EFFICIENT SEPARATIONS & PROCESSING CROSSCUTTING PROGRAM

**Technology Summary
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EFFICIENT SEPARATIONS AND PROCESSING CROSSCUTTING PROGRAM TECHNOLOGY SUMMARY

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INTRODUCTION

The Office of Environmental Management (EM) is responsible for cleaning up the legacy of radioactive and chemically hazardous waste at contaminated sites and facilities throughout the U.S. Department of Energy (DOE) nuclear weapons complex, preventing further environmental contamination, and instituting responsible environmental management. Initial efforts to achieve this mission resulted in the establishment of environmental restoration and waste management programs. However, as EM began to execute its responsibilities, decision makers became aware that the complexity and magnitude of this mission could not be achieved efficiently, affordably, safely, or reasonably with existing technology.

Once the need for advanced cleanup technologies became evident, EM established an aggressive, innovative program of applied research and technology development. The Office of Technology Development (OTD) was established in November 1989 to advance new and improved environmental restoration and waste management technologies that would reduce risks to workers, the public, and the environment; reduce cleanup costs; and devise methods to correct cleanup problems that currently have no solutions.

In 1996, OTD added two new responsibilities—management of a Congressionally mandated environmental science program and development of risk policy, requirements, and guidance. OTD was renamed the Office of Science and Technology (OST).

THE EM ORGANIZATION

OST is one of seven Deputy Assistant Secretarial Offices within EM. Each Deputy Assistant Secretarial Office is discussed here, with the exception of OST (EM-50), addressed in detail later in this Introduction.

Office of the Assistant Secretary for Environmental Management (EM-1)

The Office of the Assistant Secretary for Environmental Management provides centralized direction for waste management operations, environmental restoration, and related applied research and development programs and activities within DOE. The Office of the Assistant Secretary develops EM program policy and guidance for the assessment and cleanup of inactive waste sites and facilities, and waste management operations; develops and implements an applied waste research and development program to provide innovative environmental technologies to yield permanent disposal solutions at reduced costs; and oversees the transition of contaminated facilities from various departmental programs to environmental restoration. The Assistant Secretary provides guidance to all DOE Operations Offices. Organizational relationships are shown in Figure A.

Figure A. Office of Environmental Management Organization Chart

The Office of Management and Evaluation (EM-10)

The Deputy Assistant Secretary for Management and Evaluation serves as the Assistant Secretary's principal advisor on all administrative functions and activities for EM line offices. Responsibilities include personnel administration; training and career development; total quality management; organization and manpower management; cost and performance management; space and logistics management; acquisition, procurement, and contracts management; general administrative support services; and automated data processing, automated office support systems, and information resources management.

The Office of Planning, Policy, and Budget (EM-20)

The Office of Planning, Policy, and Budget analyzes and provides support on policy and planning issues associated with environmental compliance and cleanup activities, waste management, nuclear materials and facilities stabilization, overall budget and priority setting analyses, nuclear nonproliferation policy practices, and the ultimate disposition of surplus materials and facilities. This Office is also responsible for the review, coordination, and integration of inter-site, interagency and international planning activities related to these issues. The Office coordinates policy and procedural issues associated with the external regulation of the environmental restoration, waste management, and nuclear materials and facility stabilization programs.

The Office of Waste Management (EM-30)

The Office of Waste Management provides an effective and efficient system that minimizes, treats, stores, and disposes of DOE waste as soon as possible in order to protect people and the environment from the hazards of those wastes. The Office carries out program planning and budgeting, evaluation and intervention, and representation functions associated with management

of radioactive high-level, transuranic, and low-level waste; hazardous and sanitary waste; and mixed waste.

The Office of Environmental Restoration (EM-40)

The Office of Environmental Restoration remediates departmental sites and facilities to protect human health and the environment from the risks posed by inactive and surplus DOE facilities and restores contaminated areas for future beneficial use. This Office provides program direction for and management of environmental restoration activities involving inactive sites and facilities, including the decontamination of surplus facilities.

The Office of Nuclear Material and Facility Stabilization (EM-60)

The Nuclear Material and Facility Stabilization program mission is to protect people and the environment from the hazards of nuclear materials and to deactivate surplus facilities in a cost-effective manner. The Office provides program planning and budgeting, evaluation and intervention, and representation functions associated with the stabilization of nuclear materials and the deactivation of surplus facilities.

The Office of Site Operations (EM-70)

Acting to eliminate barriers and ensure that field concerns are recognized in major EM decisions, the Office of Site Operations acts as a focal point and champion for the Operations Offices and field sites, serving as facilitator, coordinator and ombudsman for crosscutting issues and topics raised by the various EM elements. The Office of Site Operations provides Headquarters policy direction for landlord planning and budgeting and sets policy and guidance to improve the effectiveness of crosscutting environment, transportation management, and waste minimization activities.

THE OFFICE OF SCIENCE AND TECHNOLOGY (EM-50)

OST manages and directs focused, solution-oriented national technology development programs to support EM by using a systems approach to reduce waste management life-cycle costs and risks to people and the environment. OST programs involve research, development, demonstration, testing, and evaluation of innovative technologies and technology systems that meet end-user needs for regulatory compliance. Activities include coordination with other stakeholders and the private sector, as well as collaboration with international organizations. In 1994, the EM program identified five major problem areas on which to focus its technology development activities (later two were combined), and implemented Focus Areas to address these problems. In addition, some needs were identified that were common to all the Focus Areas, and three Crosscutting Programs were created to address them.

OST programs establish, manage, and direct targeted, long-term research programs to bridge the gap between broad fundamental research that has

wide-ranging application and needs-driven applied technology development research. OST expects to produce technologies to answer the needs of its major customers within EM for innovative science and technology through

Figure B. Organization Chart of the Office of Science and Technology

integration of basic research programs, applied research programs (Focus Areas and Crosscutting Programs), industry partnerships, and technology transfer activities.

Three offices comprise OST: the Office of Science and Risk Policy, the Office of Technology Systems, and the Office of Technology Integration. The organization for OST is shown in Figure B.

OFFICE OF SCIENCE AND RISK POLICY (EM-52)

The Office of Science and Risk Policy manages EM's Science Program and the formulation of risk policy. The mission of this office includes the development of a targeted, long-term basic research agenda for environmental problems so that "transformational" or breakthrough approaches can lead to significant reduction in the costs and risks associated with the EM Program. This Office also bridges the gap between broad fundamental research that has wide-ranging applicability, such as that performed in DOE's Office of Energy Research, and needs-driven applied technology development that is conducted in EM's Office of Technology Systems. This Office was designed to focus the country's science infrastructure on critical national environmental management problems.

The Science Program draws on information from its DOE customers to identify necessary basic research. The Science Program concentrates its efforts on the characterization of DOE's wastes and contaminants, interactions of

radioactive elements with biosystems in various natural media and waste forms, extraction and separation of radioactive and hazardous chemical contaminants, prediction and measurement of contaminant movement in DOE facilities' environments, and formulation of scientific bases for the risks associated with DOE-based contaminants.

Risk policy activities within this Office involve the development of policies, procedures, and guidance to ensure that EM activities in preventing risks to the public, workers, and the environment are within prescribed, acceptable levels. Risk evaluation methods and event and consequence analyses provide DOE with a basis for assessing both the risk and any actions being considered to reduce that risk. The Office of Science and Risk Policy ensures that advances in risk evaluation methods are integrated into coherent decision-making processes regarding risk acceptability. Decision-making processes must meet DOE missions while protecting public health, worker health and safety, ecosystem viability, and cultural and national resources.

OFFICE OF TECHNOLOGY SYSTEMS (EM-53)

OST programs involve research, development, demonstration, testing, and evaluation activities designed to produce innovative technologies and technology systems to meet national needs for regulatory compliance, lower life-cycle costs, and reduced risks to the environment. To optimize resources, OST has streamlined technology management activities into a single focus team for each major problem area. To ensure programs are based upon user needs, these teams include representatives from user offices within EM. There are four major problem areas upon which technology development activities are focused.

- Mixed Waste Characterization, Treatment, and Disposal
- Radioactive Tank Waste Remediation
- Subsurface Contaminants
- Decontamination and Decommissioning

Mixed Waste Characterization, Treatment, and Disposal Focus Area

DOE stores 167,000 cubic meters of mixed low-level and transuranic waste from over 1,400 mixed radioactive and hazardous waste streams at 38 sites. The Mixed Waste Characterization, Treatment, and Disposal Focus Area provides an integrated, multi-organizational, national team to develop treatment systems for the department's inventory of mixed radioactive and hazardous waste and to dispose of these low-level and transuranic waste streams in a manner that regulatory requirements.

This Focus Area plans to demonstrate three technologies to treat at least 90 percent of DOE's stored mixed waste inventory by the end of FY97. The

outcome will be waste forms that are reduced in volume, as compared to the volume of stored mixed waste, and meet regulatory requirements for safe, permanent disposal. Technology development is being conducted in the areas of thermal and nonthermal treatment emissions, nonintrusive drum characterization, material handling, and final waste forms.

Radioactive Tank Waste Remediation Focus Area

The Radioactive Tank Waste Remediation Focus Area develops technologies to safely and efficiently remediate over 300 underground storage tanks that have been used to process and store more than 100 million gallons of high-level radioactive and chemical mixed waste. Technologies are needed to characterize, retrieve, and treat the waste before radioactive components are immobilized. All this must be done in a safe working environment. Emphasis is placed on in situ or remotely handled processes and waste volume minimization.

Research and development of technologies in this area is aimed at enabling tank farm closure using safe and cost-efficient solutions that are acceptable to the public and that fulfill Federal Facility Compliance Act requirements of site regulatory agreements.

Subsurface Contaminants Focus Area

The Subsurface Contaminants Focus Area is developing technologies to address environmental problems associated with hazardous and radioactive contaminants in soil and groundwater that exist throughout the DOE complex, including radionuclides, heavy metals, and dense, nonaqueous phase liquids. More than 5,700 known DOE groundwater plumes have contaminated over 600 billion gallons of water and 50 million cubic meters of soil. Migration of these plumes threatens local and regional water sources, and in some cases has already adversely impacted off-site resources. In addition, the Subsurface Contaminants Focus Area is responsible for supplying technologies for the remediation of numerous landfills at DOE facilities. These landfills are estimated to contain over 3 million cubic meters of radioactive and hazardous buried waste, some of which has migrated to the surrounding soils and groundwater. Technology developed within this specialty area will provide effective methods to contain contaminant plumes and new or alternative technologies for remediating contaminated soils and groundwater. Emphasis is placed on the development of in situ technologies to minimize waste disposal costs and potential worker exposure by treating plumes in place. While addressing contaminant plumes emanating from DOE landfills, the Subsurface Contaminants Focus Area is also working to develop new or alternative technologies for the in situ stabilization and nonintrusive characterization of these disposal sites.

Decontamination and Decommissioning Focus Area

The Decontamination and Decommissioning Focus Area is developing technologies to solve the department's challenge of deactivating 7,000

contaminated buildings and decommissioning 700 contaminated buildings. It is also responsible for decontaminating the metal and concrete within those buildings and disposing of 180,000 metric tons of scrap metal. Technology development for decontamination and decommissioning focuses on large-scale demonstrations, each of which incorporates improved technologies identified as responsive to high-priority needs. All technologies will be considered for eventual deployment, and side-by-side comparisons of improved technologies are being performed using existing commercial technologies as baselines.

CROSSCUTTING PROGRAMS

In addition to work directed to specific Focus Areas, EM is engaged in research and development programs that cut across these problem areas. Technologies from these Crosscutting Programs may be used within two or more of the Focus Areas to help meet program goals. These programs complement and facilitate technology development in the Focus Areas as shown in Figure C. The Crosscutting Programs are:

- Characterization, Monitoring, and Sensor Technologies,
- Efficient Separations and Processing, and
- Robotics Technology Development Program.

Characterization, Monitoring, and Sensor Technologies Crosscutting Program

DOE is required to characterize more than 3,700 contaminated sites, 1.5 million barrels of stored waste, 385,000 m³ of high-level waste in tanks, and from 1,700 to 7,000 facilities before remediation, treatment, and facility transitioning commence. Monitoring technologies are needed to ensure worker safety and effective cleanup during remediation, treatment, and site closure.

Figure C. Relationships between Focus Areas and Crosscutting Programs

Efficient Separations and Processing Crosscutting Program

Separations and selected treatment processes are needed to treat and immobilize a broad range of radioactive wastes. In some cases, treatment technologies do not exist; in others, improvements are needed to reduce costs and secondary waste volumes and to improve waste form quality. This Crosscutting Program concentrates efforts on specific high-priority needs as defined by the Focus Areas, then evaluates and adapts the technologies for other applicable Focus Areas.

This program is working to meet Federal Facilities Compliance Act milestones and other regulatory requirements, and to develop separations and treatment technologies that minimize risk, the volume of waste requiring deep, geological disposal, and secondary waste volumes.

Robotics Technology Development Crosscutting Program

Existing technologies are often inadequate to meet EM's mission needs both at a reasonable cost and under conditions that promote adequate worker safety. Robotic systems reduce worker exposure to the absolute minimum while providing proven, cost-effective, and, in some cases, the only acceptable approach to problems.

Robotics remote systems development work occurs in three areas. Remote systems for decontamination and dismantlement of facilities will reduce or eliminate extensive worker radiation protection requirements and increase productivity. Robotic systems for characterization and retrieval of stored tank waste will allow work to proceed within the radiation fields in the waste storage area. Automated chemical/radiological analysis systems are estimated to provide a cost benefit of \$10.5 billion from FY96 through FY00.

INDUSTRY AND UNIVERSITY PROGRAMS

Industry and University programs provide to the Focus Areas and the Crosscutting Programs the capability to involve private industry, universities, and other interested parties in their program through direct procurement with DOE. The public-private partnerships that are established encourage the enhancement and commercialization of technologies developed by the private sector through pilot- and field-scale demonstration at DOE sites. The integration of industry, academia, and the DOE laboratories allows all aspects of the technology to be evaluated, including worker safety and health, commercial potential, and technical merit.

Industry and University activities support more than 100 agreements with the private sector. These agreements include the Small Business Innovative Research (SBIR) program, international activities, stakeholder activities, worker safety and health activities, and commercialization initiatives, as well as the direct support to the Focus Areas. For information on how to participate in

these programs, see the "DOE Business Opportunities" section at the end of this book.

OFFICE OF TECHNOLOGY INTEGRATION (EM-54)

The Office of Technology Integration addresses issues that affect the involvement of critical external entities such as production/waste sites, users, the public, tribes, regulators, and commercial parties. The office is involved in the assessment, acceptability, availability, and use of improved technical solutions by providing uniform guidance, tools, and initiatives to support the Office of Technology Systems. This office also sponsors efforts to encourage and promote the involvement of affected parties' in regulatory issues.

In addition, the Office of Technology Integration sponsors domestic and international technology transfer programs within OST and coordinates planning and cost-benefit analyses with other EM organizations.

THE EFFICIENT SEPARATIONS AND PROCESSING CROSSCUTTING PROGRAM OVERVIEW

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

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

A key goal of the ESP is to apply ESP-sponsored technologies in all Focus Areas regardless of the intended application. The ESP emphasizes innovation and proof-of-principle in its tasks, and will accept higher risks because of the greater probability of payoff when averaged over all Focus Areas. Focus Area staff help decide whether specific ESP tasks begin or continue. For example, Focus Area representatives reviewed FY96 ESP proposals.

TECHNOLOGY NEEDS

A wide range of wastes and associated environmental problems exists at more than 100 contaminated installations in 36 states and territories because of half a century of nuclear processing activities undertaken by DOE and its predecessors. The cost of cleaning up this legacy is estimated to be tens of billions of dollars. The ESP was initiated 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 less expensive disposal.

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

SCOPE OF SEPARATIONS

The ESP provides the following categories of separations:

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

CURRENT PROGRAM

The ESP conducts primarily laboratory research to create new chemical separations technologies and processes. These technologies must be able to scale up economically, without introducing 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 complement new separations strategies. The ESP currently funds 32 multiyear tasks that address high-priority waste remediation problems. Fifty percent of these tasks include university staff; approximately 50% have outside collaboration from industry.

PRODUCT LINES

ESP technologies have been put into the following product lines:

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

SHORT-LIVED RADIONUCLIDES

The Short-Lived Radionuclides product line provides technology to remove radionuclides with short half-lives such as radioactive cesium, strontium, and

tritium. Cesium and strontium are the main heat and penetrating-radiation emitters in high-level waste (HLW). The Hanford and Savannah River sites contain the largest volume of this waste. Removal of cesium and strontium will reduce the volume of HLW needing geologic disposal, and greatly reduce worker exposure to radiation in waste treatment facilities. The current baseline technologies for cesium and strontium are unacceptable and require improvement.

Tritium-contaminated water at Hanford and Savannah River poses risk to the public if accidentally released. Tritium contamination also exists at other sites and in spent fuel cooling ponds. The Hanford Site's Tri-Party Agreement currently requires that tritiated water be treated or removed.

This product line has successfully developed ion exchange materials capable of removing cesium and strontium from both alkaline and acid streams, and is developing technology capable of separating tritium at the concentrations found in groundwater and in fuel storage pools.

LONG-LIVED RADIONUCLIDES

The Long-Lived Radionuclides product line provides technology to remove radionuclides with long half-lives such as uranium, plutonium, and technetium. Uranium and plutonium contamination is widespread throughout the DOE complex, often at low concentrations in large volumes, thus making disposal very expensive. Technetium is a major contributor to long-term risk assessment, and may be a problem material in vitrification of Hanford wastes. The current technetium removal technologies produce large volumes of secondary waste, and are unable to effectively treat technetium in groundwater.

This product line has developed technology to remove plutonium residues at Rocky Flats, and polymer technology capable of treating contaminated process and waste streams. Various tasks in this product line focus on other means to safely remove the long-lived radionuclides of concern for safe disposal.

HEAVY METALS

Several toxic metals of concern are found in various waste streams throughout the DOE complex. Mercury is one metal that concerns many of the sites involved in cleanup operations. Mercury in mixed-waste streams destined for vitrification poses a chemical processing problem. The mercury is volatilized and requires additional offgas treatment for removal. The heavy metals product line will develop technologies to remove toxic metals found in waste streams that could pose problems in downstream processing.

WASTE PROCESSING AND TREATMENT

The Waste Processing and Treatment product line involves treatment processes that remove the materials described in the previous product lines (Short-Lived Radionuclides, Long-Lived Radionuclides, and Heavy Metals), along with other distinct separation needs such as nitrite and nitrate removal. Other technologies included in this product line are the development of membranes to remove various radionuclides; technologies to remove organic material, nitrates, and nitrites, which will reduce the amount of low-level waste (LLW); filtration processing as a pretreatment step to remove solids; and hot cell studies to understand and improve the removal rates of various radionuclides.

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SHORT-LIVED RADIONUCLIDES

The Short-Lived Radionuclides product line provides technology to remove radionuclides with short half-lives such as radioactive cesium, strontium, and tritium. The removal of ^{137}Cs and ^{90}Sr from waste streams has been one of the major concerns for the ESP program since its creation in 1991. Because this research is reaching its maturity, the funding for this product line has been decreasing. This product line has produced several successful technologies, including the crystalline silicotitanate (CST) ion exchange material, which will be the first material tested in the Radioactive Tank Remediation Focus Area's demonstration on 25,000 gallons of Oak Ridge National Laboratory's Melton Valley Storage Tank (MVST) waste.

Bench-scale testing is continuing on various ion exchange materials to determine the most efficient technologies for removing radioactive cesium and strontium from both acidic and alkaline waste streams. The current technology available for removing tritium from groundwater requires a large investment in both capital equipment and energy requirements. Membranes that remove tritium from contaminated water are being developed to overcome the expenses of current technology.

ESP-supported technologies in this product line include:

- Crystalline Silicotitanates for Cesium/Strontium Removal
- Separation Technologies for the Treatment of Idaho National Engineering Laboratory Wastes
- Evaluation of Improved Techniques for Removing Strontium and Cesium from Process Waste water and Groundwater
- Separation of Tritiated Water from Water Using Composite Membranes
- Extension of Studies with Commercial Technologies for Technetium and Cesium Removal from Environmental Systems: Field Tests

1.1

CRYSTALLINE SILICOTITANATES FOR CESIUM/ STRONTIUM REMOVAL

TECHNOLOGY NEEDS

The DOE has more than 200 tanks being used to process and store radioactive waste byproducts generated by weapons materials production facilities. These tanks contain tens of millions of gallons of highly radioactive supernatant, salt cake, and sludges. The waste streams will include both highly alkaline and highly acidic solutions. The major radioactive constituents are isotopes of cesium, strontium, and transuranics.

The technology developed and demonstrated in this work is needed to remediate radioactive wastes currently contained in storage tanks. Specifically, a new class of inorganic ion exchangers called crystalline silicotitanates (CSTs) will be used to develop advanced, efficient radioactive waste separation technologies.

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

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

TECHNOLOGY DESCRIPTION

In this task, CSTs have been developed that exhibit very high selectivity for cesium and strontium in the highly alkaline radioactive wastes at the Hanford Site and other DOE sites. Tests have also shown that CSTs have high selectivity for cesium in acidic and neutral solutions. The ESP is supporting an effort at Sandia National Laboratories (SNL) and Texas A&M University to further develop and characterize the important chemical and physical properties that will determine the applicability of CST to radioactive waste treatment at Hanford and other DOE facilities.

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

Attrition resistance was measured by the standard UOP industrial shaker test on fresh samples and those exposed to a waste simulant for 7 days at ambient temperature. The best materials were tested under flow conditions in a 1cm diameter column with flow rates of 1 to 3 column volumes (CV) per hour. Samples were collected until at least the 70% breakthrough point was achieved. No shrinkage, swelling, gas evolution, or void formation was observed in the IONSIV® IE-911.

BENEFITS

Based on these and other test results, IONSIV® IE-911 has many potential benefits over competing ion exchangers. It has high capacity for cesium at any pH range (14 to 0) and an excellent capacity for strontium over a pH range from 14 to neutral (7). The kinetics are very good at 3 CV/h and will be evaluated at higher flow rates as development continues. Because it is nonregenerable and would be used once, significant cost savings will be possible due to less complex processing equipment and a smaller facility.

The cesium-loaded exchanger has excellent radiation stability to 109 Rads (Si) and studies are in progress to assess its use as a potential cesium interim or final waste form. Direct incorporation into glass appears to be feasible based on PNNL tests that show the historical 1% TiO_2 in glass limit is very conservative and TiO_2 concentrations up to 5% or higher are possible. Commercial samples of IONSIV® IE-911 will be available early in 1996 to confirm these test results with actual wastes at the various DOE facilities.

COLLABORATION/TECHNOLOGY TRANSFER

A CRADA exists between SNL and UOP Molecular Sieves to scale up synthesis of the CST and convert the fine powder into an engineered form. SNL and UOP have collaborated with WHC and PNNL to obtain guidance on the required performance characteristics of the engineered form.

Texas A&M University and SNL researchers are collaborating to further develop and characterize CST chemical and physical properties.

ACCOMPLISHMENTS

- Batch tests with the West Valley THOREX solutions (0.9 M Na⁺, pH 12) and a developmental IONSIV® IE-911 resulted in K_d values of >10,000 mL/g. A column test with a flow rate of 0.8 CV/h was conducted at Sandia with simulated waste, and no cesium was measured up to 450 CV. Based on these results, an actual waste test was conducted at West Valley.
- Batch tests with ORNL W-27 simulant (4.77 M Na⁺, 4.85 M NO₃⁻, pH = 12.5) were conducted with developmental IONSIV® IE-911 materials. K_d values of 530 mL/g were measured and Lot 38 B was selected for column tests. A 1cm (diameter) x 10cm (length) column was tested with W-27 simulant at a flow rate of 3 CV/h. Cesium concentrations were measured and the 50% breakthrough volume was found to be 500 CV, which was in agreement with that predicted from the batch K_d measurement.
- Extensive testing was conducted on IONSIV® IE-911, Lot 38B, in DSSF-5 solutions. Average K_d measurements are about 500 mL/g. These data have been used by UOP to further the development of IONSIV® IE-911. A column experiment at 3.75 CV/h with 10 ppm cesium indicated a 50% breakthrough point of 500 CV.
- Tests to remove cesium and strontium from groundwater simulating Cs and Sr waste that are found at INEL's TAN have been conducted using IONSIV® IE-911 Lot 38 B. Batch K_d s of greater than 104 mL/g for cesium and 2×10^5 mL/g for strontium were measured. A column test was conducted at 10 CV/h to 4550 CV. During the test, no cesium breakthrough and only slight strontium breakthrough was measured. The DF for cesium was greater than 500 and strontium was greater than >1600.
- Samples of IONSIV® IE-910 and IONSIV® IE-911 were loaded with cesium and irradiated to 10⁸ and 10⁹ Rads (Si) under a range of test solutions and conditions. No significant degradation was observed under all test conditions.

TTP INFORMATION

The Crystalline Silicotitanates for Cesium/Strontium Removal technology development activities are funded under the following technical task plan (TTP):

TTP No. AL26C311 "Crystalline Silicotitanates for Cesium/Strontium Removal"

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1.2

BENCH-SCALE TESTING FOR SEPARATION OF IDAHO NATIONAL ENGINEERING LABORATORY WASTE

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 they were solidified in a fluidized-bed calciner. The solid calcine is stored in stainless-steel bins within concrete vaults.

In April 1992, DOE discontinued reprocessing of spent nuclear fuel and shifted the focus of the Idaho Chemical Processing Plant (ICPP) to management and disposition of accumulated radioactive wastes. Currently approximately 1.8 million gallons of acidic, radioactive liquid waste, which is not amenable to calcination, and approximately 3800 m³ of calcine exist at the ICPP. Legal drivers and agreements exist that obligate the INEL to develop, demonstrate, and implement technologies for treatment and interim storage of the radioactive liquid and calcine wastes. Per these agreements, all high-level radioactive waste must be treated and removed from INEL by the year 2035.

Remediation efforts will begin in FY97 to remove volatile organic compounds (VOCs) and radionuclides (cesium and strontium) from groundwater located at INEL's TAN facility. A plume of VOCs and radionuclides has spread from the former TSF-05 injection well, and a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) remediation action is under way.

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

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

TECHNOLOGY DESCRIPTION

INEL is collaborating with several DOE and international organizations to develop and evaluate:

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

In FY93 a joint development program was established within the ESP to evaluate technologies currently under development in the former Soviet Union for treating high-level radioactive waste. This joint program between the Khlopin Radium Institute of St. Petersburg, Russia, and INEL has been developing and testing two technologies for the removal of radionuclides from INEL acidic waste. The two solvent extraction technologies are a phosphine oxide derivative process for removing actinides and technetium and a cobalt dicarbollide derivative process for the simultaneous removal of cesium and strontium from acidic waste.

The Russian process flowsheets have been modified to enhance extraction performance and to improve the safety characteristics of the processes. Current FY96 work scope includes testing the modified cobalt dicarbollide process with actual waste in centrifugal contactors at the INEL.

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

Testing of the engineered form of these technologies with actual waste is planned for FY96 in conjunction with the producers of these materials, namely UOP Molecular Sieves for the CSTs, the Czech Technical University for the PAN composites, and the Institute of Physical Chemistry, Moscow, Russia, for the CuFC/silica composite, provided material is available for testing.

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

BENEFITS

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

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

COLLABORATION/TECHNOLOGY TRANSFER

INEL collaborated with the following groups for this work: Khlopin Radium Institute, St. Petersburg, Russia; the Institute of Physical Chemistry, Moscow, Russia; Czech Technical University; UOP Molecular Sieves; AlliedSignal, Inc.; 3M; and Parsons Environmental Services.

ACCOMPLISHMENTS

- Testing was completed on the modified cobalt dicarbollide process, which incorporated a nonaromatic diluent and the phosphine oxide derivative processes in centrifugal contactors using simulated INEL acidic liquid waste. The testing was conducted jointly with Khlopin Radium Institute scientists at INEL. Cesium and strontium removal efficiencies of 98.9% and 99.89%,

respectively, were achieved using 24 stages of centrifugal contactors. The centrifugal contactors were specifically designed for the transuranic element extraction (TRUEX) process, which has different hydrodynamic properties than the cobalt dicarbollide process. Specifically, the centrifugal contactors were designed for a less-dense organic phase. The cobalt dicarbollide solvent is more dense than the aqueous waste. In addition, phase disengagement properties of the TRUEX and cobalt dicarbollide processes are quite different.

- Testing of the commercial Russian sorbent on simulated INEL acidic tank waste was performed in batch contacts and column tests. The cesium distribution coefficient obtained was 3000, and the maximum sorbent capacity measured was 144 g Cs/kg resin. Results of dynamic column tests with simulated waste spiked with ^{137}Cs indicate that greater than 99.5% of the cesium can be removed with two columns in series at 5% breakthrough.
- Efficient removal of cesium and strontium from contaminated TAN groundwater was demonstrated using 3M web technology. Approximately 4731L (1250 gallons) of contaminated water were pumped at 1 L/min through two prefilters (2 μm and 0.1 μm), then through a strontium-specific cartridge that incorporated AlliedSignal sodium titanate, and finally through a cesium-specific cartridge that incorporated cobalt hexaferrocyanide in the web. Strontium breakthrough (50%) was achieved after processing 3028L (800 gallons) of water, and no cesium was detected (<9 pCi/L) from the system effluent for the entire duration of the test. The system ran for nearly 80 hours continuously without operational problems.

TTP INFORMATION

The Bench-Scale Testing for Separation of Idaho National Engineering Laboratory Waste technology development activities are funded under the following technical task plan (TTP):

TTP No. ID76C311 "Bench-Scale Testing for Separation of Idaho National Engineering Laboratory Waste"

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1.3

FISSION PRODUCTS SEPARATIONS TESTING

TECHNOLOGY NEEDS

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

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

TECHNOLOGY DESCRIPTION

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

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

Testing of the new materials will begin by conducting scoping tests where new treatment materials are compared with standard, commercially available materials in batch shaker tests. Sorption tests will be performed under various treatment conditions (e.g., pH, temperature, simulant waste composition) for

the most promising materials. Additional testing with actual waste water will be conducted with two or three of the most effective treatment methods. Once batch testing of a treatment method is completed, dynamic column tests will be performed using the most successful sorbents, to obtain the defining column operating parameters.

BENEFITS

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

COLLABORATION/TECHNOLOGY TRANSFER

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

ACCOMPLISHMENTS

- Batch sorption studies using treated zeolite in the waste water simulant were completed. Zeolite sorption efficiency was observed in the presence of the major cations in waste water (sodium, calcium, potassium, and magnesium). Chabazite zeolite was also used to decontaminate batch samples of actual process waste water and groundwater. The sorption characteristics of small zeolite column were determined using a waste water simulant: 50% breakthrough of strontium and cesium from a 3.85mL zeolite column occurred at 15,000 and 50,000 bed volumes, respectively.
- Batch testing of the R-F resin was conducted to determine the optimum conditions for nuclide removal in the simulant. Sorption results from several resin pretreatment methods were compared to sorption isotherms developed using the resin as received. Optimum resin performance was achieved by washing the resin with ultra-pure water.

- The cesium sorption isotherm on the resin is linear for simulant containing 10^{-9} to 10^{-4} meq/L cesium; the cesium sorption ratio in the linear range is 28,000 L/kg. The cesium sorption capacity in the waste water simulant was similar to that found using the chabazite zeolite treatment, approximately 0.1 meq/kg.
- The strontium sorption isotherm has two inflection points, possibly indicating a more complex sorption mechanism. Sorption capacity, therefore, is dependent on the ratio of sample volume-to-mass of resin used in the batch test. If this ratio is less than 0.5 mL per mg resin, the strontium sorption capacity on the resin is 600 meq/kg. If the sample volume-to-resin mass ratio is greater than 2 mL/mg, the strontium sorption capacity in the simulant is only 4 meq/kg. In comparison, the strontium sorption capacity from the same simulant using pretreated zeolite is 30 meq/kg.
- The effect of elevated sodium, potassium, magnesium, and calcium concentration on strontium and cesium sorption was studied. Strontium sorption on the resin is significantly more affected by the presence of interfering cations, as compared to that observed with the zeolite. With the addition of 4 meq/L interfering cation to the waste water simulant, the strontium sorption ratio is reduced to 0.3% of its original value. Cesium sorption is reduced by 50% for the same increase in cation concentration.
- A column study was initiated to determine the breakthrough characteristics of strontium and cesium from R-F resin. The column is sized similarly to that of the zeolite column to compare column behavior directly. Packed density of the resin column was 0.43 g/cm^3 , as compared to 0.55 g/cm^3 for the zeolite column. Fifty percent breakthrough for strontium and cesium occurred at 525 and 3800 bed volumes, respectively.
- Crystalline nonatitanate products ($\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$) are currently being evaluated with the same procedures for characterizing the zeolite and R-F resin. We received nonatitanate powder and cylindrical pellets from AlliedSignal and a 3M web membrane containing the titanate powder. Equilibrium studies were completed to determine optimum contact time for nonatitanate powder and pellets in 10 mL of waste water simulant. Maximum strontium sorption on samples containing 5 to 100 mg powder ranges from 2 to 24 h. Beyond the optimum mixing time, strontium desorbs from the powder. Approximately 600 h of mixing is required for the nonatitanate pellets to obtain maximum strontium sorption. Beyond this time, strontium also desorbs from the pellets.

TTP INFORMATION

The Fission Products Separations Testing technology development activities are funded under the following technical task plan (TTP):

TTP No. OR16C312 "Fission Products Separations Testing"

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1.4

SEPARATION OF HTO USING MEMBRANES TRITIUM MEMBRANE TEST

TECHNOLOGY NEEDS

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

TECHNOLOGY DESCRIPTION

Polymeric composite membranes are being developed to remove tritium from contaminated water at DOE sites. Industrial membrane systems are being developed that have proven to be energy efficient, and membrane technologies such as reverse-osmosis have been well developed for desalination and other industrial/municipal applications. Aromatic polyphosphazene membranes are being investigated because they have excellent radiological, thermal, and chemical stability. The FY96 effort is directed toward delineating a potential mechanism, providing a statistical approach to data acquisition, refining a mass balance, and designing a staged array module. The major milestones of this project are directed at several issues, including a statistical approach to experimental design and mass balances, calculations from a designed module staged array, and a determination of the mechanism of the HTO separation.

In FY95, we showed that the poly[bis(phenoxy)phosphazene]-based membrane can consistently achieve 30% reduction in a single pass, from 3 $\mu\text{Ci/L}$ (K-East Basin water). The FY96 work is directed primarily at a basic understanding of the HTO separation. Thus, a series of mass balance experiments will be conducted to confirm the preliminary FY95 results. Experiments will follow statistically designed parameters. The designed experiments will examine factors that might impact the HTO separation, such as pH, ion type/concentration, and temperature.

Staff at the University of Idaho and the University of Washington will provide spectroscopic data on the possible mechanism of the HTO separation. SpinTek Membrane Systems (Huntington Beach, CA) will assist in the study of water permeation through the membranes. Several critical factors must be determined if the system is to be implemented. We expect to examine N-Basin water (39 $\mu\text{Ci/L}$) during FY96 as well as water with a much higher tritium content. Experiments with water in the milliCurie per liter or higher range will require coordination with regulatory and technical personnel and possibly other DOE sites. The data from this experiment is crucial because it will allow us to determine further design parameters for the staged array system. Once most of the mechanism information and membrane property data are obtained, we will calculate the hypothetical separation of the HTO from water in the cascade.

BENEFITS

Waters containing unacceptable tritium concentrations (above environmental release limits or drinking water standards) are released at DOE sites, including Hanford, Savannah River, INEL, LLNL, BNL, and Mound. One example involves the C-O18H Treatment Facility at Hanford (to treat 242A evaporator waste water), which will discharge (1.4 million gallons) of treated condensate containing tritium averaging 6.3 $\mu\text{Ci/mL}$ through the year 2015. Currently, water from some test wells at Hanford contain tritium concentrations approaching 6×10^7 pCi/L. The Tri-Party Agreement requires that the HTO in the K-East Basin (spent nuclear fuel storage) be treated or relocated. Currently, there are no acceptable removal options for tritium remediation other than migration with time through geologic formations. This work will reduce the risk to the environment and public, reduce the costs for ultimate disposal for the tritium-containing water, and provide a way to recover the tritium in a concentrated form for disposal or use.

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

COLLABORATION/TECHNOLOGY TRANSFER

This work is a collaborative effort between PNNL, WHC, and SpinTek Membrane Systems. Atomic Energy Canada, Limited, has also expressed interest in the membrane process and has entered into a proprietary agreement with PNNL. Two meetings with Ontario Hydro personnel have been conducted.

PNNL has expanded the involvement of interested industries, including collaboration with Desalination Systems, Inc., during FY95. Liumar Technologies Corporation has examined the polyphosphazene membranes for their proprietary applications and continue to provide us with information about aqueous permeation. Separation Systems Technology, Inc. (San Diego, CA) has also provided us considerable information concerning membrane properties needed for module design. SEG/Oak Ridge has discussed their need for this technology for application to commercial nuclear power facilities.

We have obtained information concerning deuterium and tritium physical properties from both the All Russian Institute of Chemistry/Murmansk and the Association of Advanced Technologies/MINATOM (Russia). We are collaborating with the University of Idaho and the University of Washington (Center for Process Analytical Chemistry) to help further define the HTO separation mechanism spectroscopically.

To promote interest in this technology, we presented the work before the Canadian Nuclear Society and the American Nuclear Society, and have a major publication in press. A patent was also issued.

ACCOMPLISHMENTS

- A statistical design of experiments was completed, and work toward providing the necessary information is under way.
- We have deionized and distilled 10 gallons of K-East Basin water ($3 \mu\text{Ci/L}$) and used this as a source of HTO for initial experiments. Twenty gallons of N Basin water ($39 \mu\text{Ci/L}$) will also be prepared for similar use.
- Experiments were conducted with 10% carboxylated poly(diphenoxy) phosphazene, unannealed, using distilled K-East Basin water ($3 \mu\text{Ci/L}$). The experiments indicated that HTO separation is quite variable and reached 18% depletion with only one carboxylated membrane under deionized water conditions. This confirms the variability from many previous experiments with unannealed membranes.
- The annealed membranes were also examined under similar conditions (4°C and distilled K-East Basin water), but the scintillation results indicate little, if any, HTO depletion. However, the pressure stability required to maintain permeation with the annealed membranes was more consistent in contrast to the continual pressure fluctuations needed for the unannealed membranes.
- The same set of experiments (two membranes and 4°C) was performed with distilled K-East Basin HTO containing $0.001 \text{ M Na}_2\text{SO}_4$. Both membrane types provided HTO separation, with the carboxylated membrane showing up to 17% HTO depletion, after 4 hours of operation. We are currently conducting

membrane experiments with 0.01 M and 0.1 M Na_2SO_4 solutions as well as with similar calcium salt concentrations. Although the initial experiments have not been completed, the current data suggest that hydration shell involvement may be a significant part of the HTO separation mechanism.

- Liumar Technologies Corporation of Ottawa, Ontario, is determining the coating conditions of the poly(diphenoxy)phosphazene with material from Ethyl Corp. They are also attempting to establish the nanofiltration characteristics of the membrane using various molecular weight polyethylene oxides.

TTP INFORMATION

The Separation of HTO Using Membranes and Tritium Membrane Test technology development activities are funded under the following technical task plan (TTP):

TTP No. RL36C311 "Separation of HTO Using Membranes" and TTP No. RL46C311 "Tritium Membrane Test"

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1.5

EXTENSION OF STUDIES WITH 3M EMPORE™ AND SELENTEC MAG*SEPSM TECHNOLOGIES FOR TECHNETIUM AND CESIUM REMOVAL FROM ENVIRONMENTAL SYSTEMS: FIELD TESTS

TECHNOLOGY NEEDS

Removing contaminants from large volumes of water, such as the ocean or a river, is a difficult task. The current accepted method of sampling ocean and river water for radionuclide contaminants is very costly and labor intensive. Large volumes of the water must be shipped to laboratories such as those at SRTC at considerable expense. At SRTC, 20 L of water are processed (for technetium and cesium) through a 2mL ion exchanged column to concentrate the radionuclide so that it can be counted directly on the resin or eluted and counted in the eluate. A 100L sample is needed for each plutonium analysis. After concentration, elution with acid generates a concentrated solution that can be further concentrated by evaporation and analyzed by sophisticated instruments capable of detecting very low levels of radioactivity.

TECHNOLOGY DESCRIPTION

In this task, researchers at SRTC are examining two new ion exchange-related technologies to improve environmental sampling and make it more cost effective. Selentec, Inc.'s MAG*SEPSM technology uses small (70- to 250µm) magnetite particles coated with ion exchange resin to contact dilute aqueous solutions for the selective removal of ions from those solutions. The particles can then be quickly recovered from the solution and sent for analysis. If eluted, they can be reused at least 10 times, based on lab studies at SRTC. Those studies have shown that particles incorporating TEVA™ resin, a product of Eichrom Industries, are very efficient for recovering technetium from ocean and river water. Particles incorporating SRTC's resorcinol-formaldehyde (R-F) resin have been shown to be very effective for quantitatively concentrating cesium ion.

The 3M Empore™ filter is a Teflon mesh material that securely holds high loadings of ion exchange resin among its fibers. Solutions pass through the filter material; a reasonably high flow rate affords contact of the liquid with the ion exchanger, which extracts ion of interest. Lab studies at SRTC have shown that small filters impregnated with TEVA™ and R-F resins extract TcO₄⁻ and Cs⁺, respectively, from ocean and fresh water as well as their 2-mL column counterparts used in the currently accepted procedure, but at far greater processing rates than those afforded by a column.

Laboratory studies and one field test show that the Selentec MAG*SEPSM and the EM EmporeTM filter, associated with an appropriate ion exchange resin, can concentrate ⁹⁹Tc, ¹³⁵Cs, and ¹³⁷Cs from large volumes of ocean and river water for analysis.

This task will focus on more field testing of the sampling concepts to validate methods so that sampling procedures can be published and adopted by other environmental samplers.

BENEFITS

Field testing of these two technologies for environmental sampling will lead to a validated method that will streamline sampling and monitoring techniques. Real-time sampling can be done so water will not have to be shipped and stored until ready for sample preparation for analysis. The costs for sampling and analysis should be reduced significantly in as much as small (gram quantities) samples of particles or filter discs already containing the ions to be analyzed, and not the water, will be returned to the lab.

The percent recoveries of ions removed by the 3M filter are quantitative enough in lab tests to indicate that an automated system under consideration should be useful in unmanned environmental monitoring tasks. MAG*SEPSM particles will be especially useful in sampling waters with high concentrations of suspended solids because prefiltration of the samples will not be needed. The magnet will easily separate particles from nonmagnetic sediment, making prefiltration unnecessary.

Once these sampling methods are validated, it is expected that the basic concept of using these two technologies can be expanded to decontaminate drummed wastes that are stored at each DOE site.

COLLABORATION/TECHNOLOGY TRANSFER

Many technology transfer opportunities exist within this project. Validation of sampling procedures will enable use of the MAG*SEPSM particles and 3M EmporeTM filters by environmental samplers everywhere. For example, a successful demonstration of the MAG*SEPSM particles with Mississippi River water convinced a sampling team to test the technology of the Ob River in Russia for technetium detection. SRTC researchers will test an automatic sampler adapted to accommodate the 3M Empore filter medium with TEVA resin for technetium collection in Savannah River Site streams. This will be a collaboration among SRTC, 3M, and ISCO (manufacturer of the automatic sampler) that could enable business development of sampling "kits" for unmanned environmental monitoring, for which there is a large market in the DOE complex.

Use of both technologies in selective cleanup of a wide variety of hazardous, radioactive, and mixed wastes currently stored in drums has been proposed to the Plume Focus Area as a result of the promise shown in early lab studies for the environmental sampling project. Further, there is the need to work with resin developers, in conjunction with Selentec Inc. and 3M, to enable the technologies to target an ever-wider suite of environmental pollutants that must be monitored and remediated.

ACCOMPLISHMENTS

- In FY95, both technologies were tested with the TEVA™ and R-F resins for TcO_4^- and Cs^+ , respectively.
- Two field units were developed for the MAG*SEPSM technology. The smaller unit, which affects particle contact with volumes equal to or less than 1 L was tested in New Orleans. The larger unit is designed for volumes from 1 to 20 L.
- Consultations were held with 3M about design of an autosampler and incorporation of the Empore™ membrane into its operation.
- Sodium titanate was incorporated into a small sample of the Empore™ filter and tested for plutonium removal from Arctic Ocean water. Analyses are under way.

TTP INFORMATION

The Extension of Studies with 3M Empore™ and Selentec MAG*SEPSM Technologies technology development activities are funded under the following technical task plan (TTP):

TTP No. SR16C343 "Extension of Studies with 3M Empore™ and Selentec MAG*SEPSM Technologies for Technetium and Cesium Removal from Environmental Systems: Field Tests"

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None available at this time.

2.0

LONG-LIVED RADIONUCLIDES

The Long-Lived Radionuclides product line provides technology to remove radionuclides with long half-lives such as uranium, plutonium, and technetium. Uranium and plutonium contamination is widespread throughout the U.S. Department of Energy (DOE) complex. Technetium is a major contributor to long-term risk assessment and may be a problem material in vitrification of Hanford wastes.

Technology being tested and demonstrated in this product line includes a polymer/ultrafiltration process to remove actinides. This process received an "R&D 100" award for its contribution in the electroplating industry. A high-temperature vacuum distillation technology will provide a means to remove actinides from 12 metric tons of salts at the Rocky Flats Plant. Additional studies are being conducted on solvent extraction to minimize the secondary waste and develop a more efficient extraction process. Other technologies being developed include ion exchange materials for the removal of actinides and technology to remove actinides from soils.

ESP supported technologies in this product line are:

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

2.1

HIGH-TEMPERATURE VACUUM DISTILLATION SEPARATION OF PLUTONIUM WASTE SALTS

TECHNOLOGY NEEDS

There are 16 metric tons of salts at Rocky Flats Plant containing approximately 1 metric ton of plutonium. Most of these salts (11 tons) are composed of a sodium chloride-potassium chloride matrix. The remainder consists of a calcium chloride matrix. These salt residues are the product of past plutonium processing operations. The Defense Nuclear Facilities Safety Board has expressed concern (in Recommendation 94-1) about possibly unstable residues resulting from suspension of weapons-related activities in the DOE complex. These concerns include residue salts stored at Rocky Flats.

DOE responded with commitments to mitigate the hazards associated with these residues, including mitigating the problems associated with 6000 kg of high-hazard pyrochemical salts at Rocky Flats by May 1997, and an additional 4000 kg by December 1997. The high-hazard salts are stored in drums in buildings where workers need routine access and are in proximity to the drums. These residues may pose a safety risk if the reactive metals in the residues come into contact with water, creating hydrogen gas that could cause container pressurization.

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

TECHNOLOGY DESCRIPTION

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

Distillation separation is based on the large difference in vapor pressures at high temperature between most chloride salts that constitute pyrochemical residues and the actinide oxides. However, the plutonium content in these salts is usually a form of plutonium trichloride. Vapor pressure differences

between alkali and alkaline earth chlorides and plutonium trichloride are too small to effect a good separation, therefore PuCl_3 must be converted to an oxide through an oxidation process. Staff at LANL have developed a process that uses carbonate salts to act as an oxidant. This process has proven very effective in converting all plutonium species into plutonium dioxide. This oxidation process can be ultimately combined with a distillation separation process.

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

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

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

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

BENEFITS

Separating the plutonium from the waste salts will lead to a large reduction in the cost of disposal, even if the salts do not meet LLW disposal criteria. Present Waste Isolation Pilot Plant (WIPP) Waste Acceptance Criteria (WAC) would result in a maximum plutonium loading per 55-gallon drum of 23 g. In the best

possible circumstance this would lead to more than 50,000 drums. Efforts are underway to modify the WIPP WAC to allow 200 g of plutonium per drum. This would still result in 8000 drums.

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

COLLABORATION/TECHNOLOGY TRANSFER

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

ACCOMPLISHMENTS

- Experiments with both uncontaminated and plutonium contaminated salts have unequivocally established that kilogram quantities of alkali metal chloride salts can be distilled per unit operation per day. Excellent mass balance has been achieved with both distilled salt (>99.5%) and distillation heel (>99.9%).
- Tests with salts (approximately 50 kg) containing plutonium have successfully separated alkali metal chloride salts from the actinide content of the residue. The plutonium concentration of the salts was reduced from the tens of percent level to the parts-per-million level.
- Salts pretreated by a molten carbonate oxidation process were found to be excellent feed for the distillation separation process. These results led to funding by DOE EM-60 for design and procurement of full-scale, production capable equipment. This equipment is scheduled to begin processing salt residues at LANL in March 1996. The processing campaign will serve as a pilot-scale demonstration for Rocky Flats.

TTP INFORMATION

The High-Temperature Vacuum Distillation Separation of Plutonium Waste Salts technology development activities are funded under the following technical task plan (TTP):

TTP No. AL16C321 "High-Temperature Vacuum Distillation Separation of Plutonium Waste Salts"

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None available at this time.

2.2

WATER-SOLUBLE CHELATING POLYMERS FOR REMOVAL OF PLUTONIUM AND AMERICIUM FROM WASTE WATER

TECHNOLOGY NEEDS

Alternative technologies are needed to treat radioactive waste water 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 into the environment.

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

Sludge handling and disposal is becoming more expensive as burial requirements increase and approved burial sites become less available. More stringent discharge regulations have been enacted by DOE, the 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 LANL Waste Treatment Facility. Precipitation technology cannot consistently meet current discharge limits for some metals. Even lower discharge limits are anticipated in the future. The longer-term goal of moving to closed-loop, zero-discharge systems for water handling will require new approaches and new combinations of technology.

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

TECHNOLOGY DESCRIPTION

Polymer filtration is a technology being developed to recover valuable or regulated metal ions selectively from process or waste waters. Water-soluble chelating polymers are specially designed to bind selectively with metal ions in aqueous solutions. The polymers' molecular weight is large enough so they can be separated and concentrated using available ultrafiltration technology.

Water and smaller unbound components of the solution pass freely through the ultrafiltration membrane. The polymers can then be reused by changing the solution conditions to release the metal ions, which are recovered in concentrated form, for recycle or disposal.

The basis for metal ion separation involves the retention of metal ions bound to the chelating groups of the water-soluble polymer while smaller unbound species and water pass freely through the ultrafiltration membrane (see Figure 2.2-1). The polymer filtration process allows for the selective concentration of dilute solutions

Figure 2.2-1. Metal ions bound to the chelating water-soluble polymer are retained by the ultrafiltration membrane; water and other small solute species pass through freely.

of metal ion contaminants. The reduced volume containing the polymer/metal ion complex can go directly to disposal or the metal ions can be recovered by a stripping reaction and the polymer can be recycled for further metal ion recovery. The advantage of this separation technology for dilute metal ion solutions is its rapid kinetics, which result from the homogeneity of the process. In addition, by careful selection of the

chelating functionality, selective metal ion complexation can be obtained.

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

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

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

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

BENEFITS

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

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

We also see potential application for the water-soluble polymers to decontamination and decommissioning work. The polymer solution can be used to wash surfaces and remove contaminating metal ions. The metal ions would then be concentrated and recovered through the ultrafiltration operation and the polymer reused for further cleaning. Water-soluble polymers related to

those prepared for this project have already shown promise for removing lead from soils at Superfund sites, and this work is proceeding to the demonstration phase. Other polymers have been developed for removing mercury contamination, controlling acid-mine-drainage, and removing technetium from groundwater. We are currently searching for demonstration sites for these applications.

COLLABORATION/TECHNOLOGY TRANSFER

Specific immediate customers for this technology are EM-30's Waste Treatment Facility at LANL and Defense Program's projects at LANL that cannot operate fully without the operations at the Waste Treatment Facility.

While application of the polymer filtration technology to electroplating operations is nearest to commercial deployment, we expect the prototype equipment that has been developed for these markets to be readily transferable to operations within the glove box environment at the LANL Plutonium Facility. The effort within EM-60 to stabilize residues and wastes at DOE facilities as a result of the Defense Nuclear Facility Safety Board's Recommendation 94-1, may also require this technology in the near term.

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

ACCOMPLISHMENTS

- A series of water-soluble polymers functionalized with phosphonic acid, acylpyrazolone, and hydroxamic acid chelating groups were prepared for evaluation and 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. Polymer concentration is generally about 1 wt%, and the solution is filtered through an ultrafiltration membrane with the appropriate molecular weight cutoff.
- To date, the phosphonic acid derivatives have shown the best properties for removing plutonium and americium in the target solutions. Therefore, FY96 demonstration tests will concentrate on using the phosphonic acid-containing polymers.
- A polymer filtration apparatus was deployed for tests on actual waste solutions in the LANL Plutonium Facility. We tested the polymer filtration process on 7 L of wash solutions with initial pH of 1.5. The water-soluble chelating polymer was added, and the pH was adjusted with potassium

hydroxide to the range of 5 to 6. The final permeate volume was approximately 6.75 L and the retentate volume was approximately 0.25 L. The alpha activity due to plutonium and americium was reduced from 75,400 cpm/mL in the original solution to 333 cpm/mL in the permeate (well below the discard limits for the industrial waste line).

- 10 L of nitric acid distillate (approximately 1 N) was run from an evaporator being tested to recycle nitric acid. About 1 L of 10 N potassium hydroxide solution was added to neutralize the acid and give a final pH of 8 to 8.5. The final permeate volume was approximately 10.5 L and the retentate volume was approximately 0.5 L. Permeate rates were in the range of 1 L every 12 to 16 minutes. The alpha activity was reduced from 4288 cpm/mL to 97 cpm/mL. A demonstration unit will be designed, built, and tested in FY96 on waste water produced in LANL's Plutonium Facility.
- Four patent applications were filed in May 1995 that cover a variety of polymer filtration applications including the removal of radioactive metal ions from waste water streams.

TTP INFORMATION

The Water-Soluble Chelating Polymers for Removal of Plutonium and Americium from Waste water technology development activities are funded under the following technical task plan (TTP):

TTP No. AL16C322 "Water-Soluble Chelating Polymers for Removal of Plutonium and Americium from Waste water"

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2.3

ADVANCED INTEGRATED SOLVENT EXTRACTION SYSTEMS

TECHNOLOGY NEEDS

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

TECHNOLOGY DESCRIPTION

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

The first objective of the program involves development and testing of a new technetium selective resin (ABEC-5000) and a new cesium-strontium selective resin (Diphonix-CS) that should have applicability for removing technetium, cesium, and strontium from the highly alkaline supernatant liquid in the single- and double-shell storage tanks at Hanford. Studies will involve the measurement of the influence of major constituents and radiolysis on the uptake and recovery of technetium by the

Figure 2.3-1. Advanced Integrated IX Systems

ABEC-5000 resin and on the uptake and recovery of cesium and strontium by the Diphonix-CS resin. After completion of these initial characterization studies, the two resins will be tested in a column mode using simulated alkaline waste. Figure 2.3-1 depicts the Advanced Integrated IX Systems in individual columns or in a mixed-bed mode.

The second major task is to develop an advanced acid-side SX process that will remove in one step ^{90}Sr , ^{99}Tc , ^{137}Cs , and TRUs from acidic HLW. Lanthanides would also be extracted together with TRUs. The process is called TOREX (for total radionuclide extraction) and is based on the use of a mixture of strontium-, cesium-, TRU- and technetium-selective extractants in a novel combined phase modifier-diluent reagent (Figure 2.3-2).

Figure 2.3-2. Advanced Integrated SX Systems

The TOREX process is designed to remove the desired radioisotopes at high nitric acid concentration and achieve recoveries at low acid concentrations. Selective stripping of strontium and cesium from TRUs and technetium is possible. The major advantage in performing a

TOREX-type process is the significant reduction in the size of the processing facility to pretreat HLW. Studies in FY96 will focus on developing and batch testing the TOREX process solvent.

The second part of the advanced integrated SX program is continuation of the development of a front-end combined cesium extraction-strontium extraction (CSEX-SREX) process. This combined CSEX-SREX system has been tested in a batch countercurrent mode in FY95. Acidic waste simulant from Lockheed Idaho Technology Company (LITCO) was used for the test and results were very favorable. Advantages of a combined CSEX-SREX extraction process at the beginning of a pretreatment sequence include removal of all the major gamma emitters and the need for considerably less shielding in all subsequent processing. Proof-of-principle studies were carried out in FY95. FY96 studies will involve the hot testing of the process in a continuous countercurrent solvent extraction mode using Argonne National Laboratory (ANL) centrifugal contactors.

BENEFITS

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

COLLABORATION/TECHNOLOGY TRANSFER

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

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

ACCOMPLISHMENTS

- The Combined CSEX/SREX Process for the simultaneous extraction of cesium and strontium from acidic nitrate media was successfully batch tested in a countercurrent mode using a dissolved calcine waste simulant from LITCO. The process uses a solvent formulation comprised of 0.05 M di-t-butylcyclohexano-18-crown-6, 0.1 M Crown 100' (a proprietary cesium-selective macrocyclic polyether), 1.2 M tri-n-butylphosphate, and 5% (n/n) lauryl nitrile in an isoparaffinic hydrocarbon diluent. The countercurrent test run indicates that more than 98% of the cesium and strontium initially present in the feed solution can be removed in only four extraction stages. Both cesium and strontium are readily recovered by stripping the process solvent with 0.1 M HNO_3 .
- Considerable progress was made to date on the synthesis and characterization of both ABEC-5000 and Diphonix-CS resins. The ABEC-5000 resin has been evaluated for technetium uptake as a function of sodium hydroxide concentration and as a function of sodium nitrate, nitrite, carbonate, aluminate, and citrate concentration in 2 and 4 M NaOH. The distribution ratios of technetium are in the range of 10^2 to 10^3 units and are very insensitive to the above list of anions over a wide range of concentrations. Technetium uptake measurements with simulated 101-SY, neutralized current acid waste, and single-shell tank waste solutions have also been made. The dry weight D_{Tc} is in the 1×10^2 to 2×10^2 range with all three waste solutions. Elution units of technetium from packed bed with H_2O has also been demonstrated.

TTP INFORMATION

The Advanced Integrated Solvent Extraction Systems technology development activities are funded under the following technical task plan (TTP):

TTP No. CH26C321 "Advanced Integrated Solvent Extraction Systems"

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BIBLIOGRAPHY OF KEY PUBLICATIONS

None available at this time.

2.4

THERMALLY UNSTABLE COMPLEXANTS PHOSPHATE IMMOBILIZATION OF ACTINIDES

TECHNOLOGY NEEDS

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

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

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

Phosphate mineralization is a concept that can potentially immobilize radioactive metal ions in the environment. It is a safe, simple, and inexpensive

alternative to pump-and-treat methods for groundwater decontamination or the installation of massive barriers to prevent nuclide migration (in situ grouting). Alternatively, it could be applied as a finishing step following the removal of most of the radionuclides from the site. The process could be applied to waste disposal sites (used either before or after burial) such as Hanford and INEL, areas of accidental environmental contamination (Fernald, Rocky Flats), or even to commercial mill tailings piles.

TECHNOLOGY DESCRIPTION

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

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

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 geomedias and synthesized analogs. Verification of reduced "solubility" (not thermodynamic solubility products, but actual radionuclide concentrations) of actinide ions in the III, IV, V, and VI oxidation states as a function of pH and phosphate concentration is a primary goal. Ultimately, the concept could be developed to treat various mill-tailings piles in addition to those media contaminated with transuranics.

BENEFITS

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

The principal benefits to be derived from the demonstration of this process are to eliminate the need for pumping groundwater or excavating 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.

ACCOMPLISHMENTS

As initially conceived, this program was to rely on the class of compounds called Thermally Unstable Complexants (TUCS). These ligands, diphosphonic acid chelating agents were designed to spontaneously decompose under suitable conditions, but proved too robust for the purpose under environmental conditions. The organophosphate complexing agent phytic acid (Figure 2.4-1) (myo-inositol(hexakisphosphoric acid)) was then identified as a potential substitute for the phosphonate chelating agents. Phytic acid has much better characteristics for the design objective than the phosphonate TUCS compounds. It is a natural product and forms insoluble salts with polyvalent cations (Ca^{2+} , for example), thus potentially serving as a cation exchanger. It is known to be a readily hydrolyzed releasing phosphate, and the organic residue (inositol) does not complex metal ions and will not interfere with the mineralization process.

Figure 2.4-1 Structure of the organophosphate complexing agent phytic acid.

The rate of production of phosphate from phytate as a function of temperature and pH has been investigated using spectrophotometric techniques and Nuclear Magnetic Resonance (NMR) spectroscopy. Independent of the starting pH, all systems tend toward a final pH of 6, buffered by the $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ hydrolysis product. NMR spectroscopy indicates inositol as the major immediate organic product. No evidence was found for significant buildup of intermediate inositol(phosphate) species ($\text{I}(\text{PO}_4\text{H}_2)_{6x}$). Extrapolation of the rate parameters using the Arrhenius relationship at pH 5 and 6 gives the lifetime for phytate 104 ± 22 years at pH 5.1 and 156 ± 42 years at pH 6.0. Reports indicate that microbiological effects can shorten this lifetime by orders of magnitude. Other reports have implicated polyvalent metal ions in accelerated phytate hydrolysis. The lifetime of phytic acid in the environment becomes immaterial if it functions in the intermediate term as an effective cation exchange medium.

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

The "solubility" of europium, uranyl, and neptunium (V), as a function of pH and phosphate concentration in a synthetic groundwater solution ($I=0.1 \text{ M}$, $[\text{NaHCO}_3]=0.5 \text{ mM}$), has been determined in a series of experiments using radiotracers. Solid films of metal nitrates, hydroxides, citrates, and TRUEX process solvent solutions were deposited on glass surfaces and contacted with the synthetic

groundwater solutions. In both the europium and uranyl systems, the concentration of the radionuclide in the synthetic groundwater was controlled by phosphate even at 0.1 mM total phosphate. Europium concentrations were less than 2×10^{-9} M even at the lowest phosphate concentration. Uranyl concentrations were below 2×10^{-7} M in the presence of phosphate with concentrations decreasing at higher pH. Each of these solubility limits is at least 10 times lower than that observed in the absence of phosphate and generally consistent with thermodynamic calculations. NpO_2^+ concentrations were not appreciably affected by phosphate except at $[\text{PO}_4]_t > 1.0$ mM and at pH 7-8. Under these conditions, neptunium solubility is controlled at about 10^{-6} M. Ongoing experiments are investigating the effect of coprecipitation on $[\text{NpO}_2^+]$ in solution.

TTP INFORMATION

The TUCS/Phosphate Immobilization of Actinides technology development activities are funded under the following technical task plan (TTP):

TTP No. CH26C322 "Thermally Unstable Complexants (TUCS)/Phosphate Immobilization of Actinides"

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None available at this time.

2.5

SELECTIVE IN SITU SORPTION OF TECHNETIUM FROM GROUNDWATER

TECHNOLOGY NEEDS

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

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

TECHNOLOGY DESCRIPTION

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

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

Further improvements can be made to our best candidate resins to increase both the K'_d , $K'_d(\text{eq})$, and especially the kinetic behavior. In the first few months of FY96, we will finalize the resin synthesis and development portion of this project, and begin testing the best candidate resins under flow-through column conditions using first more realistic groundwater simulants and then using actual technetium-contaminated groundwater (available from Paducah).

As only equilibrium selectivity has been investigated to date, we plan in FY96 to determine selectivity under conditions of solution flow in a column where mass transport issues become important. In addition, we plan to test our best

candidate resins under actual flow-through conditions in the ground by pumping non-contaminated groundwater through the resins for a month or more (at Portsmouth), to investigate the stability of the resins to breakdown, fouling, and degradation by the environment (e.g., attack by microorganisms, etc.). Following this test, we will include our best resins in a small field demonstration using technetium-contaminated groundwater designed to generate data for scale-up to a larger field demonstration project. We want to include our optimum resin in demonstration projects at both Portsmouth and Paducah in FY97.

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

BENEFITS

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

COLLABORATION/TECHNOLOGY TRANSFER

University of Tennessee, Knoxville.

ACCOMPLISHMENTS

- We synthesized and studied a series of resins in which the properties of the resin were systematically varied. We prepared 64 synthetic resins that were tested along with seven commercial resins for sorption of pertechnetate from a groundwater test solution under 24h batch equilibrium conditions.
- We successfully met our objective in FY95 to prepare resins that would possess higher selectivity for pertechnetate over other anions, as compared with existing (commercially available) resins, while maintaining good capacity. Table 1 shows resins that have higher distribution ratios for pertechnetate both on a weight basis (K'_d) and per exchange site ($K'_d(\text{eq})$), the latter being a better indication of selectivity. The best synthetic resin with regard to overall performance has a pertechnetate distribution ratio (K'_d) of 41,700 mL/g, twice that of the best commercially available resin.

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

Table 2.5-1 Sorption results for pertechnetate from groundwater test solution (24h equilibration times) for selected synthetic and commercial anion exchange resins, with values of K'_d in descending order. Uncertainties are $\pm 5\%$.

We applied our knowledge of the properties of existing anion exchange resins in making both the chemical and physical modifications necessary to improve both the K'_d and the K'_d (eq) for pertechnetate.

TTP INFORMATION

The Selective In Situ Sorption of Technetium from Groundwater technology development activities are funded under the following technical task plan (TTP):

TTP No. OR16C311 "Selective In Situ Sorption of Technetium from Groundwater"

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2.6

TECHNETIUM AND ACTINIDE SOLVENT EXTRACTION

TECHNOLOGY NEEDS

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

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

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

TECHNOLOGY DESCRIPTION

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

The purpose of this task is to develop an efficient solvent-extraction and stripping process to remove the fission products ^{99}Tc , ^{90}Sr , and ^{137}Cs from alkaline tank wastes, such as those stored at Hanford and Oak Ridge. As such, this task expands on FY95's successful development of a solvent-extraction and stripping process for technetium separation from alkaline tank-waste solutions. This process now includes the capability of removing both technetium and strontium simultaneously. In this form, the process has been named SRTALK and will be developed further in this

program as a prelude to developing a system capable of removing technetium, strontium, and cesium.

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

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

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

In FY96 we plan to develop the process flowsheet for the solvent extraction of technetium from alkaline supernatant and water stripping as needed by potential users. For example, Pacific Northwest National Laboratory (PNNL) has proposed to test the process on simulated and actual Hanford supernatant in 2-cm centrifugal contactors. We plan to continue investigating appropriate extractants, diluents, and modifiers for the combined extraction of technetium, strontium, and cesium. Key issues are achieving high extraction and stripping ratios for all of these, as some factors that enhance cesium extraction might suppress technetium stripping. This may additionally involve some combined effort with optimizing cesium and strontium extractants.

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

BENEFITS

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

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

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

COLLABORATION/TECHNOLOGY TRANSFER

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

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

ACCOMPLISHMENTS

- A solvent-extraction and stripping process was defined for removing technetium from alkaline tank waste.
- A highly effective solvent for the process contains 4,4', (5')-di-*t*-butyldicyclohexane-18-crown-6 dissolved in TBP-modified isoparaffinic kerosene. The solvent has been tested on actual tank waste from ORNL's MVST; performance was equivalent to that obtained with waste simulants. Extraction and stripping efficiencies of 98% or better are attainable with two-stage extraction and two-stage stripping at unit phase ratio using waste simulants.
- The SRTALK process is under development to simultaneously extract technetium and strontium from alkaline tank-waste supernate. Results using a MVST simulant have shown that combined extraction and stripping efficiencies of 96% and 99% for technetium, respectively, and 62% and >99% for strontium, are attainable with two-stage extraction and two-stage stripping at unit phase ratio. Work toward increasing the extraction efficiency for strontium has produced excellent results from simple alkaline sodium nitrate solutions.
- Results to date reveal cesium extraction and stripping efficiencies from actual MVST W-29 waste of 89% and >99%, respectively, following four equal-volume cross-current extraction contacts, and four equal-volume cross-current stripping contacts using

only water. Combined technetium and cesium extraction and stripping results from MVST W-29 simulant have shown that combined extraction and stripping efficiencies of respectively 96% and 83% for technetium, and 37% and 93% for cesium, are attainable with two-stage extraction and two-stage stripping at unit phase ratio.

TTP INFORMATION

The Technetium and Actinide Solvent Extraction technology development activities are funded under the following technical task plan (TTP):

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2.7

ELECTRICALLY CONTROLLED CESIUM ION EXCHANGE

TECHNOLOGY NEEDS

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

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

TECHNOLOGY DESCRIPTION

This task proposes a new approach for radionuclide separation by combining IX and electrochemistry to provide a selective and economic separation method.

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

Although the compositions of DOE tank waste vary significantly among sites, initially our approach is limited to investigating cesium removal from Hanford tank waste using nickel hexacyanoferrate IX films. PNNL researchers have performed proof-of-principle experiments with these films and obtained encouraging results. The films show cesium selectivity in the presence of high sodium concentrations and have a lifetime approximately ten times that of traditional organic IX materials. The primary advantage to our method is that secondary waste is minimized as compared to traditional IX and electrochemical ion exchange (EIX), which rely on acid elution and caustic sodium loading process steps. These process steps and the need to control interfacial pH are eliminated by using electrochemical redox reactions within the film to control

ion binding. This task is a collaboration between PNNL, The Electrosynthesis Company (East Amherst, NY), and the University of Washington.

Our approach is to deposit nickel hexacyanoferrate films on industrially available substrates such as porous nickel electrodes. Figure 2.7-1 shows a simplified schematic of the IX process using this electroactive material. In this system, the oxidation state of the iron (+2 or +3) is easily controlled by relatively small changes in the applied voltage (from 100 to 300 mV). When a cathodic potential is applied to the film, Fe^{+3} is reduced to the Fe^{+2} state, and a cation must be intercalated into the film to maintain charge neutrality (i.e., Cs^+ is uptaken).

Figure 2.7-1. Simplified schematic of a process where the ion exchange characteristics are controlled by modulating the applied potential. The first drawing shows the film driven cathodically, causing an uptake of cesium, and the second shows the film driven anodically, causing a release of cesium.

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

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

In FY96, we will initially establish subcontracts with the University of Washington and The Electrosynthesis Company and will provide a project management plan to the ESP. One meeting with all participants will be scheduled to ensure cohesive collaboration. The experimental work at PNNL will include optimization of the deposition parameters for the nickel hexacyanoferrate film. This work will be performed in collaboration with the University of Washington and include an experimental matrix for statistical optimization of the following variables: potentiostatic/galvanostatic conditions, waveform of potential/current, deposition time, and reactant composition ($\text{KNO}_3/\text{K}_3\text{Fe(CN)}_6/\text{K}_4\text{Fe(CN)}_6/\text{KOH}$).

The synthesized films will be characterized using traditional electrochemical (voltammetry, electrochemical quartz crystal microbalance, and impedance) and

surface science (X-ray diffraction, scanning electron microscopy) techniques. The characterization will address film structure, cesium IX capacity, film stability at high pH, and cesium uptake and elution rates. In addition, the optimal loading and unloading potentials will be determined for high-surface area electrodes. These potentials should not vary significantly between the laboratory-scale and the bench-scale designs. The Electrosynthesis Company will assist PNNL in the design of a continuous-flow cell for bench-scale testing. The initial design may incorporate a nickel foam electrode with several reference electrode probes to verify the uniform potential distribution.

BENEFITS

- The benefits of potentially modulated ion exchange as applied to Hanford tank waste are listed below:
- Minimal secondary waste is generated as compared to using competing technologies such as traditional IX. Several process steps are eliminated, and the elution volume can be controlled.
- PNNL researchers have demonstrated that the IX films can be cycled at least 100 times with only a 25% loss in film activity. This is significantly higher (greater than tenfold) than the traditional IX process.
- The technical approach has enormous potential for multivalent ions, such as strontium, once a suitable electroactive film is identified for those systems.
- The uptake/elution of ^{137}Cs is controlled by the applied potential and not by the interfacial pH. Also, no hydrogen is generated during the uptake or elution process.
- Possible problems, such as uniform potential distribution, can be easily overcome with standard electrochemical engineering practices.
- This approach enables the hexacyanoferrate IX material to be reusable, while in the traditional IX configuration the material cannot be regenerated and must be discarded.

COLLABORATION/TECHNOLOGY TRANSFER

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

ACCOMPLISHMENTS

Several "proof of principle" experiments have been performed with the nickel hexacyanoferrate system to validate the approach. Nickel electrodes, with surface areas up to 100 cm^2 , were coated with a hexacyanoferrate IX film, and the iron oxidation state was modulated through the applied potential. The experiments showed that the iron oxidation state (+2 or +3) can be changed easily without water electrolysis. Figure 2.7-2 shows the redox reaction of iron (+2 and +3) in a nickel hexacyanoferrate film for 1515 cycles of sodium uptake and elution. The film is extremely reversible with a approximately 25% capacity loss (i.e., decrease in peak current) after 100 uptake/elution cycles. This stability is substantially higher than the baseline IX technology, which is estimated to be economical for only 20 to 30 cycles.

Figure 2.7-2. Cyclic voltammograms of a nickel hexacyanoferrate film at 50 mV/s in 0.5 M Na_2SO_4 showing the oxidation and reduction reactions of iron after several cycles.

We have also shown qualitatively that the deposited nickel hexacyanoferrate films are selective for cesium.

Figure 2.7-3 shows three cyclic voltammograms for a nickel hexacyanoferrate film in solutions of 0.66 mM CsNO_3 , 0.5 M Na_2SO_4 , and a mixture of 0.66 mM CsNO_3 /0.5 M Na_2SO_4 . The peak current for the pure 0.66 mM CsNO_3 solution is significantly lower than that of the pure 0.5 M Na_2SO_4 solution. This is partly due to the lower cesium concentration. The peak current in the mixture was also found to be lower than that measured in the pure Na_2SO_4 . This strongly suggests that the deposited film preferentially uptakes and elutes cesium even in the presence of a high sodium concentration (mole ratio of Na:Cs = 1500).

Figure 2.7-3. Cyclic voltammograms of a nickel hexacyanoferrate film in 0.5 M Na_2SO_4 , 0.66 mM CsNO_3 , and a mixture of 0.5 M Na_2SO_4 /0.66 mM CsNO_3 showing iron oxidation and reduction reactions.

TTP INFORMATION

The Electrically Controlled Cesium Ion Exchange technology development activities are funded under the following technical task plan (TTP):

TTP No. RL36C321 "Electrically Controlled Cesium Ion Exchange"

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None available at this time.

2.8

DERIVATIVE OF NATURAL COMPLEXING AGENTS: REMOVAL OF PLUTONIUM IN WASTE AND NEW LIGANDS BASED ON NATURAL COMPLEXING AGENTS

TECHNOLOGY NEEDS

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

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

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

TECHNOLOGY DESCRIPTION

In the natural iron(III) sequestering agents, multiple catechols (e.g., Enterobactin) or hydroxamic acids (e.g., desferrioxamine B) are combined in polydentate ligands to fully bind the metal in a six-coordinate complex. These chelate groups are ideal for sequestering many Lewis acidic metal cations and can readily be incorporated into ligands for actinide (IV) cations. We have therefore focused our efforts on the binding properties of catecholamides, terephthalamides, and hydroxypyridinones (Figure 2.8-1).

Figure 2.8-1 The powerful chelating groups catecholamide, terephthalamide, 1,2-HOPO, 3,2-HOPO and 3,4-HOPO.

Thermodynamic measurements have been made to ensure that these bidentate groups show selectivity for actinide (IV) ions over iron(III). The thermodynamic binding constants between the ligands shown in Figure 2.8-3 and the metals iron(III) and thorium(IV) have been determined and are detailed in Table 2.8-2. These measurements show that all three binding groups form 1:4 complexes with thorium(IV).

	MTA	N-Pr-1,2-HOPO	N-Pr-3,4-HOPO
PROTONATION CONSTANTS	11.1 6.1	4.96(2)	9.47(2) 3.03(4)
Fe(III) FORMATION CONSTANTS (ML)	16.4	9.0(1)	14.6(1)
ML ₂	30.9	15.8(2)	26.7(1)
ML ₃	41.8	24.1(2)	36.24(4)
Th(IV) FORMATION CONSTANTS (ML)	27.9(7)		13.5(2)
ML ₂	38.5(5)		25.0(8)
ML ₂ H	45.0(9)		
ML ₂ (OH) ₂		12.1(2)	
ML ₃	45.1(1)		35.8(2)
ML ₃ (OH)		24.9(2)	
ML ₄	50.5(1)	36.0(3)	41.8(5)

Table 2.8-2. Thermodynamic Constants determined for MTA, N-Pr-1,2-HOPO and N-Pr-3,4-HOPO.

Figure 2.8-3. Structures of the bidentate binding groups MTA, N-Pr-1,2-HOPO and N-Pr-3,4-HOPO for which stability constants with Th(IV) and Fe(III) have been determined.

Incorporating these powerful chelating groups into solid/liquid and liquid/liquid extractant systems can produce materials with potential practical application. The liquid/liquid extractants employ the simple bidentate chelating groups, modified with a wide variety of lipophilic side chains designed to systematically alter their solubility properties (Figure 2.8-4). Initial experiments have been performed to determine the distribution coefficients of the extractants between aqueous and a number of common organic phases used in separations technology. Several materials with low water solubility have been tested for their ability to extract Lewis acid metals from aqueous media under varying conditions of pH and ionic strength. Several of the 1,2-HOPO sequestering agents seem particularly promising, showing quantitative removal of Lewis acid metal ions into organic media.

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 2.8-4. Lipophilic extractants that have been synthesized.

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

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

The heterocyclic hydroxypyridinones have found a further application in the chemistry of uranium. The simple bidentate form 2:1 complexes with uranyl ion and the isolation and structural characterization of several of these complexes has been achieved. From a knowledge of these basic binding interactions we should be able to design ligands with increased specificity for $[UO_2]^{2+}$. The ligand N-methyl-3,2-HOPO-4-propylamide (Figure 2.8-5) readily forms a 2:1 complex with uranyl ion in which the HOPO ligands bind in the equatorial plane of the $[UO_2]^{2+}$ species as demonstrated by X-ray crystallography (Figure 2.8-6).

The ligands are unable to fully satisfy the coordination requirements of the metal and a final coordination site is occupied by solvent. By including an additional neutral donor into a tetradentate ligand a considerable increase in stability should be achieved, and the ligand 5-LIO-Me-3,2-HOPO (Figure 2.8-7) has been studied as a possible way to achieve this. Furthermore, increasing the length of the alkyl group on the amide provides a way to increase the lipophilicity of these neutral 2:1 complexes.

Initial animal studies show that bis bidentate hydroxypyridinone ligands show much enhanced ability to remove uranium from mice when compared to more common metal ion sequestering agents such as ethylene-diamine tetraacetic acid (EDTA) and diethyl-enetriamine pentaacetic acid (DTPA). Further work to determine the stabilities of these species by solution thermodynamics and to structurally characterize uranyl complexes

Figure 2.8-5 N-methyl-3,2-HOPO-4-propylamide.

Figure 2.8-6 X-ray crystal structure of N-methyl-3,2-HOPO-4-propylamide with uranyl ion as the DMF solvato species.

Figure 2.8-7. 5-LIO-Me-3,2-HOPO.

of bis bidentate ligands, incorporating, 3,2-HOPO, 1,2-HOPO, catechola-mides and terephthalamides is now in progress. The possibility of functionalizing these species to form lipophilic or hydrophilic species and immobilizing them on solid supports to form new extractant materials is also under investigation.

BENEFITS

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

TTP INFORMATION

The Derivative of Natural Complexing Agents: Removal of Plutonium in Waste, and New Ligands Based on Natural Complexing Agents technology development activities are funded under the following technical task plan (TTP):

TTP No. SF26C311 "Derivative of Natural Complexing Agents: Removal of Plutonium in Waste" and

TTP No. SF16C311 "New Ligands Based on Natural Complexing Agents"

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None available at this time.

3.0

HEAVY METALS

Several toxic metals of concern (e.g., mercury) are found in various waste streams throughout the U.S. Department of Energy (DOE) complex. Many pretreatment, immobilization, and storage processes and methods are impacted negatively by the presence of toxic metals. This product line is pursuing technology that removes these metals safely and efficiently.

Ongoing research in this product line includes the development of molecular modeling technology to determine the best sorbents to remove toxic metals, while avoiding the costly expense of performing detailed laboratory tests. The development of polymer pendant ligands for rapid and selective removal of toxic metals is also being studied.

Efficient Separations and Processing-supported technologies in this product line are:

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

3.1

LIGAND MODELING AND DESIGN

TECHNOLOGY NEEDS

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

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

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 applications for the cost-effective removal of specific radionuclides from nuclear waste streams.

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

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

BENEFITS

This new technology—the design criteria coupled with the computer-based molecular model—enables one to assess the reactivity of an organic ligand

toward a target metal ion on the basis of molecular structure. This capability can be used to screen potential ligands before undertaking the time and expense associated with synthesis and testing.

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

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

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

COLLABORATION/TECHNOLOGY TRANSFER

PNNL staff are collaborating with:

- Norman Allinger, University of Georgia, author of MM3--adding a methodology for treating high-coordinate metal complexes to the next scheduled release of the software, MM3(96)
- Philip Horwitz and co-workers at Argonne National Laboratory--performing calculations to optimize the performance of the SREX ligand and to design a selective ligand for radium.
- Bruce Moyer and co-workers at Oak Ridge National Laboratory--performing calculations to identify structural factors that control reactivity in benzocrowns and improve the cesium/sodium selectivity that can be obtained with ligand-bearing benzoether groups.
- IBC Advanced Technologies--providing design criteria, MM3 parameters, and a conformer searching algorithm to their in-house theoretician, Robert Hancock.

ACCOMPLISHMENTS

- The inexpensive, off-the-shelf molecular model MM3 was configured to handle aliphatic crown ether ligands and their complexes with the alkali and alkaline earth metal ions.
- MM3 demonstrated that it can 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 crown ethers have been developed.
- MM3 is currently being applied to the design and screening of aliphatic crown ether ligands for the separation of cesium and radium and the optimization of the SREX reagent.
- MM3 is being extended to treat metal complexes with ligands bearing benzo ether donor atoms such as benzocrown ethers, calixarenes, and spherands.

TTP INFORMATION

The Ligand Modeling and Design technology development activities are funded under the following technical task plan (TTP):

TTP No. RL36C331 "Ligand Modeling and Design"

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3.2

REMOVAL AND RECOVERY OF TOXIC METAL IONS FROM AQUEOUS WASTE SITES USING POLYMER PENDANT LIGANDS

TECHNOLOGY NEEDS

Efficient removal or recovery of Resource Conservation and Recovery Act (RCRA) metals and radionuclide from aqueous wastes at DOE sites will benefit from improved ion exchange materials. The cost of developing and deploying advanced ion exchange materials will remain small compared to the cost of major competing technologies, such as precipitation or indiscriminate separation of all metal ions from wastes.

TECHNOLOGY DESCRIPTION

The purpose of this project is to develop polymer pendant ligand technology to remove and recover toxic metal ions from aqueous wastes. Polymer pendant ligands are organic ligands anchored to crosslinked, modified divinylbenzene-polystyrene beads that can selectively complex metals ions. The objectives include synthesizing selective polymer pendant ligands for removal and recovery of ions, determining the kinetics of the process, and transferring the technology to our industrial partner, AquaEss, San Jose, California, who performs application studies and will eventually implement the technology.

Studies in FY94 and FY95 focused on acid mine waste water (e.g., pH 2.5) represented by the Berkeley Pit at Butte, Montana, with emphasis on removing iron(III), aluminum, chromium(III), copper(II), zinc, manganese(II), magnesium, nickel(II), and silver. Because iron is the dominant cation in the Berkeley Pit, we focused on devising iron-selective ligands to remove this species first. AquaEss has developed a strategy for using this kind of ligand for acid waste water.

In FY96, we are focusing on removing RCRA metal ions, including silver, mercury(II), lead, cadmium, and copper(II). This application of the technology is opposite to that for acid mine waste water dominated by iron(III). Instead, ligands are needed to remove RCRA metal ions in the presence of modest iron(III) cations. AquaEss has begun devising column processing strategies for using such ligands.

COLLABORATION/TECHNOLOGY TRANSFER

AquaEss, San Jose, California

Robert Albright, Consultant

ACCOMPLISHMENTS

During FY94 and FY95, we developed selective polymer pendant ligands to remove and recover Fe^{3+} ion (Berkeley Pit acid mine waste water). The polymer pendant catecholligand derivatives, sulfonated catechol and sulfonated 3,3-LICAMS (Figure 3.2-1), are structurally similar to biological ligands that selectively sequester Fe^{3+} .

PS-3,3-LICAMS and PS-CATS removed Fe^{3+} ions from aqueous acidic waste waters (pH values of 0.5 to 2.5) with high capacities (0.8 to 1 mmol/g beads) and excellent removal kinetic rates ($2.4 \times 10^{-4} \text{ s}^{-1}$). Recovery of Fe^{3+} from the beads and then reuse of the beads was readily accomplished using a 2 N H_2SO_4 solution.

In subsequent application studies, AquaEss used column experiments with the above-mentioned polymer pendant ligands that showed a displacement phenomena occurred that can be used to separate Fe^{3+} ions from Al^{3+} , Cr^{3+} , Cu^{2+} , Zn^{2+} , Mn^{2+} , Mg^{2+} , and Ni^{2+} ions.

PS-SED, 1.12 mmol/g, anchored on modified, macroporous 6% polystyrene-divinylbenzene beads, is highly selective for Ag^+ ions at pH 3.0 in the presence of a variety of competing tri- and divalent metal ions such as Fe^{3+} , Cr^{3+} , Al^{3+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Mg^{2+} , Mn^{2+} , and Pb^{2+} (batch experiments).

When Hg^{2+} ions are added to the other ions, including silver, the PS-SED ligand is selective for the mercury. In the absence of mercury and silver, the ligand is moderately selective for lead over cadmium and other ions; except copper competes significantly. In the absence of lead, the ligand is moderately selective for cadmium over other ions, except copper. The selectivity of the ligand for the cations investigated is: $\text{Hg(II)} > \text{Ag} > \text{Cu(II)} > \text{Pb} > \text{Cd} > \text{Fe(III)}$ approximately Al approximately $\text{Cr(III)} > \text{Ni(II)} > \text{Zn}$ approximately $\text{Co(II)} > \text{Mn(II)} > \text{Mg}$.

AquaEss performed a column experiment with the PS-SED beads with a synthetic waste water that contained 200 ppm each of Ag^+ , Hg^{2+} , Pb^{2+} , Cd^{2+} , and Fe^{3+} ions at pH 3, representing a combination of RCRA metal ions

Figure 3.2-1 PS-CATS AND PS-3,3-LICAMS

Figure 3.2-2. PS-SED

that pervade DOE sites. All the Ag^+ , Hg^{2+} , and Pb^{2+} ions (200 ppm each) were removed from solution at pH 3 and retained on the column; while Cd^{2+} and Fe^{3+} ions were mostly retained on the column (approximately 75%), both were evident at column breakthrough by the familiar displacement phenomena. Therefore, Fe^{3+} ions form kinetically and thermodynamically less stable complexes with PS-SED in comparison to Ag^+ , Hg^{2+} , and Pb^{2+} , while Cd^{2+} ions appear to be influenced by the presence of Fe^{3+} and Pb^{2+} ions, and this phenomenon is now being investigated.

TTP INFORMATION

The Removal and Recovery of Toxic Metal Ions from Aqueous Waste Sites Using Polymer Pendant Ligands technology development activities are funded under the following technical task plan (TTP):

TTP No. SF16C331 "Removal and Recovery of Toxic Metal Ions from Aqueous Waste Sites Using Polymer Pendant Ligands"

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4.0

WASTE PROCESSING AND TREATMENT

The Waste Processing and Treatment product line involves treatment processes that remove the materials described in the previous product lines (Short-Lived Radionuclides, Long-Lived Radionuclides, and Heavy Metals), along with other distinct separation needs such as nitrite and nitrate removal.

Many of the ion exchange materials developed in the Short-Lived Radionuclides product line are being tested in column-size equipment to determine various parameters needed for scale-up. The removal of sodium, organics, nitrates, and nitrites can significantly reduce the volume of wastes needing final disposal.

Efficient Separations and Processing-supported technologies in this product line include:

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

4.1

IMMOBILIZATION OF FISSION PRODUCTS IN PHOSPHATE CERAMIC WASTE FORMS

TECHNOLOGY NEEDS

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

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

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

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

TECHNOLOGY DESCRIPTION

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

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

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

In this new project, major tasks include: (1) demonstrating the S/S of waste streams containing fission products, (2) scaling up the phosphate-bonded immobilization technology for field applications, and (3) transferring the phosphate-bonded immobilization technology to end users. During FY96, we will focus on developing appropriate phosphate-bonded ceramic waste forms with optimized process parameters, using specific surrogate fission-product waste streams, and demonstrating their effective stabilization.

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

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

During FY96, we will develop durable final waste forms using chemically bonded phosphate ceramics and simulated fission-product-rich waste stream. Three different phosphate systems (zirconium, magnesium, and titanium) will be investigated. We will identify one or more suitable phosphate systems for the waste stream under consideration (based on the requirements of individual waste streams) and then develop the waste forms with optimized properties. The detailed approach for the FY96 task will be as follows:

- Identification, Fabrication, and Characterization of Candidate Phosphate Systems:
 - Identify the phosphate systems applicable to particular waste streams, based on physical and chemical properties and thermodynamic stability.
 - Fabricate dense and strong monolithic ceramics at bench scale, using low-temperature processing routes.
 - Perform microstructural and mechanical characterizations and durability studies of monolithic phosphate ceramics.
- Development of Optimized Simulated Wastes Forms with Radionuclide Surrogates:
 - Incorporate surrogate wastes in phosphate matrices with various waste loadings at bench scale. These surrogate wastes will be modeled on the compositions of actual fission-product waste streams at DOE sites.
 - Determine the integrity of simulated waste forms by standard performance tests such as compression strength (ASTM C 39), leaching behavior (ANS 16.1), 90 day water immersion test, mechanical stability after thermal cycling (ASTM B 553), and radiation stability.
 - Collaborate with the University of Illinois at Urbana-Champaign on extensive microstructural and mineralogical evaluations on the simulated final waste forms to establish the stabilization mechanisms and the fate of the contaminants in the waste forms.

BENEFITS

- This work will provide a novel low-temperature process for treating and stabilizing fission products generated from D&D processes and cleanup of HLW tanks. This technology will complement high-temperature processes to treat fission-product wastes.
- This technology directly addresses waste streams at various DOE sites, primarily at Hanford and Savannah River. In addition, this work will be critical to the ongoing cleanup work at Rocky Flats, Idaho National Engineering Laboratory, Los Alamos National Laboratory, and Oak Ridge National Laboratory.
- The technology generates no secondary wastes. Moreover, the approach is relatively low-cost and has only minimal energy requirements, making it extremely attractive for providing a high return on investment.

COLLABORATION/TECHNOLOGY TRANSFER

During the initial stages of the project, the University of Illinois at Urbana-Champaign (Advanced Center for Cementitious Materials) will

collaborate in the mineralogical evaluations and identification of stabilization mechanisms for the contaminants in phosphate ceramics.

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

ACCOMPLISHMENTS

This is a new initiative, accomplishments will be discussed in future issues of this publication.

TTP INFORMATION

The Immobilization of Fission Products in Phosphate Ceramic Waste Forms technology development activities are funded under the following technical task plan (TTP):

TTP No. CH26C344 "Immobilization of Fission Products in Phosphate Ceramic Waste Forms"

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None available at this time.

4.2 COMPREHENSIVE SUPERNATANT TREATMENT

TECHNOLOGY NEEDS

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

TECHNOLOGY DESCRIPTION

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

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

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

BENEFITS

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

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

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

COLLABORATION/TECHNOLOGY TRANSFER

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

ACCOMPLISHMENTS

- Approximately 1 L of supernatant from MVST W-25 was prepared for batch tests.
- Distribution coefficients (K_d) and percentage removal of cesium from MVST W-25 supernatant were measured using R-F resin, CST, Duolite CS-100, granular and powdered potassium cobalt hexacyanoferrate, and composite microspheres containing sodium and potassium cobalt hexacyanoferrates in hydrous titanium oxide and phosphate. In typical experiments, 10 mL of supernatant was mixed with 50 mg of sorbent for periods ranging from 15 minutes to 144 hours. The cesium K_d s were 34 to 44 mL/g for CS-100, 138 to 764 mL/g for the R-F, 451 to 958 mL/g for the CST, and 26,000 to 46,000 mL/g for granular potassium cobalt hexacyanoferrate.
- Nine different ion exchangers have been tested to determine strontium removal from MVST supernatant: Amberlite IRC-718, sodium titanate, CST, R-F, hydrous titanium oxide/polyacrylonitrile (TiO-PAN), sodium titanate/polyacrylonitrile (NaTiO-PAN), titanium monohydrogen phosphate microspheres, Duolite C-467, and Chelex 100. The inorganic ion exchangers outperformed the organic resins in removing strontium, with the fine powders of NaTiO and CST giving best results. Of the organic resins tested, Duolite C-467 gave the most favorable results.
- Several sorbents, including Reillex™ HPO, Reillex™ 402, Amberlite IRA-904, and Amberlite IRA-400, were tested in batch tests for removing pertechnetate from MVST supernatant. All of the anion exchangers removed the pertechnetate anion reasonably well. The hydroxide forms of the exchange-

ers appeared to be superior to the nitrate forms. Overall, the hydroxide form of Reillex 402 gave the most promising results.

TTP INFORMATION

Comprehensive Supernatant Treatment technology development activities are funded under the following technical task plan (TTP):

TTP No. OR06C341 "Comprehensive Supernatant Treatment"

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4.3

HOT DEMONSTRATION OF PROPOSED COMMERCIAL NUCLIDE REMOVAL TECHNOLOGY

TECHNOLOGY NEEDS

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

TECHNOLOGY DESCRIPTION

This task covers the development and operation of an experimental test unit located in a hot cell at ORNL. This equipment is designed to test radionuclide removal technologies under continuous operation on actual ORNL MVST supernatant, Savannah River HLW supernatant, and Hanford supernatant. The latter two may be simulated by adding the appropriate chemicals and/or nuclides to the MVST supernatant.

The technologies tested will be housed in modules that can be attached to the experimental system inside the hot cell and continuously fed the test supernatant until the nuclide of interest exhausts the module capacity. This task complements the work being done under the ESP task "Comprehensive Supernatant Treatment" by using larger scale, continuous equipment to verify and expand the batch studies done by that task.

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

To test materials provided by the ESP, the experimental unit will be operated at a scale of 1 to 2 L per test. Testing will consist of using the modules or systems supplied by the ESP for cesium removal until the unit has reached its capacity. MVST supernatant, Savannah River HLW supernatant, Hanford

supernatant, and MVST supernatant modified to simulate Hanford or Savannah River supernatant will pass through the module at a prescribed flow rate, and the effluent from the module will be passed through a gamma detector for analysis on line. The effluent will also be collected in fractions for later analysis as required. The volume of supernatant passed through the test module until 50% breakthrough (or other appropriate end point) and exhaustion of capacity are determined. The capability for testing actual supernatant treatment technologies can be used for other tests based on requests by the Tanks Focus Area (TFA) and the ESP.

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

The final product will be a data base and a final report that summarizes the results and makes recommendations for unit operations that could be used to separate and concentrate radionuclides from DOE storage tank supernatant at Oak Ridge and other DOE sites.

BENEFITS

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

COLLABORATION/TECHNOLOGY TRANSFER

Ultimately, the technologies being developed will be transferred to an end user with the help of the TFA. The results of these tests will be compared to the batch results and small column tests results obtained in the Comprehensive Supernatant Treatment task. The results will be used to supply the TFA's Cesium Removal Demonstration Project with the information to determine design parameters. The rate of removal, resin required, and regeneration requirements are important design parameters, and the loading capacity of each sorbent will help to determine the size of the column required and will also help define the final volume of solid waste to be disposed. The materials supplied to remove ^{99}Tc may be produced and tested in other ESP programs.

ACCOMPLISHMENTS

- Experimental equipment for the cesium removal project was installed in the hotcell, and procedures used during the experiment and several ion-exchange material tests were completed.
- The feed supernatant for the tests was obtained from MVST W-27 in April 1995. Approximately 56 L of the supernatant is in storage in building 4501. Tank W-27 supernatant is at pH 7.2 and has the lowest potassium and ^{137}Cs levels of the available tanks, allowing the supernatant to be more easily handled than those from other tanks. For some absorber tests, this supernatant will be adjusted back to the pH standard in other tanks, pH approximately 12.5 to 13.0. Analysis of the present sample after pH adjustment to 12.8 and filtration showed approximately 9.3×10^{-6} Ci/mL of ^{137}Cs .

R-F Resin Test Results:

The first experiment used R-F resin obtained from Savannah River Technology Center. The feed rate during operation was approximately 1.4 mL/min, and resulted in a feed rate of approximately 7 CV/h. The original 12.5 cm³ of resin shrank to 11.5 cm³ when feed started to flow through the bed and remained at that volume through the run. The fractions were weighed, and samples taken for counting the ^{137}Cs . The column volumes to 50% breakthrough were about 45. During the run, about 0.5 L of feed containing 4.42 mCi of ^{137}Cs was fed to the column.

In a second experiment with R-F resin, the feed rate through the bed was reduced to 2.8 to 3.0 CV/h. During the first 4 CV of feed through the bed, the bed volume decreased from the original 12.5 to 10.6 cm³, which changed the CV/h rate to 2.9 to 3.0. After approximately 25 CV, the bed volume was 10.2 cm³. The final bed volume after the run was 9.9 cm³. The 50% breakthrough occurred at approximately 40 CV, and the shape of the curve was very similar to that in the first R-F run.

Another experiment used CS-100. Feed rate through the column was set at 0.7 cm³/min, 2.9 bed volumes/hour, and was constant through the run. Flow continued until more than 60% breakthrough had been achieved. The run was continued to more than 80% breakthrough. The column volumes to 50% breakthrough were approximately 12.5. During operation, the column bed height remained constant, and no change in color or appearance was seen.

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

TTP INFORMATION

The Hot Demonstration of Proposed Commercial Nuclide Removal Technology technology development activities are funded under the following technical task plan (TTP):

TTP No. OR06C342 "Hot Demonstration of Proposed Commercial Nuclide Removal Technology"

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None available at this time.

4.4

DEVELOPMENT AND TESTING OF INORGANIC SORBENTS FOR RADIONUCLIDE AND HEAVY METAL SEPARATIONS

TECHNOLOGY NEEDS

Inorganic ion exchange materials, such as hexacyanoferrates, titanates, phosphates, and hydrous metal oxides, have high selectivities and efficiencies for separating and removing fission products (e.g., cesium, europium, cerium, ruthenium, zirconium, and strontium), actinides, and other elements (such as silver, lead, mercury, nickel, zinc, chromium, and fluoride) from aqueous waste streams. However, in most cases, these sorbents are available commercially only as fine powders or as unstable granular particles that are not readily adaptable to continuous processing such as column chromatography.

Some of these powders are also made as pellets by using binding materials; however, the binders tend to lessen the number of exchange sites that are available for use. The binders tend to block pores and passageways to the exchange sites within the structures and adversely affect the loading and kinetic behavior of the exchangers.

Preparation of inorganic ion exchangers as microspheres improves the flow dynamics for column operations and expands their practical applications. One disadvantage of many of the inorganic ion exchangers that are made as powders, granular material, or pellets is the lack of reproducibility as sorbents. These materials are prepared in batch processes in which chemical and physical gradients can occur that cause variances in the crystal morphology and compositions of the products. These same materials, when made by the internal gelation process, are more reproducible. Furthermore, in a few cases, the densities and porosities of an exchanger made as microspheres can be tailored by varying the chemical and physical process parameters; this allows some control over the selectivity and loading behavior of the exchanger.

TECHNOLOGY DESCRIPTION

The objectives of this task are to develop, (using the internal gelation process), prepare, and test microspheres and granular forms of inorganic ion exchangers to remove radionuclides and heavy metals from waste streams occurring at various sites. Several inorganic materials, such as hexacyanoferrates, titanates, phosphates, and oxides have high selectivities and efficiencies for separating and removing radionuclides such as uranium, technetium, cesium, and strontium, and metals such as cobalt, silver, zinc, and zirconium from aqueous waste streams. However,

these sorbents frequently exist only as powders and consequently are not readily adaptable to continuous processing, such as column chromatography.

Making these inorganic ion exchangers as microspheres or granular forms improves the flow dynamics for column operations and expands their practical applications. Microspheres of several materials have been prepared at ORNL, and the effectiveness of zirconium monohydrogen phosphate and hydrous titanium oxide microspheres for removing radionuclides from hot cell waste solutions has been demonstrated.

This program involves the preparation of both inorganic ion exchangers in the form of microspheres, and microspheres in which the ion exchanger powders are homogeneously dispersed throughout the microspheres, to produce materials that would be useful for continuous processing of contaminated streams.

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

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

BENEFITS

The internal gelation process was originally developed as a process for preparing UO_2 microspheres and nuclear fuels for light water and fast breeder reactors. Making inorganic ion exchangers as microspheres by the internal gelation process is a spin-off of these highly developed fuel technologies. The major benefit of this program is to further develop the technology for use in making inorganic ion exchangers more usable for large scale column use.

These materials could have several advantages in treating a variety of waste streams.

Inorganic ion exchangers (e.g., hydrous titanium oxide, hydrous zirconium oxide, hydrous iron oxide, hydrous aluminum oxide, hydrous cerium oxide, potassium cobalt hexacyanoferrate, titanium phosphate, zirconium phosphate, polyantimonic acid, ammonium molybdophosphate, manganese dioxide, sodium titanate) could be useful for treating supernate solutions, low-level liquid wastes, contaminated groundwater, contaminated surface water (including acid mine drainage), and soil leachates.

Some Specific Site Applications Include:

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

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

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

COLLABORATION/TECHNOLOGY TRANSFER

Making inorganic ion-exchangers in a usable form as microspheres using the internal gelation process is amenable to commercialization. The large-scale

engineering of the internal gelation process has already been developed for nuclear fuels. The same equipment designs with minor modifications could be used to make large quantities of the ion exchange microspheres. Private industry has expressed interest in licensing and expanding the use of the technology.

ACCOMPLISHMENTS

This is a new task for FY96. However, accomplishments include the following:

- Microspheres of several materials have already been developed and prepared at ORNL by the internal gelation process.
- Hydrous titanium oxide and titanium monohydrogen phosphate microspheres and microspheres of these materials embedded with very fine particles of potassium cobalt hexacyanoferrate were used to successfully remove highly radioactive fission products from hot cell waste solutions.
- In small batch tests, mixed microspheres also removed cesium and strontium from supernatant taken from the Melton Valley Storage Tank facility at ORNL.

TTP INFORMATION

The Development and Testing of Inorganic Sorbents for Radionuclide and Heavy Metal Separations technology development activities are funded under the following technical task plan (TTP):

TTP No. OR16C342 "Development and Testing of Inorganic Sorbents for Radionuclide and Heavy Metal Separations"

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4.5

MAGNETIC-SEEDING FILTRATION

TECHNOLOGY NEEDS

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

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

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

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

TECHNOLOGY DESCRIPTION

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

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

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

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

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

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

After completing these controlled studies that will define the effects of the governing parameters on particle removal, testing will be aimed at contaminant removal by precipitation and sorption processes. Laboratory testing will be conducted using materials characteristic of the ORNL NGLLLW precipitation process and with several types of sorbent particles. In addition, solid-liquid separation tests will be conducted with surrogates or samples of waste streams that are identified during a survey of DOE sites. The applicability of the process will be further tested through pilot demonstration of magnetic-seeding filtration with the NGLLLW process and/or other waste streams.

BENEFITS

This project will benefit all DOE sites by (1) evaluating the capabilities of magnetic-seeding filtration for solid/liquid separations, (2) providing data for

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

COLLABORATION/TECHNOLOGY TRANSFER

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

ACCOMPLISHMENTS

This is a new initiative, accomplishments will be discussed in future issues of this publication.

TTP INFORMATION

The Magnetic-Seeding Filtration technology development activities are funded under the following technical task plan (TTP):

TTP No. OR16C343 "Magnetic-Seeding Filtration"

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None available at this time.

4.6

SALT SPLITTING WITH CERAMIC MEMBRANES

TECHNOLOGY NEEDS

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

TECHNOLOGY DESCRIPTION

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

The technology being developed involves using an electrochemical salt-splitting process based on inorganic ceramic membranes, as shown in Figure 4.6-1. In this process, the waste is added to the anode compartment of the electrochemical cell, and an electrical potential is applied to the cell, subsequently driving sodium ions through the membrane while most other cations (e.g., K^+ , Cs^+) are rejected by the membrane. The charge balance in the cell is maintained by the electrolysis of water. The accumulation of potentially flammable gas mixtures can be prevented by providing adequate volumes of a sweep gas or by using oxygen and a gas diffusion electrode. As H^+ is generated in the anode compartment, the pH drops while the production of OH^- in the cathode compartment results in a rise in pH as sodium hydroxide is produced.

Figure 4.6-1. Schematic of an electrochemical process using the NaSICON membrane. Anolyte Composition: Hanford Simulant: 1.5 M NaNO_3 , 0.2 M $\text{Al}(\text{NO}_3)_3$, 1 M NaOH Catholyte Composition: 1 M NaOH Temperature: 70 C Applied Potential: 8-10V

The ceramic membranes are from a family of materials known in the electrical battery industry as sodium, super fast ionic conductors (NaSICON). The unique characteristic of NaSICON ceramics is that they possess channels within the crystal structure for fast sodium ion conduction. Silica tetrahedral "rings", 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 rare earth (RE) ions (i.e., $\text{Na}_x\text{RESi}_4\text{O}_{12}$).

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

Initial investigations were directed at selecting and modifying membrane compositions compatible with the expected chemical and radioactive environment. FY96 work consists of completing a preconceptual design of a ceramic membrane-based salt splitting process for sodium separation and caustic recycle, manufacture and nonradioactive demonstration testing of a unit cell of this design, preparing for radioactive testing, and an applications study. The preconceptual design is primarily to distinguish critical issues for testing and provide a vision for potential users. Work in FY97 is expected to include one or more bench-scale demonstrations with actual wastes and nonradioactive testing of the process at the pilot scale.

BENEFITS

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

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

The efficiency and chemical stability of some cesium ion exchange materials is decreased at high pH levels. For example, the distribution coefficient (K_d) for a powder form of crystalline silicotitanate (TAM-5-11) was reported to increase from about 150 mL/g at pH 14 to about 1600 at pH 12 in a Hanford simulant. This difference would result in a tenfold reduction in the required amount of exchanger. This reduction in pH would also permit the use of granular potassium cobalt hexacyanoferrate(II). This material has extremely high cesium K_d s but has not been considered for application at Hanford because it is unstable in solutions having a pH above 13.

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

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

COLLABORATION/TECHNOLOGY TRANSFER

Collaborations are under way with Westinghouse Savannah River Company in the design of electrochemical cells for radioactive waste processing and assessment of caustic recycle applications for alkaline supernates and sludge leaching/washing solutions. A sodium-bearing waste simulant will be provided

for an initial nonradioactive test at INEL. WHC will participate in design reviews of the preconceptual design, applications studies and process demonstrations on Hanford supernate, if applicable.

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

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

Anil Virkar and Jan-Fong Jue, University of Utah, participated in this task in FY95 and continue membrane development. Materials and Systems Research is funded under the Small Business and Innovative Research program to examine new types of NaSICON membranes.

ACCOMPLISHMENTS

- Rare earth-based NaSICON (RE-NaSICON) membranes were fabricated, tested, and evaluated against an initial set of criteria developed on the basis of potential applications. These tests confirmed the high selectivity of RE-NaSICON for sodium ions relative to hydronium, cesium, aluminum, and strontium ions in alkaline waste and slightly acidic solutions.

Figure 4.6-2. Bench-scale process demonstration with Hanford waste simulant.

- Testing of membrane samples irradiated with a ^{60}Co gamma source indicated an initial decrease in conductivity that recovered after current was passed.
- Ionic conductivities and current densities achieved in dysprosium-based NaSICON were comparable to those of bipolar or cationic organic membranes.

Excellent compatibility with basic or even slightly acidic solutions was observed; however, mass loss and surface cracks were observed in strong acids.

- Recirculating cell experiments with an advanced RE-NaSICON membrane were conducted at Ceramtec Inc. to demonstrate sodium removal from a Hanford tank waste simulant. The anolyte pH decreased from 12.6 to about 7 as 60 g of sodium ions were transported through the advanced RE-NaSICON membrane (Figure 4.6-2). As pH levels decreased to below 9, precipitation of aluminum hydroxide occurred. However, the throughput of the cell appeared to fall only slightly.

TTP INFORMATION

The Salt Splitting with Ceramic Membranes technology development activities are funded under the following technical task plan (TTP):

TTP No. RL36C341 "Salt Splitting with Ceramic Membranes"

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4.7

DEVELOP AND TEST SORBENTS - SUBTASK: COMPARISON OF ORGANIC AND INORGANIC ION EXCHANGE MATERIALS FOR BATCH CONTACT REMOVAL OF CESIUM AND STRONTIUM FROM TANK WASTE

TECHNOLOGY NEEDS

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

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

TECHNOLOGY DESCRIPTION

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

During FY95, experimental work at PNNL focused on batch distribution (K_d) testing in actual and simulated Hanford wastes, chemical and radiolytic stability of exchangers, column ion exchange testing in simulated Neutralized Current Acid Waste (NCAW), various site demonstrations (INEL and West Valley Nuclear Services (WVNS), PNNL used subcontractor technologies), and technetium and strontium removal from groundwater and LLW. This summary focuses on the actual waste testing and results from the subtask on geologic barriers.

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

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

Simulant testing was conducted to develop procedures for contacting the actual waste and to provide data over a wider range of experimental conditions.

BENEFITS

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

COLLABORATION/TECHNOLOGY TRANSFER

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

ACCOMPLISHMENTS

- Seven ion exchange materials were evaluated for cesium, strontium, and metals uptake in side-by-side comparison tests using actual and simulated 101-AW DSSF waste. Actual waste testing required only 270 mL of solution and provides an estimation of the column loading performance of the seven materials. Results are summarized in Table 4-7.1 at the initial feed conditions of 5.0 M sodium, 0.48 M potassium, 23° C, and a Na/Cs mole ratio of 78,000. The equilibrium data are given as K_d (exchanger mass basis) and values (exchanger volume basis) to illustrate the effect of the bed density on the apparent performance. The value is useful for sizing ion exchange columns, and the K_d value is pertinent for assessing the impact of converting the loaded materials into a final waste form.

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

^aion exchange material density measured on a dry weight basis in 2 M NaOH unless otherwise noted

^bbulk powder density (dry weight basis)

^cmeasured in NCAW waste simulant

^dnot applicable, strontium ion exchange material

Table 4.7-1 Actual waste testing results at feed conditions (5 M Na, 0.48 M K, and Na/Cs = 78,000)

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

- In FY95 comparative tests were made of a variety of strontium ion exchange materials, both in groundwater and HLW systems. This testing demonstrated: (1) a strong selectivity for strontium of silicotitanate, titanate, zeolitic, and micaceous ion exchangers relative to an organic resin exchanger (R-F), (2) a relatively slow approach to equilibrium (2 weeks for most exchangers) at the temperatures typical of groundwater systems, and (3) the need to incorporate an estimate of surface area into any measurement of the selectivity of an ion exchanger.
- In FY96, focus is on testing of surfactant-modified inorganic exchangers for removal of pertechnetate from LLW and groundwater. This work has demonstrated very high degrees of removal (K_ds as high as 400,000 mL/g) and shown that the adsorption can be nearly perfectly described by the Langmuir isotherm equation.

TTP INFORMATION

The Comparison of Organic and Inorganic Ion Exchange Materials for Batch Contact Removal of Cesium and Strontium from Tank Waste technology development activities are funded under the following technical task plan (TTP):

TTP No. RL36C342 "Develop and Test Sorbents - Subtask: Comparison of Organic and Inorganic Ion Exchange Materials for Batch Contact Removal of Cesium and Strontium from Tank Waste"

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4.8

DEVELOP AND TEST SORBENTS - SUBTASK: MEMBRANE-BASED SEPARATION TECHNOLOGIES FOR CESIUM, STRONTIUM, AND TECHNETIUM

TECHNOLOGY NEEDS

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

TECHNOLOGY DESCRIPTION

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

Subtask work began in FY92 to develop improved molecular recognition technology agents and implement their use in the form of flow-through membranes. After selecting novel separation agents, the capacities, distribution coefficients as a function of feed composition, physical properties, and chemical and radiolytic stability of materials with demonstrated potential for application in radiochemical separations, were determined.

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

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

BENEFITS

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

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

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

COLLABORATION/TECHNOLOGY TRANSFER

In this subtask, PNNL is collaborating with 3M, St. Paul, Minnesota, working in cooperation with IBC Advanced Technologies, American Fork, Utah. Work has also been done in cooperation with AlliedSignal, Inc., and UOP Molecular Sieves, Des Plaines, Illinois; West Valley Nuclear Services, Inc., West Valley, New York; Idaho National Engineering Laboratory (INEL), and Westinghouse Savannah River Company.

ACCOMPLISHMENTS

- In FY95, a successful hot cell experiment was conducted at INEL, in which the technology removed cesium and strontium from acid radioactive waste.
- In FY95 and FY96, technology demonstrations were conducted at the West Valley Demonstration Project and at Test Area North (TAN) at INEL on dilute, moderate pH waste. A modular processing skid including active adsorber cartridges and effective prefilters, was developed as part of the West Valley demonstration; a duplicate unit was used at INEL.
- At West Valley, the system removed technetium and cesium from process water running at 0.1 gal/min for 8 days—a volume of approximately 1500 gallons. The technetium cartridge was loaded to a 50% breakthrough after processing about 90 gallons, and the cesium cartridge ran for 40 hours (approximately 250 gallons) with no detectable breakthrough. The cesium in the feed was present at 1200 pCi/L, while the detection limit for the cartridge effluent was about two orders of magnitude lower. These results were particularly encouraging because the feed had already been processed through traditional ion exchange columns.
- During an 80 h demonstration at TAN, cesium and strontium were removed to below drinking water standards. 1250 gallons were processed at a flow rate of 0.25 gal/min. Strontium was loaded to a 50% breakthrough after about 800 gallons. No detectable cesium breakthrough occurred for the entire demonstration, with a detection limit of 9 pCi/L. Again, this water had already been through the

groundwater treatment facility. All other attempts to achieve this level of cesium contamination at TAN had been unsuccessful.

- More technology demonstrations will be made during FY96, with the goal of applying the technology on an increasingly large scale in preparation for transfer to EM-30 and/or EM-40 in FY97.

TTP INFORMATION

The Membrane-Based Separation Technologies for Cesium, Strontium, and Technetium technology development activities are funded under the following technical task plan (TTP):

TTP No. RL36C342 "Develop and Test Sorbents - Subtask: Membrane-Based Separation Technologies for Cesium, Strontium, and Technetium"

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4.9

DEVELOP AND TEST SORBENTS - SUBTASK: CESIUM AND STRONTIUM ION SPECIFIC EXCHANGERS

TECHNOLOGY NEEDS

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

Although contributions from this task would address a variety of problems in the DOE complex, specific applications to high-level waste tanks have been targeted. Groundwater streams are also treatable with the same or related materials. The goal for FY96 is to prepare, characterize, and scale-up inorganic ion exchangers tailored for use with specific DOE waste streams, and to work with DOE sites to demonstrate the effectiveness of these exchangers under realistic conditions.

TECHNOLOGY DESCRIPTION

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

In FY95, the effort included exchanger screening (subcontracted to Professor Abraham Clearfield at Texas A&M University), exchanger preparation, and exchanger testing. The program thus allows the smooth and rapid transition of materials from laboratory discovery, through process development, scale-up, formation into engineered form materials, and testing by DOE sites where strontium or cesium problems exist.

In FY96, our primary goal will be demonstration of our strontium removal technology at DOE sites. We will work with interested sites to evaluate samples onsite, and thereby qualify our materials. The screening focus this year will be the development of cesium-specific exchangers for use in non-alkaline streams, while exchanger preparation and scale-up will focus on preparation of sodium nonatitanate for strontium uptake.

BENEFITS

Because the cost of nuclear waste treatment is strongly dependent on the volume of this waste, highly selective ion exchangers, which can remove

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

COLLABORATION/TECHNOLOGY TRANSFER

Our principal goal for FY96 is to transfer technology in the form of supply of inorganic ion exchangers to potential users or national labs working closely with potential users. Collaborations currently under way with 3M, Savannah River, PNNL, and ORNL will continue, and we expect new opportunities to demonstrate our technology to be identified during the year.

ACCOMPLISHMENTS

We distributed our first product widely within DOE for testing. This product, sodium nonatitanate, is a layered inorganic ion exchanger that is highly selective for strontium from alkaline feeds, regenerable, and radiation hardy. It can be prepared currently at the 10 kg batch scale. The material can be formed into durable, alkaline-stable pellets for use in ion exchange columns. It is available for testing in both powder and pellet form.

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

Samples of our sodium nonatitanate powder were tested at PNNL, SRTC, Los Alamos National Laboratory, and ORNL. Many tests are still in progress, but where complete, show that sodium nonatitanate is highly selective for removing strontium from aqueous streams, and also has an affinity for americium, uranium, and plutonium.

3M used larger samples to prepare Empore™ membranes that were used successfully to remove strontium from Test Area North injection well water at INEL. Engineered form exchangers are currently being tested at PNNL and ORNL.

A new phosphate-type ion exchanger was developed that can be prepared as a granular material, and shows a K_d for Cs of 25,000 mL/g from 0.1 M nitric acid. Capacities are expected to be high. We plan to scale-up this process as soon as this optimization and testing are complete.

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

TTP INFORMATION

The Cesium and Strontium Ion Specific Exchangers technology development activities are funded under the following technical task plan (TTP):

TTP No. RL36C342 "Develop and Test Sorbents - Subtask: Cesium and Strontium Ion Specific Exchangers"

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4.10

CHEMICAL DERIVATIZATION TO ENHANCE CHEMICAL/OXIDATIVE STABILITY OF RESORCINOL-FORMALDEHYDE RESIN

TECHNOLOGY NEEDS

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

TECHNOLOGY DESCRIPTION

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

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

Structure/function studies for R-F resin were initiated at PNNL under the Advanced Processing Technology Initiative (APTI) in FY94. These studies undertook preparation and characterization of R-F resin synthesized under a variety of conditions to establish the primary structure of the resin and to identify some of the important synthetic parameters critical for obtaining a quality ion-exchange product.

Modification of the R-F resin will incorporate information from the earlier studies on structure/function relationships to prepare resins that are chemically more resistant to oxidation but retain high cesium ion selectivity. The technical approach includes design and synthesis of resorcinol derivatives, which are alkylated or

otherwise functionalized, such that an aromatic ring carbon para to a ring hydroxyl group is more resistant to oxidation.

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

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

BENEFITS

This work will likely result in organic ion-exchange resins that combine both high selectivity for cesium ion and significantly improved chemical stability under typical conditions encountered during processing of tank wastes. These materials are primarily designed to remove radioactive cesium from alkaline waste tank supernates at the Hanford and Savannah River sites, but will be useful to other DOE sites throughout the country for cleanup of radioactive waste streams contaminated with ^{137}Cs . The resin will be more chemically stable, and thus the amount of secondary waste will be reduced.

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

COLLABORATION/TECHNOLOGY TRANSFER

The R-F resin was developed and is supplied by Savannah River Technology Center. Collaboration is under way with researchers in fluorine chemistry at the University of Idaho to prepare the fluorinated materials required to synthesize the new resins; these efforts are also being integrated with Boulder Scientific Company, Mead, Colorado.

ACCOMPLISHMENTS

- Structure/function studies for R-F resin performed at PNNL under APTI have provided information that can now be used to design and synthesize resins that retain high selectivity for cesium, yet have a much lower susceptibility to chemical oxidation. This R&D work is applicable to phenolic-based condensation resins in general.
- Collaboration is under way with researchers in fluorine chemistry at the University of Idaho to prepare the fluorinated materials required to synthesize the new resins; these efforts are also being integrated with our industry partner (Boulder Scientific Company, Mead, Colorado).

TTP INFORMATION

The Chemical Derivatization to Enhance Chemical/Oxidative Stability of Resorcinol-Formaldehyde Resin technology development activities are funded under the following technical task plan (TTP):

TTP No. RL36C343 "Chemical Derivatization to Enhance Chemical/Oxidative Stability of Resorcinol- Formaldehyde Resin"

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4.11

SELECTIVE CRYSTALLIZATION OF TANK SUPERNATANT LIQUID

TECHNOLOGY NEEDS

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

TECHNOLOGY DESCRIPTION

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

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

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

A process flowsheet was developed in the laboratory using simulated wastes and demonstrated with actual wastes from three Hanford Site waste tanks. The waste is first washed with water or dilute caustic to dissolve the soluble inorganic salts. The liquid phase is then acidified with nitric acid, which converts NaOH , Na_2CO_3 , and NaNO_2 to NaNO_3 , allowing recovery of most of the sodium in the waste. The acidified solution is evaporated until NaNO_3 crystals begin to form. The slurry is cooled to precipitate more NaNO_3 , then is

filtered or centrifuged to separate the crystals from the mother liquor. The soluble radionuclides stay in the mother liquor, except for the fraction that remains occluded within the NaNO_3 crystals or adheres to the surfaces. The crystals are further decontaminated by recrystallizing from water repeatedly until the desired level of decontamination is achieved.

BENEFITS

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

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

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

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

COLLABORATION/TECHNOLOGY TRANSFER

Under a contract with the University of Arizona, fundamental crystallization parameter studies were conducted under the direction of Dr. Alan Randolph. Randolph, a world-class crystallization expert with expertise in Hanford Site waste chemistry, was instrumental in selecting the design of Hanford's 242-A

and 242-S evaporator/crystallizers that have been used here since the mid-1970s to reduce the volume of tank waste.

Environmental regulations governing reuse and disposal options for the recovered salts were reviewed under a contract with the consulting firms CH2M Hill and IT Corporation.

ACCOMPLISHMENTS

Initial flowsheet conditions were developed using simulated wastes.

- Process feasibility was demonstrated when essentially nonradioactive sodium nitrate was recovered from samples of waste from high-level waste tanks 101-SY and 102-AN.
- Experiments with simulated waste explored the effects of crystallization parameters on the size and crystal habit of product NaNO_3 crystals. Data were obtained to allow prediction of decontamination factor as a function of solid/liquid separation parameters.
- Experiments with actual waste from tank 101-SY were conducted to determine the extent of contaminant occlusions in NaNO_3 crystals. The occlusion rate determines the theoretical maximum decontamination factor for a single-stage crystallization, and therefore defines the size (number of required stages) of an operating plant.
- Fundamental crystallization parameter studies (crystal nucleation rates and growth rates) were conducted under a contract with the University of Arizona.
- A detailed process flowsheet and computer model were created using a steady-state process simulator software program also being used by the TWRS program for their waste pretreatment and disposal projections. Therefore, evaluations can be made to the effect of the clean salt process on the low-level waste volume and composition resulting from the TWRS baseline flowsheet.
- Environmental regulations governing re-use and disposal options for the recovered salts were reviewed under a contract with the consulting firms CH2M Hill and IT Corporation. Current regulations, which could be revised, preclude the free release of the recovered salts for offsite uses or disposal, regardless of the level of decontamination (*de minimis* rule). The regulations encourage reuse and recycling of the salts within the DOE complex, wherever genuine beneficial uses of the salts can be identified. Several such uses were discussed in the consulting firm's final report.

TTP INFORMATION

The Selective Crystallization of Tank Supernatant Liquid technology development activities are funded under the following technical task plan (TTP):

TTP No. RL46C341 "Selective Crystallization of Tank Supernatant Liquid"

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TECHNICAL LIAISON WITH THE INSTITUTE OF PHYSICAL CHEMISTRY (RUSSIAN ACADEMY OF SCIENCE)

TECHNOLOGY NEEDS

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

TECHNOLOGY DESCRIPTION

DOE has engaged the Institute of Physical Chemistry of the Russian Academy of Science (IPC/RAS) to conduct studies of the fundamental and applied chemistry of the transuranium elements (TRU, primarily neptunium, plutonium, and americium) and technetium in alkaline media. This work is supported by DOE because the radioactive wastes stored in underground tanks at DOE sites (Hanford, Savannah River, and Oak Ridge) contain TRU and technetium, are alkaline, and the chemistries of TRU and technetium are not well developed in this system. Previous studies at the IPC/RAS centered on the fundamental chemistry and on coprecipitation. In FY96, the work will focus more on the applied chemistry of TRU and technetium in alkaline media and work will continue on the coprecipitation task.

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

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

RAS must be verified with genuine wastes available at the Hanford Site. Results from the IPC/RAS and Hanford Site studies will be disseminated in technical publications and presentations.

BENEFITS

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

Results to date from the IPC/RAS show the solubilities of the TRU and technetium are strongly dependent on the oxidation state, and can be altered successfully by various common chemical oxidants and reductants. This can lead to a promising method for removing plutonium; similar results are possible for neptunium.

COLLABORATION/TECHNOLOGY TRANSFER

The task is a collaboration with the Institute of Physical Chemistry, Russian Academy of Science, Moscow, Russia.

ACCOMPLISHMENTS

In 1994, the IPC/RAS prepared a technical literature review of the chemistry of the TRU and technetium in alkaline media. This review was edited and published by the liaison as a WHC document in May 1995. Eleven tasks to investigate the chemistry of the TRU and technetium were proposed by the IPC/RAS; four were selected by the DOE for FY95 support:

- Oxidation and reduction reactions and reagents for neptunium, plutonium, americium, and technetium
- Solubilities of neptunium, plutonium, americium, and technetium as functions of oxidation states, hydroxide concentration, and presence of other bulk waste components
- Reactions and reagents suitable to coprecipitate neptunium and plutonium in the (V) and (VI) oxidation states
- Gamma radiolysis reactions of neptunium, plutonium, and technetium
- Draft technical reports on the four tasks received in September 1995, and due in January 1996, are being edited for publication as contractor documents.

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

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

The solubilities of neptunium(IV) and plutonium(IV) hydrous oxides (in the presence of hydrazine) were 10^{-6} to 10^{-5} M for neptunium, and 10^{-7} to $10^{-5.5}$ M for plutonium as NaOH concentration increased from 2 to 14 M. The solubilities of pentavalent neptunium, plutonium, and americium were similar above 6 M NaOH increasing from $10^{-3.7}$ to $10^{-3.5}$ M at 14 M NaOH. Technetium(IV) and (V) solubility measurements are very sensitive to air oxidation; in the presence of hydrazine, solubilities range from 5×10^{-6} to 5×10^{-4} M. Electrodeposited $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ has a solubility of 6.3×10^{-7} M in 4 M NaOH.

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

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

TTP INFORMATION

Technical Liaison with the Institute of Physical Chemistry technology development activities are funded under the following technical task plan (TTP):

TTP No. RL46C342 "Technical Liaison with the Institute of Physical Chemistry (Russian Academy Of Science)"

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4.13

ELECTROCHEMICAL TREATMENT OF LIQUID WASTES

TECHNOLOGY NEEDS

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

TECHNOLOGY DESCRIPTION

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

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

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

In the electrochemical destruction of sodium nitrate and nitrite, sodium hydroxide is the major liquid phase product of the process. If the sodium hydroxide could be recovered and recycled, significant reduction in the quantity of waste requiring disposal would be realized. Onsite use of the recovered sodium hydroxide would

include neutralization of fresh waste and as a corrosion inhibitor in the waste storage and evaporation facilities. Thus, the quantity of sodium hydroxide that would be available for recovery and recycle would be increased by converting the sodium nitrate and nitrite into sodium hydroxide.

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

BENEFITS

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

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

COLLABORATION/TECHNOLOGY TRANSFER

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

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

ACCOMPLISHMENTS

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

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

TTP INFORMATION

The Electrochemical Treatment of Liquid Wastes technology development activities are funded under the following technical task plan (TTP):

TTP No. SR16C341 "Electrochemical Treatment of Liquid Wastes"

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BIBLIOGRAPHY OF KEY PUBLICATIONS

Hobbs, D.T. *Summary Technical Report on the Electrochemical Treatment of Alkaline Nuclear Wastes*. WSRC-TR-94-0287, Westinghouse Savannah River Company, Aiken, South Carolina (1994).

Pakalapati, S.N.R., B.N. Popov, and R.E. White. *Model for EDTA Destruction in a Parallel Electrochemical Reactor*. WSRC-TR-95-0406, Westinghouse Savannah River Company, Aiken, South Carolina (1995).

Prasad, S.A., A.E. Farrell, J.W. Weidner, and R.E. White. *Interim Report on the Flowsheet Model for the Electrochemical Treatment of Liquid Radioactive Wastes*. WSRC-RP-94-1149, Westinghouse Savannah River Company, Aiken, South Carolina (1994).

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

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

TECHNOLOGY DESCRIPTION**High-Level Waste:**

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

The liquid recycled from the vitrification plant also requires cesium separation. Cesium in the recycle stream occurs because some cesium is volatilized during vitrification of the sludge and is removed by scrubbing and flushing the offgas system. Current plans are to evaporate the solutions in high-level waste evaporators and return the concentrated solutions to the existing process for removal of cesium. Tests of cesium removal from this stream are planned for mid-FY96.

Sodium titanate developed by AlliedSignal, Inc., under ESP funding has been tested for use in the SRS process. Tests were done with several different samples (dry solids and slurries) with simulant and actual waste solutions to determine the strontium decontamination factor (DF) using a procedure previously developed to ensure that purchased material met plant specifications for strontium removal. The highest DF obtained with AlliedSignal material was 101, which although lower than the desired DF of 150, is better than that obtained with current large-scale samples of vendor material.

Absorption of uranium and plutonium from the solutions has also been tested to ensure removal without nuclear criticality problems.

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

Reactor Basin Water:

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

Currently, no integrated systems have been demonstrated that remove radionuclides and 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.

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

Sampling Seawater:

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

Empore™ (3M) membranes were tested for removal of cesium, plutonium and technetium from seawater. Technetium was separated and concentrated from seawater with Teva™ (Eichrom Industries) resin incorporated in an Empore™ membrane. Initial bleedthrough was observed; however, spiking the solution with ^{99}Tc allows recoveries to be calculated to give the desired accuracy. Testing was done with several different concentrations of technetium with no change in the amount of recovery.

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

Plutonium was adsorbed from seawater with an Empore™ membrane containing sodium titanate. Recovery calculations were complicated by inadvertent contamination; however, the tests demonstrated the feasibility to the point that 3M and ISCO, a manufacturer of environmental sampling equipment, will collaborate to provide equipment for field testing of both freshwater and seawater under another ESP task during FY96.

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

Catalytic Exchange for Aqueous Detritiation:

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

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

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

BENEFITS

This task provides a method for testing ESP-developed separations materials and processes on actual tank waste solutions as well as contaminated reactor basin and ground waters. Thus, developers are provided with the opportunity to test their technology on actual wastes while providing new technology to treat SRS wastes. Testing of sodium titanate has resulted in an alternative material for Sr and TRU removal from SRS HLW supernatant solutions. This material meets all specifications for decontamination and particle size which the present vendor of monosodium titanate has not done. A demonstration of 3M web technology on R reactor basin water will provide a technology for separation of PCBs and radionuclides while minimizing mixed waste.

COLLABORATION/TECHNOLOGY TRANSFER

In this task, testing is being done on materials developed by AlliedSignal, Inc., Des Plaines, Illinois; Eichrom Industries, Darien, Illinois; 3M, St. Paul, Minnesota; Selentec, Atlanta, Georgia; and UOP Molecular Sieves, Des. Plaines, Illinois.

TTP INFORMATION

Advanced Separations at Savannah River Site technology development activities are funded under the following technical task plan (TTP):

TTP No. SR16C342 "Advanced Separations at Savannah River Site"

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BIBLIOGRAPHY OF KEY PUBLICATIONS

None available at this time.

DOE BUSINESS OPPORTUNITIES FOR TECHNOLOGY DEVELOPMENT

WORKING WITH THE DOE OFFICE OF ENVIRONMENTAL MANAGEMENT

The Office of Environmental Management (EM) provides a range of programs and services to assist private sector organizations and individuals interested in working with DOE in developing and applying environmental technologies. Vehicles such as research and development contracts, subcontracts, grants, and cooperative agreements enable EM and the private sector to work collaboratively. In FY95, 39 percent of Office of Science and Technology (OST) funding went to the private sector, universities and other federal agencies. EM's partnership with the private sector is working to expedite transfer of newly developed technology to EM restoration and waste management organizations, industry, and other federal agencies.

Several specific vehicles address institutional barriers to effective cooperation and collaboration between the private sector and DOE. These mechanisms include contracting and collaborative agreements, procurement provisions, licensing of technologies, consulting arrangements, reimbursable work for industry, and special consideration for small businesses.

INFORMATION ON EM

The EM Center for Environmental Management Information provides the most current facts and documents related to the EM program. Through extensive referrals, the Center connects stakeholders to a complex-wide network of DOE Headquarters and Operations Office contacts.

To obtain information from the EM Center for Environmental Management Information, write or phone:

EM Center for Environmental Management Information
U.S. Department of Energy
P.O. Box 23769
Washington, DC 20026-3769
1-800-736-3282
cemi@dgs.dgsys.com

THE COOPERATIVE RESEARCH AND DEVELOPMENT AGREEMENT

The Cooperative Research and Development Agreement (CRADA) is a written agreement between one or more federal laboratories and one or more

nonfederal parties through which the government provides personnel, facilities, equipment, and other resources, with or without reimbursement, to support a shared research agenda. The nonfederal parties may also provide funds, personnel, services, facilities, equipment, intellectual property, or other resources to support the research. DOE developed a modular CRADA to be responsive to the needs of participants while protecting the interests of the government and its taxpayers. DOE also has issued the small business CRADA to expedite agreements with small businesses and other partners that meet DOE's requirements. During FY95, EM entered into more than 60 CRADAs.

THE RESEARCH OPPORTUNITY ANNOUNCEMENT

The Research Opportunity Announcement (ROA) is a solicitation for industry and academia to submit proposals for potential contracts in basic and applied research, ranging from concept feasibility through proof-of-concept testing in the field. This mechanism is used when EM is looking for multiple solutions for a given problem. ROAs are issued annually by EM. The EM ROA provides multiple awards and is open all year. ROAs are announced in the *Commerce Business Daily*, and typically published in the *Federal Register*.

For questions on ROAs, contact:

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To learn about EM Technology business opportunities, connect to the METC Homepage:

<http://www.metc.doe.gov/business/solicita.html>

THE PROGRAM RESEARCH AND DEVELOPMENT ANNOUNCEMENT

EM uses the Program Research and Development Announcement (PRDA) to solicit proposals from nonfederal parties for research and development in areas of interest to EM. The PRDA is used for projects that are in broadly defined areas of interest where a detailed work description might be premature. It is a tool to solicit a broad mix of applied research, development, demonstration, testing, and evaluation proposals.

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To learn about EM Technology business opportunities, connect to the METC Homepage:

<http://www.metc.doe.gov/business/solicita.html>

THE SMALL BUSINESS INNOVATION RESEARCH PROGRAM

The Small Business Innovation Research (SBIR) Program promotes small business participation in government research and development programs. This legislatively mandated program is designed for implementation in three phases from feasibility studies through support for commercial application. DOE publishes solicitation announcements through the Small Business Innovation Research Office each year to define research and development areas of interest.

For further information about SBIR programs, contact:

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(301) 903-5707
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BUSINESS AGREEMENTS

Cost-Shared Contracts

Nonfederal parties working under DOE contract can agree to share some of the cost of developing a technology for a nonfederal market. This arrangement may involve cash, in-kind contributions, or both.

Grants and Cooperative Agreements

These contractual arrangements provide the recipient with money and/or property to support or stimulate research in areas of interest to DOE. DOE regularly publishes notices concerning grant opportunities in the *Commerce Business Daily*.

Research and Development Contracts

This acquisition instrument between the government and a contractor provides supplies and services to the government. DOE may enter directly into research and development contracts, and DOE laboratories and facilities can subcontract research and development work to the private sector. Announcements on requests for proposals are published in the *Commerce Business Daily* and are available through the EM Homepage on the Internet: www.em.doe.gov

Licensing Technologies

DOE contractor-operated laboratories can license DOE/EM-developed technology and software. In situations where DOE retains ownership of a new technology, the Office of General Counsel serves as licensing agent. Licensing activities are conducted according to existing DOE intellectual property provisions and can be exclusive or nonexclusive, for a specific field of use, for a geographic area, United States or foreign usage. Information on licensing technologies may be obtained by contacting the Office of Research and Technology Applications (ORTA) representatives listed later in this section.

Technical Personnel Exchange Arrangements

Personnel exchanges provide opportunities for federal or DOE laboratory scientists to work together with scientists from private industry on a mutual technical issue. Usually lasting one year or less, these arrangements foster the transfer of technical skills and knowledge. These arrangements require substantial cost-sharing by industry, but DOE has an advanced class patent agreement in place for this provision and the rights of any resulting patents become the property of the private industry participant. Contact an ORTA representative for more information.

Consulting Arrangements

Consulting arrangements are formal, written agreements in which a DOE laboratory or facility employee may provide advice or information to a nonfederal party for the purpose of technology transfer, or a nonfederal party may consult with the laboratory or facility. Laboratory/facility employees participating in this exchange of technical expertise must sign a nondisclosure agreement. Contact an ORTA representative for more information.

Reimbursable Work for Industry

This concept enables DOE personnel and laboratories to perform work for nonfederal partners when laboratories or facilities have expertise or equipment not available in the private sector. Reimbursable Work for Industry is usually termed "work for others." An advanced class patent waiver gives ownership of any inventions resulting from the research to the participating private sector company. Contact an ORTA representative for more information.

Office of Research and Technology Applications

Each federal laboratory has an Office of Research and Technology Application. These offices serve as technology transfer agents for the federal laboratories. They coordinate technology transfer activities among laboratories, industry, and universities. ORTA offices license patents and foster communication between researchers and technology customers.

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PERIODIC TABLE Of the Elements

1 H Hydrogen	2 He Helium																
3 Li Lithium	4 Be Beryllium	5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon										
11 Na Sodium	12 Mg Magnesium	13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon										
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	57 *La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium	
87 Fr Francium	88 Ra Radium	89 +Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium	

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ACRONYMS

AMP	ammonium molybdophosphate
ANL	Argonne National Laboratory
APTI	Advanced Processing Technology Initiative
CRADA	Cooperative Research and Development Agreement
Ci	Curie
CPU	Central Processing Unit
CST	crystalline silicotitanate
CV	column volumes
cpm/mL	counts per minute per milliliter
CSEX-SREX	cesium extraction-strontium extraction
CuFC	copper hexaferrocyanide
D&D	decontamination and decommissioning
DF	decontamination factor
DOE	Department of Energy
DSSF	double-shelled slurry feed
DTPA	diethylenetriaminepentaacetic acid
DWPF	defense waste processing facility
EDTA	ethylenediaminetetraacetic acid
EIX	electrochemical ion exchange
EM	Office of Environmental Management
EM-30	Office of Waste Management
EM-40	Office of Environmental Restoration
EM-50	Office of Science and Technology
EM-60	Office of Facilities Transition and Management
EPA	Environmental Protection Agency
ESP	Efficient Separations and Processing Crosscutting Program
g	gram
HLW	high-level waste
HTO	tritiated water

ICPP	Idaho Chemical Processing Plant
INEL	Idaho National Engineering Laboratory
IPC/RAS	Institute of Physical Chemistry/Russian Academy of Science
IX	ion exchange
K_d	distribution coefficient
LANL	Los Alamos National Laboratory
LBNL	Lawrence Berkeley National Laboratory
LDR	land disposal restriction
LLNL	Lawrence Livermore National Laboratory
LITCO	Lockheed Idaho Technology Company
LLLW	liquid low-level waste
LLW	low-level waste
Ln	lanthanide
M	molar
MCL	maximum contaminant level
mL	milliliter
μCi	microcurie
MVST	Melton Valley Storage Tank
N	normality
NaSICON	sodium super ion conductors
NaTiO-PAN	sodium titanate/polyacrylonitrile
NCAW	neutralized current acid waste
nCi	nanocurie
NGLLLW	newly generated liquid low-level waste
nM	nanometer
NiFC	nickel hexaferrocyanide
NIU	Northern Illinois University
NMR	Nuclear Magnetic Resonance
ORNL	Oak Ridge National Laboratory
PAA	polyantimonic acid
pCi/L	picoCuries per liter

PEG	polyethylene glycol
PNNL	Pacific Northwest National Laboratory
ppm	parts per million
PTFE	polytetrafluoroethylene
PUREX	plutonium uranium extraction
R&D	research and development
RCRA	Resource Conservation and Recovery Act
RE	rare earth
R-F	resorcinol-formaldehyde (resin)
SREX	Strontium Extraction Process
SRS	Savannah River Site
SRTC	Savannah River Technology Center
SST	sodium silicotitanate
S/S	solidification/stabilization
SX	solvent extraction
TAN	Test Area North (at INEL)
TBP	tributyl phosphate
TFA	Tank Focus Area
THOREX	thorium extraction
TiO-PAN	titanium oxide/polyacrylonitrile
TOREX	total radionuclide extraction
TPB	tetraphenylberate
TRU	transuranic (elements)
TRUEX	transuranic element extraction
TSCA	Toxic Substances Control Act
TTP	Technical Task Plan
TUCS	thermally unstable complexants
TV	test volumes
TWRS	Tank Waste Remediation System
UT	University of Tennessee
VOC	volatile organic compound

WAC	waste acceptance criteria
WHC	Westinghouse Hanford Company
WIPP	Waste Isolation Pilot Plant
WVNS	West Valley Nuclear Services