as shown in Table 1.

Table 1. Analyzed RCRA metal concentrations (ppm) in waste solutions before and after SAMMS treatment

	Hg	Ag	Cr	Pb	Ba	Zn	Na
Before:							
WW at pH 3	6.20	1.80	1.79	7.22	7.18	3.96	2220
WW at pH 7	6.00	0.45	1.13	5.25	7.12	2.75	2212
WW at pH 9	6.35	1.04	0.58	2.90	7.15	1.32	2222
Oil-1	12.10						
After:							
SAM-1-3	0.0108	<.005	1.45	1.66	7.60	3.93	2236
SAM-1-7	0.0064	<.005	0.70	0	7.35	2.23	2202
SAM-1-9	0.0056	<.005	0.71	0	7.40	1.41	2218
SAM-2-3	0.0008	<.005	1.67	2.26	8.64	5.06	2185
SAM-2-7	0.0008	<.005	0.07	0	8.21	1.54	2114
SAM-2-9	0.0007	<.005	0	0	8.82	1.19	2201
SAM-1-Oil	0.635						
SAM-2-Oil	0.066						

Table 2. Testing Parameters

	Types of Wastes	V_{waste}/V_{SAMMS}	K_d of Hg	Remaining Hg in Waste (ppb)
SAM-1-3	Wastewater at pH 3	97	55670	10.8
SAM-1-7	Wastewater at pH 7	97	90974	6.4
SAM-1-9	Wastewater at pH 9	97	110056	5.6
SAM-2-3	Wastewater at pH 3	38	290588	0.8
SAM-2-7	Wastewater at pH 7	38	281213	0.8
SAM-2-9	Wastewater at pH 9	38	340141	0.7
SAM-1-Oil	Waste pump oil	100	1806	635
SAM-2-Oil	Waste pump oil	20	3647	66

SAMMS reduced the Hg concentration from 6.35 ppm to 0.7 ppb (below the drinking water limit of 2 ppb) by just one treatment of wastewater 38 times its volume. The distribution coefficient is as large as 340,000 with the presence of large concentrations of other cations (e.g., 2220 ppm Na). Other RCRA metals (Pb, Ag, and Cr) were also reduced to below RCRA levels at pH 7 and 9. SAMMS reduced the Hg level from 12.1 ppm to 0.066 ppm (hazardous waste limit is 0.2 ppm) by treating 20 times the waste oil volume once. The RCRA-laden SAMMS can be disposed directly as solid wastes because they passed TCLP tests by showing up to 1000 times lower release of RCRA metals (Table 3).

The preparation of these SAMMS is not yet fully optimized, and the materials tested and reported here had a small surface coverage of the functional groups (approximately 25% of a fully dense monolayer). Recent improvements in the procedure have provided higher (76%) levels of surface coverage and greater improvements are expected in final optimization of the SAMMS synthesis.

Field-scale demonstrations of the SAMMS technology using actual DOE wastes at DOE sites are being planned for FY 1998 and FY 1999.

Table 3. TCLP Leachate Concentrations (ppm)

	Hg	Ag	Cr	Pb	Ba	Ni	Zn
SAM-1-Oil	0.0043	0	0	0	0.37	0.10	0.57
SAM-2-Oil	0.0018	0	0	0	0.18	0	0.29
SAM-1 (pH 3,7,9)	0.0009	0	0.24	0	0.70	0.20	1.05
SAM-2-3	0.0006	0	0.07	0	0.58	0.06	0.33
SAM-2-7	0.0006	0	0	0	0.55	0	0.31
SAM-2-9	0.0002	0	0	0	0.44	0	0.30
EPA TCLP Limits	0.2	5.0	5.0	5.0	100		
Land Disposal Restrictions	--	0.072	5.2	0.51		0.32	
Drinking Water Limit	0.002						

Note: "0" concentration means the concentration below the detection limits of ICP-AES.

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Simultaneous Treatment of Chlorinated Organics and Removal of Metals and Radionuclides with Bimetals and Complexing Acids—Application to Surfactant Solutions

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EM Focus Areas: subsurface contaminants; mixed waste characterization, treatment, and disposal

Technology Needs

DOE is responsible for a variety of complex and unique waste materials. Chief among these in terms of volume are mixed radioactive and hazardous wastes. Examples include barrels of soil containing uranium (U), technetium (Tc), and chlorinated hydrocarbons at the Paducah facility, groundwater contaminant plumes of Tc and trichloroethene (TCE) at Paducah and Portsmouth, and waste streams with U and carbon tetrachloride at Hanford. Separation and treatment technologies for similar wastes are needed at virtually every DOE facility. Because the metallic/radioactive portion of the waste stream cannot be destroyed, the goal of treatment technologies aimed at multiple contaminants is to separate and destroy the organic portion, and to minimize the volume contaminated with metallic or radioactive wastes.

Currently available methods for separation and treatment of radioactive mixed waste are typically energy-intensive, and often require high temperatures. Passive methods that operate at ambient temperatures are needed. The purpose of this task is to develop bimetallic substrates, using a base metal such as iron and a promoter metal such as palladium (Pd), to provide a passive, low-energy solution to a substantial portion of DOE's mixed-waste problem.

Technology Description

This technology consists of a porous medium that can simultaneously dechlorinate hazardous organics such as TCE and polychlorinated biphenyls (PCBs) at the same time that it removes metallic and hazardous wastes from a solvent/surfactant solution. The porous medium consists of a bimetallic substrate such as palladized iron (Pd/Fe). Palladium is readily chemically plated on iron and preliminary studies suggest that only 0.05 to 0.1% Pd is needed for an efficient reaction. Thus, the cost of the material is reasonable especially if it is long-lived or can be regenerated.

Field implementation would consist of the passage of a surfactant-laden, mixed waste through a column or bed of the bimetallic substrate. The organic component of this mixed waste may contain semivolatile compounds such as PCBs or pesticides and herbicides. The bimetal simultaneously removes radionuclides and metals and degrades halogenated hydrocarbons. Virtually any concentration can be treated; it being a matter of sizing the reactor correctly. Following reaction of the bimetal with the waste stream, the resulting effluent will consist of an uncontaminated aqueous solution of surfactant or solvent that can be reused. The bimetal would then be rinsed with a dilute mineral acid or a mild complexing acid (e.g., oxalic or citric acid) to regenerate the surface and to remove sorbed metals and non-hazardous organic residue. The latter effluent would be low-level radioactive waste in some cases, but it would now be much easier to manage and be of a lower volume than the original mixed waste.

Benefit to DOE/EM

The potential benefits of this approach are the simplicity of the system and its applicability to surfactant/solvent extracts of a wide variety of mixed wastes. In principle, a mixed-waste solution comprised of organic hazardous waste and radioactive waste, in the presence of a surfactant and/or solvent, is contacted with the bimetallic substrate. Chlorinated organics such as PCBs or TCE are degraded to nonchlorinated, relatively harmless byproducts. The solution containing the surfactant or solvent can then be reused. Similarly, the bimetallic material is then rinsed with a dilute mineral acid or mild complexing acid both to remove and further concentrate the radioactive/metallic wastes and to regenerate the bimetal for reuse. The ultimate benefit to DOE, therefore, is the development of a low-energy, ambient temperature method for simultaneous treatment of solvent/surfactant solutions that contain hazardous and radioactive wastes.

Technology Transfer/Collaborations

Previous work on Pd/Fe has attracted the involvement of a technology transfer company, Research Corporation Technologies, and a potential manufacturer of the bulk material, Johnson-Matthey Corporation. For example, Research Corporation Technologies has provided some past support (materials and supplies) to the development effort. Likewise, Johnson-Matthey has been developing manufacturing methods for providing the material in bulk. Both companies are expected to participate to some extent in the current effort. Other collaborators include researchers at the University of Arizona, who assist with the surface analyses, and at the Colorado School of Mines, who will participate in the field design and full-scale demonstration.

Scientific Background

Metallic reduction of organic compounds, primarily with zinc (Zn) or Fe powder, is a classical organic reaction that has been utilized for more than a century. Recent research, however, has shown that dramatic improvements in rate and selectivity may be obtained by employing bimetals.[1] The investigators for this proposal have developed a Pd/Fe bimetallic material that may have significant environmental and industrial applications.[2,3]

The potential applications of Pd/Fe are quite distinct from those of zero-valance iron.[4-9] The reaction mechanisms are different and the zero-valance iron reaction is much slower. For example, Pd/Fe dechlorinates PCBs at ambient temperature and pressure and retains its reactivity in the presence of alcohols and surfactants[10,11]—conditions under which zero-valence iron is essentially unreactive.[12]

The enhanced reactivity of palladized iron is believed due to hydrogenation[13] because Pd has the ability to intercalate hydrogen into its lattice. Thus, the chlorinated organic compound is adsorbed to the Fe surface and reacts with the hydrogen intercalated by the Pd.

Technical Approach

The technical approach consists of a laboratory and field phase. The laboratory work is focusing on the nature of the Pd adherence to Fe. The importance of these experiments is to determine the optimum manner for plating Pd in order to obtain maximum longevity of use. This work is focusing on the effects of purity and surface area of the base metal. It is suspected, for example, that a less-pure Fe source may result in some Pd not adhering adequately to the Fe surface. Likewise, if the Fe surface area is too high, it may be that Pd-containing particles will be lost from the reactor as the Fe corrodes. Thus, unlike the reaction with zero valence iron, which is directly proportional to surface area, Pd/Fe probably has an optimum surface area. These effects will be studied by conducting a comprehensive series of kinetic experiments to determine relative and long-term reactivity. Surface area determinations by multi-point BET with nitrogen and surface analyses with an array of methods (e.g., proton-induced x-ray emission, x-ray photoelectron spectroscopy, etc.) will be used to evaluate the materials before and after use to develop the best approach for preparation, use, and regeneration of the material.

The laboratory tests will be used to design a full-scale field test that will use actual DOE waste and will be performed onsite. The field test will be performed on an existing waste stream or else the waste stream will be generated by performing an extraction of stored waste material. Data from the field test will be used to develop baseline cost and efficiency estimates for comparison with other available technologies.

Accomplishments

This project was initiated in November 1996. However, some preliminary data had already been obtained to demonstrate the proof of principle. For example, Figure 1 shows the removal of TCE and PCBs in 2% aerosol surfactant by a packed column of Pd/Fe. The degradation half-life of TCE was approximately 1-1/2 min and was approximately 6 min for PCBs. Some of the PCBs and byproducts probably adsorb to the iron surface. However, previous studies have shown that, given sufficient reaction time, PCBs are completely dechlorinated to biphenyl.

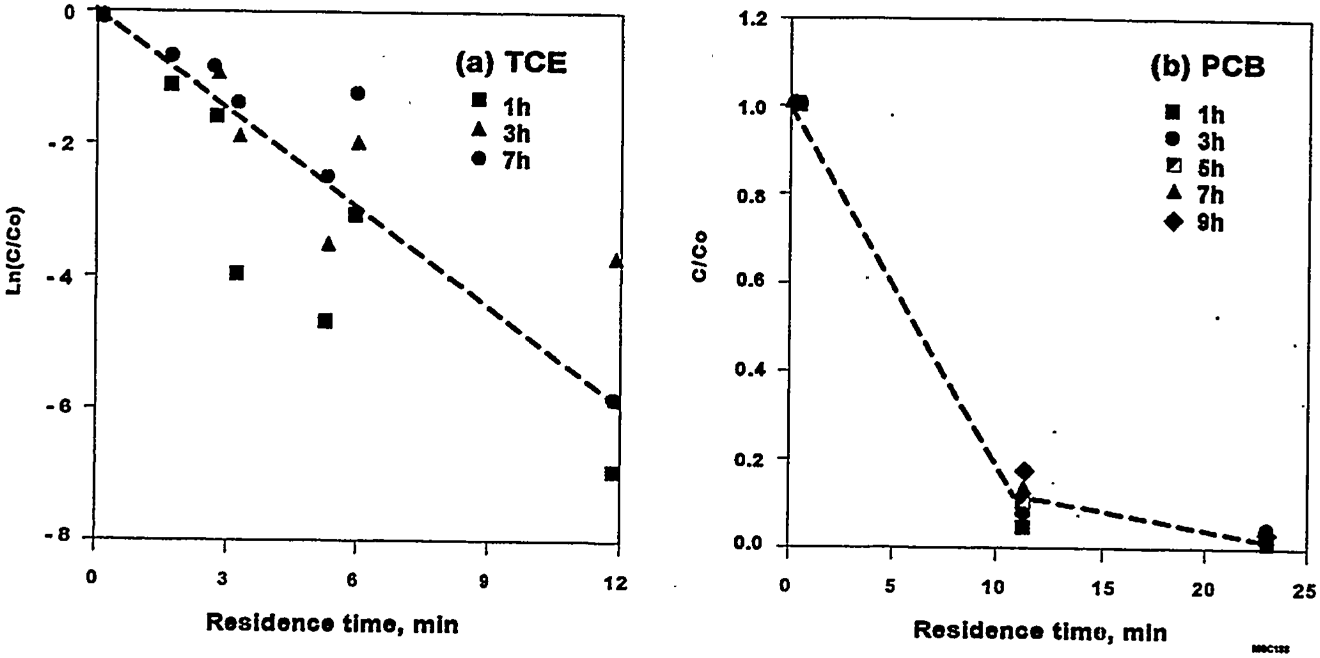

Figure 1. Degradation of TCE (a) and PCB (b) in two packed columns (connected in series) with Fe-Pd filings in 2% aerosol surfactant and 2% isopropanol. Samples were taken at the inlet, outlet, and between the two columns at various time intervals.

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Recyclable Bio-Reagent for Rapid and Selective Extraction of Contaminants from Soil

Henry L. Lomasney, ISOTRON® Corporation

EM Focus Areas: decontamination and decommissioning; subsurface contaminants; mixed waste characterization, treatment, and disposal

Technology Description

This Phase I Small Business Innovation Research program is confirming the effectiveness of a bio-reagent to cost-effectively and selectively extract a wide range of heavy metals and radionuclide contaminants from soil. This bio-reagent solution, developed by ISOTRON® Corporation (New Orleans, LA), is flushed through the soil and recycled after flowing through an electrokinetic separation module, also developed by ISOTRON®.

Technical Approach

The process is ex situ, and the soil remains in its transport container through the decontamination process. The transport container can be a fiberglass box, or a bulk bag or "super sack." Rocks, vegetation, roots, etc. need not be removed. High clay content soils are accommodated. The process provides rapid injection of reagent solution, and when needed, sand is introduced to speed up the heap leach step. The concentrated waste form is eventually solidified. The bio-reagent is essentially a natural product, therefore any solubizer residual in soil is not expected to cause regulatory concern.

The Phase I work will confirm the effectiveness of this bio-reagent on a wide range of contaminants, and the engineering parameters that are needed to carry out a full-scale demonstration of the process. ISOTRON® scientists will work with contaminated soil from Los Alamos National Laboratory. LANL is in the process of decontaminating and decommissioning more than 300 sites within its complex, many of which contain heavy metals or radionuclides; some are mixed wastes containing TCE, PCB, and metals.

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Innovative Methods to Stabilize Liquid Membranes for Removal of Radionuclides from Groundwater

Kaaeid Lokhandwala, Membrane Technology and Research, Inc.

EM Focus Areas: subsurface contaminants

Technology Description

In this Phase I Small Business Innovation Research program, Membrane Technology Research, Inc., is developing a stable liquid membrane for extracting uranium and other radionuclides from groundwater. The improved membrane can also be applied to separation of other metal ions from aqueous streams in industrial operations.

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A New Separation and Treatment Method for Soil and Groundwater Restoration

G. Duncan Hitchens, Lynntech, Inc.

EM Focus Areas: decontamination and decommissioning; subsurface contaminants; mixed waste characterization, treatment, and disposal

Technology Description

Soil and groundwater contamination by organic compounds is a widespread environmental pollution problem. In many cases, contaminated soil is excavated and transported to a landfill or is incinerated to remove contaminants. These remediation practices are expensive, environmentally disruptive, require extensive permitting, and only move contamination from one location to another. Onsite and in situ treatment techniques offer a safer, more cost-effective, and permanent solution. Many soil and groundwater contaminants are highly volatile, enabling the use of methods such as in situ vacuum extraction and air injection for their removal. However, these methods are often difficult to use because of slow volatilization rates and the lack of effective methods to treat the extracted hazardous material.

This Phase I Small Business Innovation Research program I focuses on developing an in situ soil and groundwater remediation technique that is effective against volatile as well as nonvolatile compounds and that will shorten treatment times. The technique forms the basis of a new catalytic process to degrade extracted contaminants onsite. Key hardware elements on which the new technique is based have been proven in preliminary research. The method has a high potential for public and regulatory acceptance because of its low environmental impact.

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6. Publications, Presentations, and Patents

6. 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 number, along with the Principal Investigator's name and location.

AL132010 - Fission Separation Using Ion Exchange, Solvent Extraction, and Cobalt Dicarbollide, Moses Attrep (Los Alamos National Laboratory)

Publications

Abney KD, NC Schroeder, SA Kinkead, and M Attrep, Jr. 1992. *Separation of technetium from ruthenium after the accelerator transmutation of technetium.* LA-UR-92-39, Los Alamos National Laboratory, Los Alamos, New Mexico.

Ashley KR, JR Ball, AB Pinkerton, KD Abney, and NC Schroeder. 1994. "Sorption behavior of $^{99}TcO_4^-$ on Reillex-HPQ anion exchange resin from nitric acid solution." *Solv. Extract. Ion Exch.* 12.

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Presentations

Abney KD, NC Schroeder, and SA Kinkead. 1992. "Nuclear waste partitioning: separation of ruthenium from technetium by reaction with ozone." Presented at the 203rd American Chemical Society meeting, April 5-9, 1992, San Francisco, California.

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