

Proceedings of the

**Efficient Separations and
Processing Cross-Cutting Program
Annual Technical Exchange Meeting**

January 24-26, 1995
Gaithersburg, Maryland

Sponsored by the
Office of Research Development
Office of Technology Development
Office of Environmental Management
U.S. Department of Energy

Prepared by
Pacific Northwest Laboratory
Richland, Washington

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Summary

This document contains summaries of technology development presented at the 1995 Efficient Separations and Processing Cross-Cutting Program (ESP) Annual Technical Exchange Meeting. The ESP is sponsored by the U.S. Department of Energy's Office of Environmental Management (EM), Office of Technology Development.

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

Presenters are asked to address the following areas:

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

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

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The Efficient Separations and Processing Cross-Cutting Program

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

Introduction

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

To improve focus on DOE's most pressing environmental restoration and waste management problems, the Assistant Secretary for EM established a working group in August 1993 to implement a new approach to environmental research and technology development. The goal of this new approach is to conduct a research and technology development program to overcome major obstacles in the cleanup of DOE sites. Integral to this new, solutions-oriented approach is an up-front awareness of program needs obtained from customers, users, regulators, and stakeholders. These needs can then be disseminated to the suppliers of technological solutions.

DOE has established a framework and strategy for coordinating efforts among DOE organizations, contractors, the national laboratories, other government agencies, the scientific community, industry, academia, and the public. Full implementation of the new approach is planned for FY 1995-96. The new strategy will build on existing programs and will seek continual improvement of all EM operations and processes.

Before implementing the new approach, EM's Office of Technology Development carried out an aggressive national program of applied research and development to meet environmental restoration and waste management needs based on the concepts of Integrated Programs and Integrated Demonstrations. These concepts, introduced in 1989, were engineered to manage the research, development, demonstration, testing, and evaluation activities within DOE.

Environmental Research and Technology Development

EM has defined focus areas responsible for environmental research and technology development throughout the DOE complex:

- **Contaminant Plume Containment and Remediation**—Plumes at DOE sites are estimated to include 600 billion gallons of contaminated groundwater and more than 200 million cubic yards of contaminated soils. Groundwater at many DOE sites is contaminated with radioactive and hazardous chemical species that are transported at various rates with groundwater movement.
- **Mixed Waste Characterization, Treatment, and Disposal**—DOE has site inventories of more than 133,000 cubic meters of mixed low-level waste—hazardous chemical components contaminated with radioactive components.
- **High-Level Waste Tank Remediation**—High-level waste exists as sludges, supernatant, calcine, and salt cake in 332 large storage tanks at DOE sites. These wastes must be retrieved, treated, and immobilized for permanent disposal.

- **Landfill Stabilization**—DOE sites include large volumes of solid and other wastes in landfills. Evolving regulations dictate that some landfills must be stabilized to prevent contamination of groundwater and loss of control over contaminants in the waste.
- **Facility Transitioning, Decommissioning, and Final Disposition**—Current projections are that as many as 5000 DOE-owned facilities that are contaminated with radioactive species on surfaces and inside equipment must be decontaminated and decommissioned over the next 30 years. Decontamination of such facilities will result in secondary wastes to be treated and disposed.

Cross-cutting technologies are those that overlap the focus area boundaries while providing simultaneous benefits. These technologies may be used in several or all focus area testing and evaluation programs.

The Efficient Separations and Processing Cross-Cutting Program

The Efficient Separations and Processing Cross-Cutting Program (ESP) was created in 1991 to identify, develop, and perfect separations technologies and processes to treat wastes and address environmental problems throughout the DOE complex. The ESP funds several multiyear tasks that address high-priority waste remediation problems involving high-level, low-level, transuranic, hazardous, and mixed (radioactive and hazardous) wastes. The ESP supports applied research and development (R&D) leading to demonstration or use of these separations technologies by other organizations within DOE-EM. It is organized as a cross-cutting program under DOE-EM's Office of Research and Development.

Technology Needs

A wide range of wastes and environmental problems exist at more than 100 contaminated installations in 36 states and territories as a result of half a century of

nuclear processing activities by DOE and its predecessors. The cost of cleaning up this legacy is estimated to be on the order of hundreds of billions of dollars. The ESP was begun because billions of dollars could be saved if new separations technologies and processes could produce even a marginal reduction in cost. Treating essentially all DOE defense wastes requires separation methods that concentrate the contaminants and/or purify waste streams for release to the environment or for down-grading to a waste form less difficult and expensive to dispose of.

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 as environmental restoration priorities have changed, the program has evolved to encompass the breadth of waste management and environmental remediation problems.

Mission and Scope

The mission of the ESP is to

- Provide separations technologies to process, concentrate, and immobilize a wide spectrum of radioactive and hazardous defense wastes at DOE sites.
- Coordinate separations technologies R&D within DOE-EM.
- Foster future expertise in separations technologies by encouraging university participation.
- Facilitate transfer of separations technologies to the U.S. industrial sector.

The ESP provides the following categories of separations functions:

- removal of dilute radionuclides from aqueous phases
- removal of dilute toxic materials from aqueous phases

- conditioning and chemical treatment of wastes to enhance separations (e.g., calcining, leaching, or dissolving sludges)
- removal of bulk constituents from waste streams to recover chemicals for recycle and waste minimization
- destruction of complexants and bulk anions.

Current Program

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

The ESP also sponsors development of improved chemical processes when needed, as well as research on chemical reactions that enhance chemical separations or eliminate a separations step by destroying a contaminant. However, where such technologies are already being pursued within EM, ESP coordinates activities.

Most separations technologies pertinent to EM waste remediation problems involve transfer of a contaminant from a liquid phase to a solid or some other liquid phase. In some cases the contaminant may originate in a solid phase, in which case some process (either leaching or dissolving) is needed to put the contaminant into a liquid as an intermediate step. Also, dissolved organic compounds can sequester contaminants and impede desired separations, in which case some process is needed to destroy the organic species. Accordingly, the ESP sponsors research on processes

such as organic destruction and leaching and dissolution of tank waste sludges to enable liquid-based separation technologies.

For the purposes of this meeting, the technologies described have been put into the following categories:

- cesium and strontium separations
- technology testing
- technetium separations and membranes
- actinide separations and new polymers
- tank waste processing.

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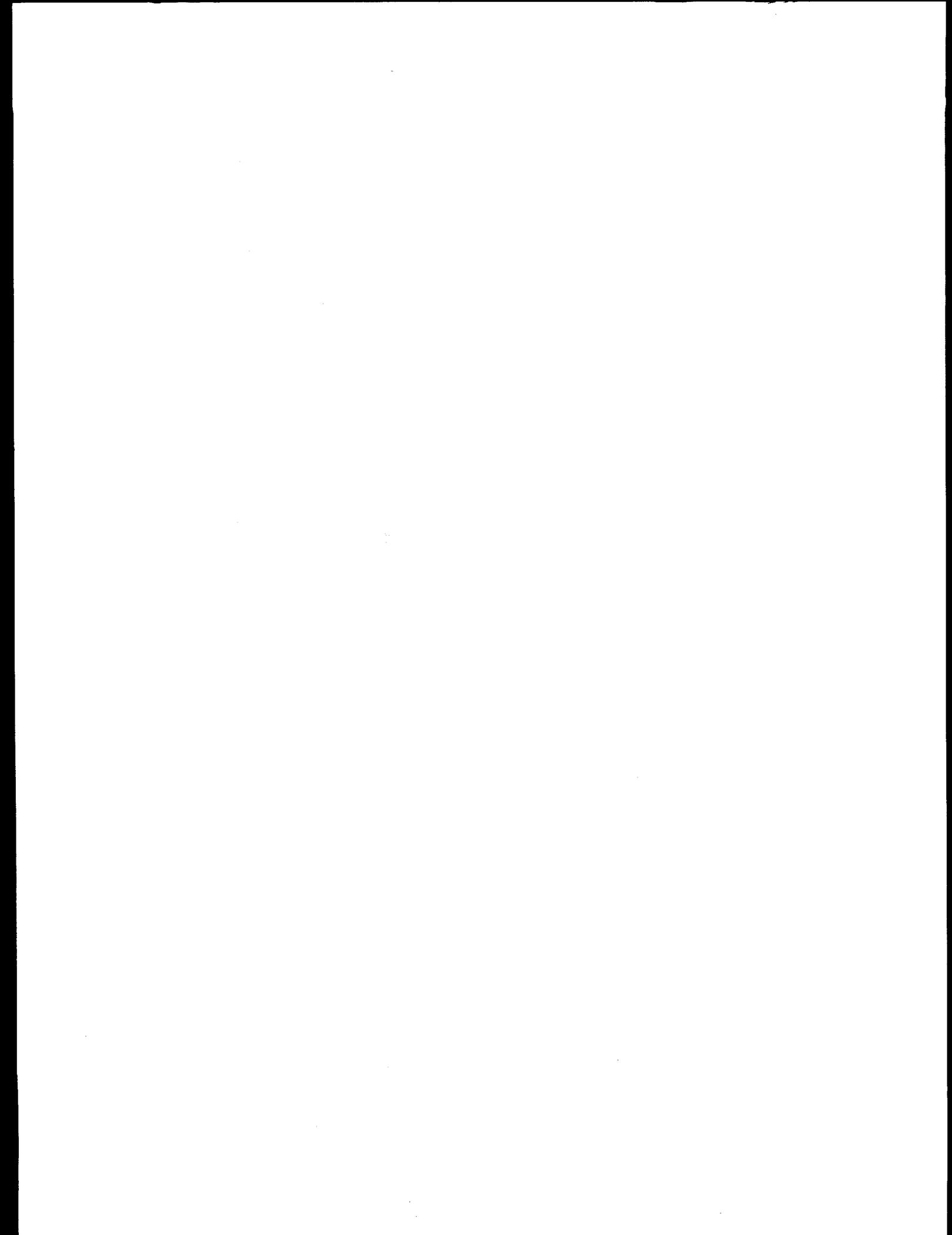
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Cesium/Strontium Separations

- Waste Separation and Pretreatment Using Crystalline Silicotitanate Ion Exchangers
- Inorganic Ion Exchange for Cesium and Strontium
- Novel Cesium, Strontium, and Technetium Ion Exchange Membrane
- Design Basis for Metal-Selective Ligands: Molecular Modeling Approach
- International Programs

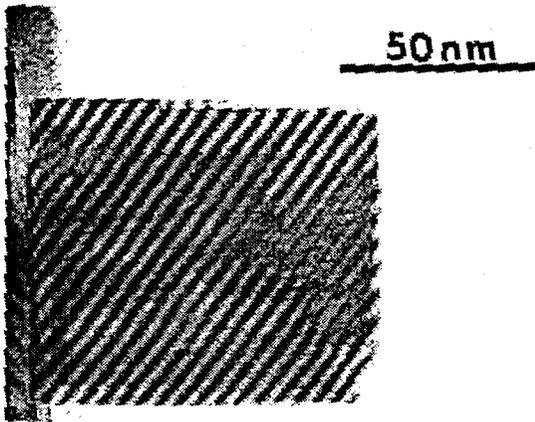


Waste Separation and Pretreatment Using Crystalline Silicotitanate Ion Exchangers

Presenters: Norm Brown, and Jim Miller, Sandia National Laboratories; John Sherman, UOP

Description

National laboratory, university, and industrial researchers are developing and evaluating inorganic crystalline silicotitanate (CST) ion-exchange materials to selectively remove ^{137}Cs and other radionuclides from a wide spectrum of radioactive defense wastes.



Transmission electron micrograph of TAM-5 phase particle of the crystalline silicotitanates

Crystalline silicotitanates comprise several phases and were invented jointly by Sandia National Laboratories and Texas A&M (TAM) University in 1992. The materials exhibit both ion-exchange properties and the capability to be ion size selective. Specifically, the TAM-5 phase has a crystalline lattice spacing that is highly selective for cesium separation even in waste streams containing very high (5 to 10 M) concentrations of sodium. The CST technology is being developed and demonstrated for the removal of radioactive materials from waste streams ranging from highly alkaline to highly acidic. The project has three primary activities:

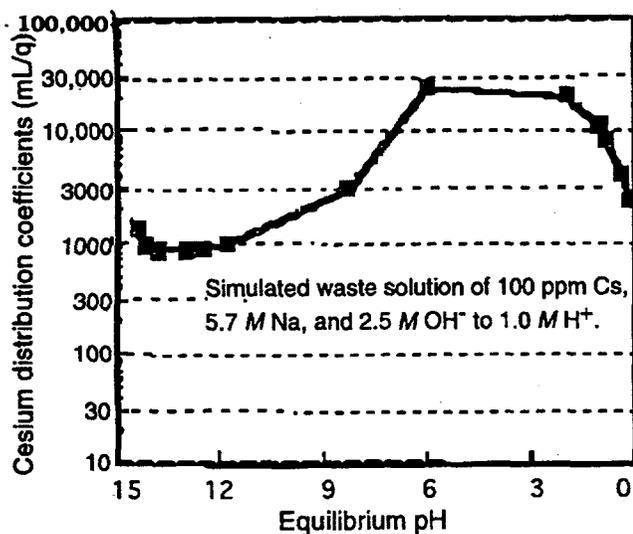
1. evaluation of the ion exchange properties of the TAM-5 powder and the CST engineered form developed by UOP, Sandia's industrial partner, especially the effects of pH and solution composition on cesium selectivity
2. stability of the TAM-5 powder in both acidic and basic solutions as well as the stability under exposure to radiation at levels of 10^9 Rads or greater
3. evaluation of the performance of the TAM-5 material in both powder and engineered form for radionuclide removal at DOE facilities, specifically at the Hanford Site, Oak Ridge National Laboratory (ORNL), Westinghouse Savannah River Company (WSRC), Idaho National Engineering Laboratory (INEL), and West Valley Nuclear Services.

Technology Needs

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

DOE has more than 200 tanks being used to process and store radioactive waste by-products 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 defense waste storage tanks. Specifically, CST ion-exchange materials and



Cesium distribution coefficients as a function of equilibrium pH

ion-exchange processes will be used to develop advanced, efficient radioactive waste separation technologies.

Accomplishments

More than 200 different syntheses of CST TAM-5 powder material have been prepared to optimize selectivity for cesium from highly alkaline waste streams. Baseline synthesis conditions were selected that were consistent with operating conditions for commercial production.

Powder synthesis has been demonstrated in a 5-gallon reactor. UOP has scaled up the lab synthesis and produced 1800 pounds of CST powder in a single commercial batch. The powder material has been characterized to determine basic physical and chemical properties, including density, particle size, surface area, powder diffraction pattern, elemental composition, water content, and cesium capacity. Cesium and strontium distribution coefficients were measured across a pH range from <0 to >14.

The TAM-5 material has high cesium selectivity over the entire pH range, but is selective for strontium (distribution coefficients >10,000 mL/g) only in neutral to

alkaline solution. The TAM-5 material also maintains high cesium selectivity over large variations in both sodium and potassium concentrations.

Stability tests show that the TAM-5 powder is stable in high pH solutions for >100 days and in low pH solutions (up to 6 M HNO₃) for at least several days. The material ion exchange performance is also stable after exposure to 10⁹ Rads.

Tests have been performed on a variety of waste compositions, both acidic and alkaline. Hanford Site, INEL, WSRC, and ORNL waste simulants have been tested as well as actual wastes at ORNL and INEL. Results show that the TAM-5 material exhibits superior cesium selectivity in all cases. Tests have also been performed on neutral-pH solutions. Cesium distribution coefficients of >500,000 mL/g have been obtained in neutral solutions, indicating the potential for using TAM-5 material for decontamination and decommissioning of nuclear facilities.

Commercialization Status

Synthesis development and evaluation efforts meet the need for commercialization of the TAM-5 material. In March 1994, Sandia teamed with UOP, a world-leader in ion-exchange material production and processes, in a Cooperative Research and Development Agreement to commercialize the TAM-5 powder and an engineered form of the material. The TAM-5 powder was commercially produced in an 1800-pound batch in September 1994. The engineered form of the material, suitable for use in ion-exchange columns, is expected to be available in mid-1995.

Collaboration/Technology Transfer

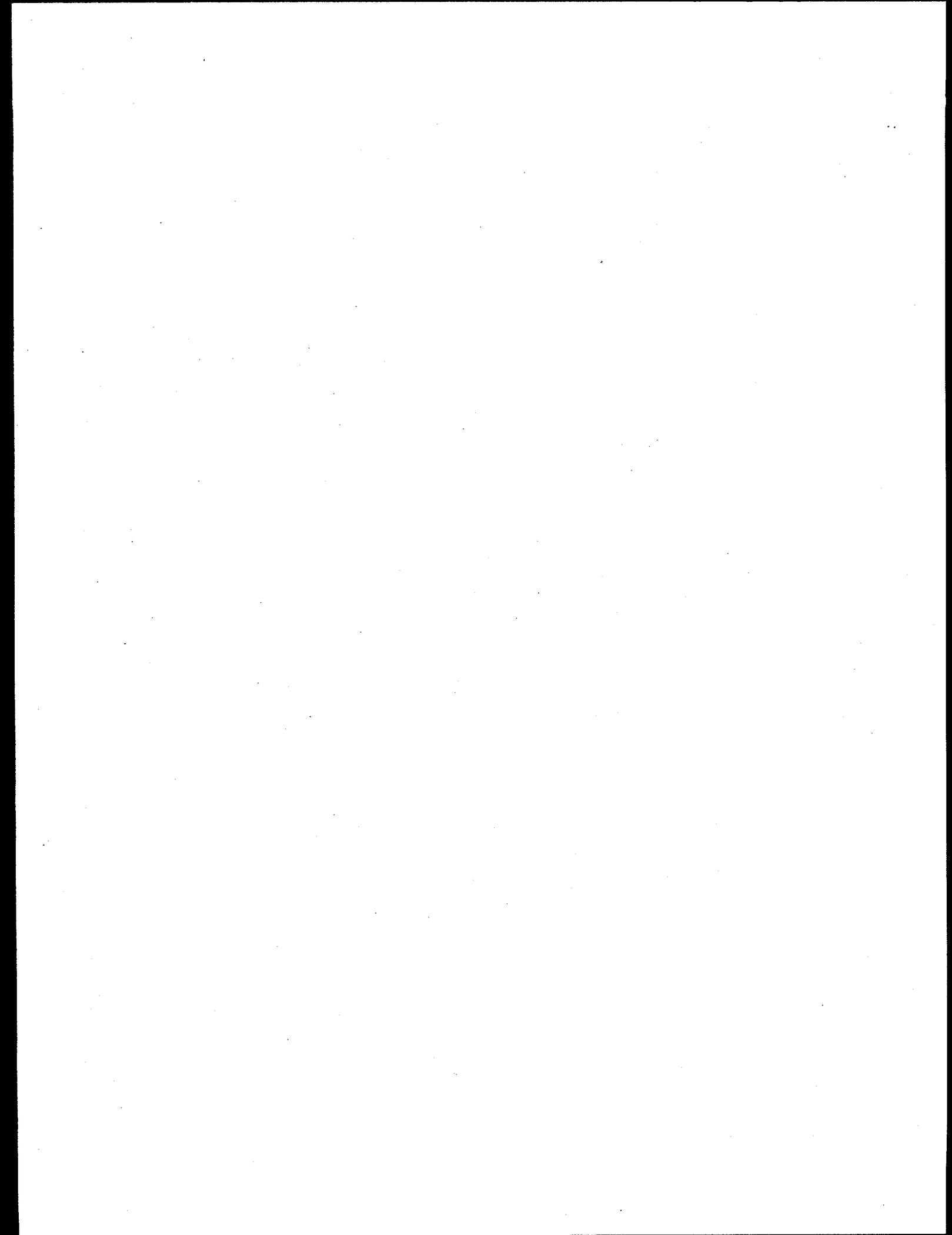
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 UOP (CRADA partner)
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Inorganic Ion Exchange for Cesium and Strontium

Presenters: Abe Clearfield, Texas A&M University; Steve Yates, AlliedSignal

Description

Pacific Northwest Laboratory (PNL) is collaborating with industry and university participants to develop high-capacity, selective, solid inorganic ion exchangers for the recovery of cesium and strontium from nuclear alkaline and acid wastes. To achieve this goal, contracts were awarded in 1992 to AlliedSignal Company, Des Plaines, Illinois, in partnership with Texas A&M University.

During 1993, they screened and developed three classes of exchangers: sodium titanates, zirconium arylphosphonate phosphates, and modified layered minerals. This included the scale-up of these materials, and a series of studies related to pelletization to a useful size range for ion exchange column use.

The preferred strontium selective exchanger for use in highly alkaline waste is a unique phase of sodium titanate, $\text{Na}_4\text{Ti}_9\text{O}_{20}$, which has a layer spacing of 10 Å. This material exhibits a strontium K_d of 21,000 mL/g from a feed containing 80 ppm strontium, 0.1 M NaOH and 5 M NaNO_3 . The material is being pelletized to a useful size range for tests in a column mode under several sets of conditions. The powder has been scaled up to the 1-kg batch size for PNL testing.

A modified sodium biotite mica and synthetic micas have been developed for the recovery of cesium from alkaline waste. Interaction of these exchangers in the presence of both potassium and cesium is being studied with the goal to produce an enhanced ion exchange material.

Pelletization screening trials are being completed that allowed evaluation of more than 20 inorganic binders for the powdered exchangers noted above. These trials resulted in the elimination of the great majority of

the binders as incompatible with the highly alkaline feed, but identified an excellent candidate for use with sodium titanate powders.

Technology Needs

EM Focus Area: high-level waste tank remediation

This project is designed to test the capacity, selectivity, and stability of selected solid ion exchangers in representative physical, chemical, and radiation environments. Emphasis is on developing and demonstrating ion exchange materials 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. A major goal for AlliedSignal/Texas A&M for FY 1995 is to continue to obtain necessary scientific and engineering information required to remove cesium and strontium from highly alkaline wastes at the Hanford Site.

Benefits

The benefits gained by developing this technology are cost reduction in separating and disposing of nuclear wastes and making technology available for selective sequestering of cesium, strontium, and technetium.

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

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

Finally, this technology applies to the environmental sector, because the materials developed for separating traces of cesium, strontium, and technetium from voluminous liquid wastes could be adapted to treat small waste streams.

Accomplishments

The crystalline form of $\text{Na}_4\text{Ti}_9\text{O}_{20}$ has been compared with other known ion exchange media to recover strontium from alkaline waste. This material appears to have the highest known distribution coefficient for strontium in the presence of 6 M sodium nitrate and >pH 13. The cellulose acetate binder first used to prepare pellets of this exchanger was found to be insufficiently durable to radiation and/or highly basic solutions. After an exhaustive survey, a binder has been selected that is stable but does not reduce the extraction capacity of the pelletized form of titanate.

The natural micas containing potassium have been replaced with synthetic micas that hold the potential to extract cesium from alkaline waste. Additional studies are being conducted to refine this powder and to prepare it for pelletization for initial field trials to recover cesium.

Collaboration/Technology Transfer

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Novel Cesium, Strontium, and Technetium Ion Exchange Membrane

Presenters: Tom Kafka, 3M; Ron Bruening, IBC Advanced Technologies

Description

Pacific Northwest Laboratory (PNL) is collaborating with industrial partners to develop high-capacity, selective solid extractants for cesium, strontium, chromium, silver, technetium, and nobel metals from nuclear wastes. The work described is one of two parallel projects to develop high-capacity, selective, solid sequestrants for the removal of specific contaminants from nuclear waste streams.

Contracts were awarded in 1992 to 3M, St. Paul, Minnesota, working in cooperation with IBC Advanced Technologies, Provo, Utah. A major emphasis during the initial work was to provide improved molecular-recognition technology agents, and to implement their use in the form of webs or structures. Novel agents have been selected for screening tests.

The capabilities, 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 are being determined.

The Empore™ extraction membrane technology developed by 3M/IBC provides a state-of-the-art method 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 placed in cartridges or filters, allowing the solution of interest to be passed through or by the web, allowing the selective solid extractant to remove the metal ion of interest. Under severe radiation fields PTFE becomes brittle, thus other materials of web construction have successfully complemented this original concept.

The membranes can achieve equal or better performance than ion exchange columns by using a very high surface area through the use of small (10 micron) active particles. No adhesive or binders are used so the full activity of the particles is retained. A polymer membrane that is more radiolytically stable (up to 300 megarad) than PTFE has been combined with active particles. Samples were sent to PNL for confirming tests using a ⁶⁰Co source. In addition, other membranes have been made with a range of support particles selected to meet DOE's needs.

Technology Needs

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

This project 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. A major goal for 3M/IBC for FY 1995 is to continue to obtain necessary scientific and engineering information required to remove cesium and strontium from highly alkaline wastes at the Hanford Site.

Accomplishments

The first opportunity to test the 3M/IBC system with actual radioactive waste was successfully completed

at the Idaho National Engineering Laboratory (INEL) using acid radioactive waste containing both ^{137}Cs and ^{90}Sr . Synthetic "mimic" wastes were used to test the system both at the 3M laboratory as well as at INEL before the actual hot cell test. The results from those tests were confirmed in actual waste testing.

The experience provided 3M/IBC/INEL/PNL staff an opportunity to obtain excellent results using a major radioactive waste stream. Additional actual waste tests are being proposed, while cartridge design, ligand-particle combinations, and web technologies are continuing to be improved.

Benefits

The benefits gained by developing this technology are cost reduction in separating and disposing of nuclear wastes and making technology available for selective sequestering of cesium, strontium, and technetium.

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

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

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Collaboration/Technology Transfer

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Design Basis for Metal-Selective Ligands: Molecular Modeling Approach

Presenter: Ben Hay, Pacific Northwest Laboratory

Description

The purpose of this work is to develop and implement a molecular design basis for organic ligand selection. These ligands 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 the development of such ligands involves lengthy programs of organic synthesis and testing, which in the absence of reliable methods for screening compounds before synthesis, then results in wasted research effort. Our approach breaks down and simplifies this costly process with the aid of computer-based molecular modeling techniques.

Commercial software for organic molecular modeling is being configured to examine the interactions between organic ligands and metal ions, yielding an inexpensive, commercially or readily available computational tool that can be used to predict the structures and energies of ligand-metal complexes. Users will be able to correlate the large body of exist-

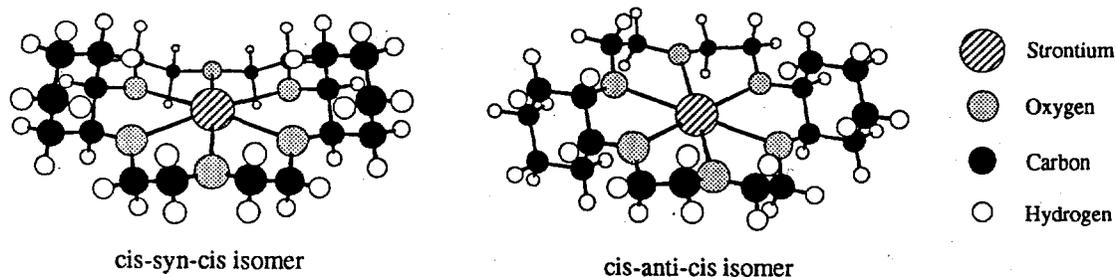
ing experimental data on structure, solution binding affinity, and metal ion selectivity to develop structural design criteria. These criteria will provide a basis for selecting ligands that can be implemented in separation technologies through collaboration with other DOE national laboratories and private industry. The initial focus will be to select ether-based ligands that can be applied to the recovery and concentration of cesium, strontium, and technetium.

Technology Needs

EM Focus Area: high-level waste tank remediation

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

The successful performance of these separation methods depends largely on the properties of the organic ligand (e.g., selectivity, binding affinities, binding kinetics, and solubility). Therefore, much effort is



Calculated structures for strontium complexes with two isomers of dicyclohexano-18-crown-6.

spent on the synthesis, characterization, and testing of a large number of ligands to find those few that have the desired properties to meet the separations process needs. The current criteria used to select ligands for a specific application are not accurate and result in more failures than successes.

Benefits

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

The cost of organic synthesis and performance testing with radioactive materials is 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 molecular modeling capability will save significant cost in ligand identification, evaluation, and deployment.

This technology will also allow the development of ligands with improved performance: 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 save money by decreasing the amount of ligand required for a process.

Problems concerning the stability of metal complexes and selectivity of complex formation are of fundamental importance. This technology has potential application to the wide variety of ligand types and associated

complexes that are being addressed by other DOE programs involving environmental cleanup, transport and disposal of environmental contaminants, development of sensors, and nuclear medicine. Private sector application of this technology in the chemical industry, medicine and pharmacology, hydrometallurgy, and geochemistry is also possible.

Accomplishments

An inexpensive, off-the-shelf molecular model (MM3) has been configured to handle aliphatic crown ether ligands and their complexes with the alkali and alkaline earth metal ions. The model has been demonstrated to 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.

The model currently is being applied to the design and screening of crown ether ligands for the separation of cesium and technetium and the optimization of the strontium extraction reagent.

Collaboration/Technology Transfer

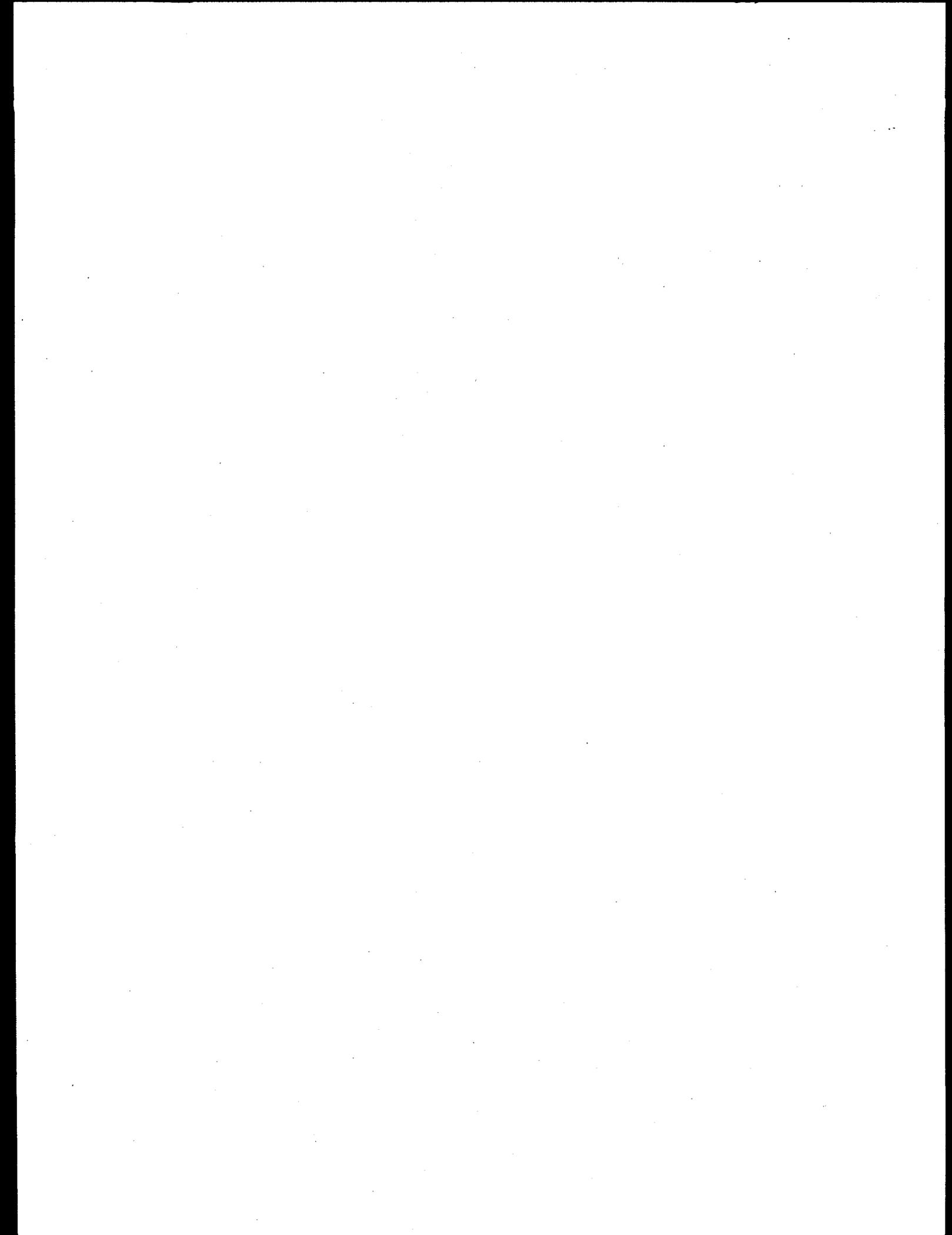
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International Programs

Presenter: Jack Watson, Oak Ridge National Laboratory

Description

The ESP seeks to develop and test the best available processing methods that are most likely to solve waste and environmental problems at DOE facilities. When foreign technologies offer significant potential benefits to DOE, the ESP engages in a limited number of international programs to test and evaluate selected technologies being developed in foreign laboratories.

Because the ESP is engaged principally in technology research and development (R&D), its contributions to developing and evaluating foreign technologies deal principally with new rather than commercially available technologies. As with the ESP R&D efforts in the U.S., the international efforts currently are concentrated on treatment of nuclear wastes.

All current ESP international efforts are in Russia and other countries formerly in the "Soviet block." Those countries have expert scientists and engineers with extensive nuclear processing experience who are working to solve nuclear waste problems in their countries, and they have usually been made available to the ESP and other U.S.-sponsored programs.

The ESP's approach to the international effort is based on identifiable DOE needs, available foreign technologies under development, and expertise of the international investigators. These activities have usually begun by assessing the capabilities and potential of potential international technologies and investigators; when appropriate, a more substantial development effort is started.

All international investigators must remain fully aware of U.S. needs, understand limitations imposed

by U.S. regulations, and transfer the technologies developed by the ESP programs to the U.S. facilities. These requirements are met in part by linking the international laboratories with appropriate DOE laboratories that know the problems that the technology will address. The DOE laboratory then works with the international participants, keeps them informed of DOE needs and regulations, and assists with testing of the technology in the U.S. To fully evaluate a waste treatment technology, it usually must be tested on real U.S. waste in the U.S.

Technology Needs

EM Focus Area: high-level waste tank remediation

The ESP international activities address any or all waste/environmental processing needs at DOE facilities, but current activities, like the overall ESP effort, are focused on the particularly important needs of high-level waste. The Khlopin Radium Institute in Saint Petersburg, Russia, is investigating the use of Russian technologies for removing cesium and strontium from acid solutions such as those at the Idaho National Engineering Laboratory (INEL). (Other U.S. activities on separation of cesium and strontium are focused largely on alkaline solutions or on non-regenerable adsorbents.)

Also under study are new methods for incorporating fine adsorbents into large porous particles, better understanding of the chemistry of actinides in complex multicomponent alkaline solutions, and innovative adsorbents and extractants for radioactive components.

Accomplishments

Laboratory studies at Khlopin have shown that cobalt dicarbollide can remove cesium and strontium effectively from simulated high-level waste like that at INEL. Engineering scale counter-current tests demonstrated that mass transfer rates and fluid hydraulic properties are suitable for implementation of the technology. Small-scale batch tests were made at INEL with real waste as a joint effort by INEL and Khlopin scientists. The extraction results were essentially the same as those predicted from laboratory tests with simulated wastes, but the Russian experts were particularly helpful in resolving early questions about the original data.

A potentially important problem with the cobalt dicarbollide process is its use of a diluent and an eluent that are listed as "hazardous" under U.S. regulations; there are no apparent difficulties with the process performance. Scientists at Khlopin have explored a number of alternate diluents and eluents that are not considered hazardous in the U.S. Further tests with the new materials are in progress.

Scientists at Khlopin have also developed and used a phosphine oxide extractant for separating actinide elements from acid high-level waste, and tests of that material were carried out on simulated and actual INEL waste. These tests were completed in parallel with the cobalt dicarbollide tests, and the results were successful and essentially the same as had been predicted. Phase stability was tested, and suitable adjustments in the extractant composition eliminated phase stability problems with the INEL wastes. This process is now an alternative to other actinide separation methods being developed in the U.S. and France.

Formulation of highly selective inorganic adsorbents into porous particles that can be used in production-scale packed adsorption columns is a problem for several promising high-level waste adsorbents and

ion exchange materials. At the Czech Technical University, a method has been studied that "traps" the fine particles into a porous polymer of polyacrylonitrile (PAN). To evaluate the potential use of this material with high-level waste, its radiation stability and chemical stability in simulated U.S. high-level waste are being evaluated. Early results are showing minimal to no chemical degradation and acceptable radiation stability over the doses reached thus far.

Other international efforts have begun at the Russian Institute for Physical Chemistry to apply their established expertise in actinide chemistry in alkaline solutions to evaluate the effects of redox conditions, radiation fields, and solution aging to the solubilities and other behavior of complex multicomponent electrolyte mixtures like those present in alkaline high-level waste at Hanford, Savannah River, and Oak Ridge.

New crown ether based extraction processes are being investigated for potential applications in the U.S. The potential for using cobalt dicarbollide bound to solid substrates as selective adsorbents for cesium is being explored by a visiting Czech scientist at the Los Alamos National Laboratory, and new selective adsorbents developed in the Czech Republic are being explored for their potential applications in the U.S.

Benefits

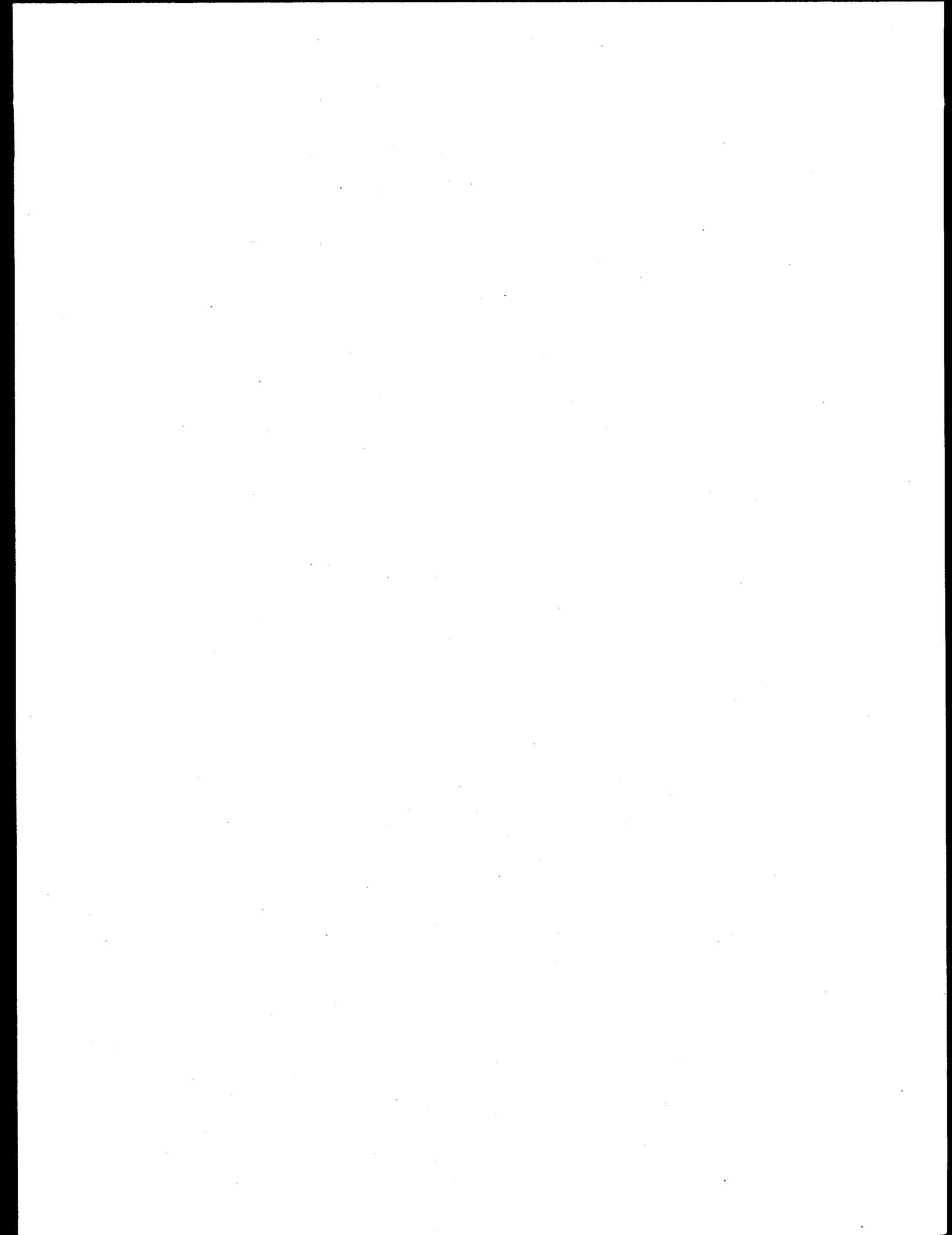
The international activities have made available highly expert scientists and engineers to work on new technologies that have not been explored fully in the U.S. Although the cost of the international effort is only a small portion of the ESP activities, it brings strong investigators to the program with new ideas and experiences; the potential "payoff" from involving such people appears to be high.

Collaboration/Technology Transfer

Khlopin Radium Institute
Czech Technical University
Russian Institute for Physical Chemistry
Russian Institute for Chemical Technology
Czech Institute for Nuclear Chemistry
Sandia National Laboratories
Idaho National Engineering Laboratory
Oak Ridge National Laboratory
Pacific Northwest Laboratory
Florida State University

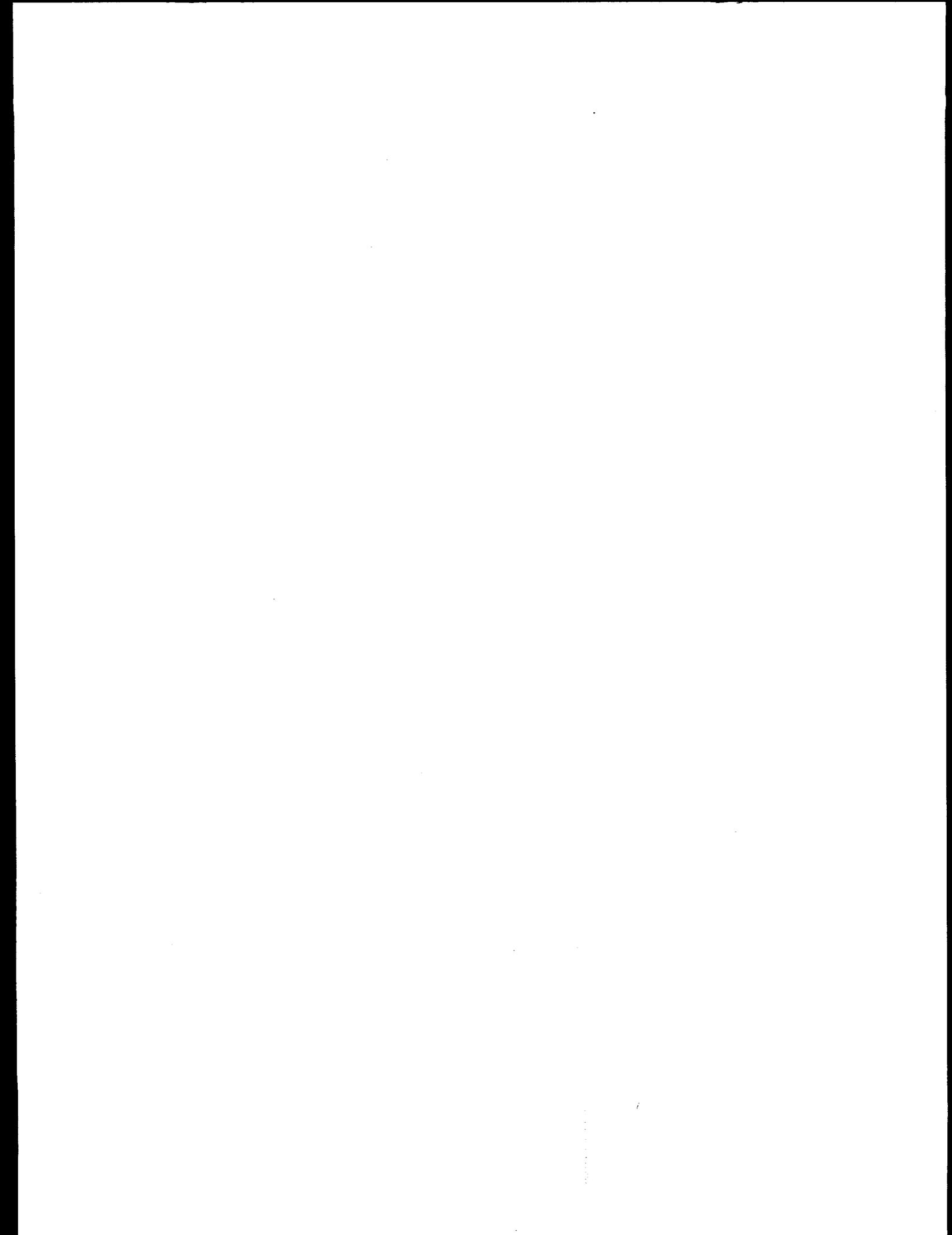
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Technology Testing

- Acidic Separation Technologies for Treatment of Idaho National Engineering Laboratory Waste
- Advanced Chemical Separations at Savannah River Site
- Evaluation of Improved Techniques for Removing Strontium and Cesium from Process Waste Water and Groundwater
- Mercury Separation from Mixed Waste



Acidic Separation Technologies for Treatment of Idaho National Engineering Laboratory Waste

Presenter: Terry Todd, Idaho National Engineering Laboratory

Description

This task investigates separation technologies for potential application to treating Idaho National Engineering Laboratory (INEL) acidic liquid wastes to remove transuranics, strontium, cesium, and technetium. Solvent extraction technologies developed in Russia for the treatment of acidic wastes have shown promise. One of these technologies, cobalt dicarbollide, will be tested in centrifugal contactors to determine its efficacy at removing cesium and strontium from acidic waste.

Other technologies, including solvent extraction and ion exchange are being investigated for the removal of cesium from the INEL waste, as well as testing of other ESP technologies on actual acidic radioactive waste for accurate performance results.

Technology Needs

EM Focus Area: high-level waste tank remediation

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

In April 1992, DOE discontinued reprocessing of spent nuclear fuel and shifted the focus of the Idaho Chemical Processing Plant (ICPP) to management and dispositioning of accumulated radioactive wastes. Currently, about 1.8 million gallons of acidic, radioactive liquid waste that is not amenable to calcination, and about 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 this radioactive liquid and calcine wastes.

Accomplishments

Two technologies developed in Russia for the treatment of radioactive liquid wastes, cobalt dicarbollide and phosphine oxide, were successfully tested on simulated waste in Russia and on the actual radioactive waste at the INEL. This collaborative effort [need to tell more about this collaboration with Russians] demonstrated the potential of the phosphine oxide process by achieving a decontamination factor for gross alpha activity of nearly 400 in three consecutive batch contacts.

Distribution coefficients for cesium and strontium in the cobalt dicarbollide process were approximately 2, and tests conducted at the Khlopin Radium Institute demonstrated a decontamination factor of 1000 for cesium in eight stages of counter-current extraction.

Web technology from 3M and IBC Advanced Technologies for the removal of cesium and strontium was successfully demonstrated on actual ICPP acidic waste. A joint team from INEL, Pacific Northwest Laboratory, 3M, and IBC performed tests at the INEL Remote Analytical Laboratory and the results from the radioactive tests confirmed the results from previous nonradioactive tests.

Benefits

The radionuclide content of the INEL wastes before separation 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.

It is possible to decontaminate the INEL wastes sufficiently to achieve NRC Class A low-level waste for the bulk constituents and the high-level waste volume resulting from the separations process would be significantly less than the original waste volume. This would result in lower facility and processing costs associated with the low-level waste stream and the much lower throughput high-level waste stream. It would also save considerable cost for interim storage and final geologic disposal of the high-level waste fraction.

Collaboration\Technology Transfer

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TTP Number ID421201

Advanced Chemical Separations at Savannah River Site

Presenters: Major Thompson, Dan McCabe, and Jane Bibler, Savannah River Technology Center

Description

Researchers at the Savannah River Site (SRS) are evaluating and testing ESP-developed materials for separating radionuclides from alkaline supernatant solutions, dissolved salt cake, and recycle water from the SRS Defense Waste Processing Facility (DWPF). The goal is to identify possible alternatives for these separations from among the materials developed at Savannah River Technology Center (SRTC) and other sites under ESP funding.

Elements of the work include acquisition of crystalline silicotitanate (CST) powder; sodium titanate powder and cobalt dicarbollide derived ion exchange material; radioactive and nonradioactive testing of the chemical properties, including reproducible demonstration of decontamination factors, for cesium, strontium, and transuranic (TRU) elements; evaluation of the materials for compatibility with the existing plant equipment and processes; and evaluation of possible direct feeding of the loaded material into the vitrifier for inclusion in the glass. The purpose is to compare accurately the technical factors between the existing process and possible alternative materials.

Technology Needs

EM Focus Area: high-level tank waste remediation

Materials need to be examined as a substitute for the tetrphenylborate (TPB) precipitation and strontium/TRU adsorption processes used in the In-Tank Precipitation Process (ITP) at SRS. The TPB precipitation has encountered difficulties because of radiolysis that produces benzene. In addition, the cesium TPB must be hydrolyzed to remove benzene before vitrifi-

cation, and problems exist with the hydrolysis process. The benzene produced by radiolysis and hydrolysis must be safely handled and destroyed by incineration. Also, the monosodium titanate used in ITP is a very fine powder that causes problems during filtration; a larger particle size material would be desirable.

During waste vitrification at the DWPF, some of the cesium volatilizes from the glass and is condensed in the offgas system, making it necessary to remove the cesium from the offgas system by scrubbing and flushing with water. This water is recycled back to the waste tanks for storage before evaporation and retreatment in ITP. However, this large volume of recycle water is not easily handled in the available tank volume. A process is desired to remove the cesium from the water before sending it to the Effluent Treatment Facility for further treatment and release to the Savannah River.

Accomplishments

Crystalline silicotitanates, developed by Sandia National Laboratories in collaboration with Texas A&M University, have been shown to adsorb cesium from solutions over a wide pH range. These CST powders have been demonstrated to remove cesium from Hanford tank waste solutions and simulated SRS tank waste solutions.

Sandia is working with UOP to produce commercial quantities of the adsorbent CST in powder form for testing, and to produce an engineered form that can be used in column adsorption. The CSTs will also adsorb strontium and TRUs similar to the existing monosodium titanate currently used in ITP. The CST

material will be tested as a possible replacement for TPB precipitation of cesium and monosodium titanate adsorption of strontium and TRUs.

Pacific Northwest Laboratory has worked with Texas A&M University and AlliedSignal Company to produce a dry sodium titanate powder that adsorbs strontium from basic solutions. The dry sodium titanate powder will be tested as a possible replacement for the monosodium titanate slurry.

Both SRTC and Clemson University have developed a cobalt dicarbollide derived ion exchange material to act as a precipitating agent for cesium. This new material is much more stable in 1 M NaOH solutions than a number of different derivatives that were previously synthesized but shown to be insoluble and unstable in the same solutions. Several preparations of the material were completed with one giving a high cesium K_d . More work is needed to improve reproducibility of the preparation and to investigate how the K_d can be improved further, and its compatibility with glass must be evaluated through testing.

Benefits

These technologies have the potential to significantly simplify and improve operations involving decontamination of aqueous waste streams by replacing

organic-containing precipitants and adsorbents, reducing the number of process steps, and removing the need to evaporate large quantities of high-activity recycle water. In addition, the safety of operations would be increased by replacing TPB with a less hazardous material.

Collaboration/Technology Transfer

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

Presenter: Debra Bostick, Oak Ridge National Laboratory

Description

This task will test new sorbent materials, ion-exchange materials, or other processes for groundwater and process waste water decontamination that might be more selective for the removal of ^{90}Sr and ^{137}Cs than standard treatment methods. These materials will be tested in the laboratory using simulated and actual waste water.

The testing will begin by conducting scoping tests where new treatment materials are compared with standard commercially available materials. Equilibrium tests will be conducted under various treatment conditions (pH, temperature, 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 processes.

Technology Needs

EM Focus Area: contaminant plume containment and remediation

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

The current treatment processes for these wastes generate large amounts of solid secondary waste that

must be disposed of as radioactive waste. Handling and disposal of these secondary wastes is expensive; therefore, new processes are needed to minimize the volume of secondary waste produced.

Accomplishments and Future Work

Materials and processes that will be investigated in the course of this study include the use of selective molecular recognition sorbents immobilized on permeable membranes by 3M, the resorcinol-formaldehyde-based resin developed by researchers at the Savannah River Site, engineered silicotitanates developed at Sandia National Laboratories, and pillared clays being developed at Texas A&M University.

Testing of the new materials was initiated by preparing a standard process water simulant, based on the composition of the process wastewater feed to the Oak Ridge National Laboratory Process Wastewater Treatment Plant (PWTP). Next, chabazite zeolite sorption was selected as the baseline treatment technology against which the new materials will be tested.

A stock quantity of TSM 300 chabazite zeolite, purchased from Steelhead Specialty Minerals in Spokane, Washington, was sized and completely converted to sodium form. Batch sorption studies using the treated zeolite in the waste water simulant were completed, determining the sorption efficiency in the presence of varying sodium, calcium, potassium, and magnesium concentrations.

The chabazite zeolite has also been used in batch testing to decontaminate an actual PWTP waste water

sample. The sorption characteristics of a small zeolite column are currently being determined using the waste water simulant.

Testing of the new materials will begin on completion of the small zeolite column study. If the membrane technology can be obtained from 3M, the SuperLig® powders and membranes will be tested similarly and results compared to those obtained using the standard chabazite zeolite treatment. If the SuperLig® materials are not available, the resorcinol-formaldehyde will be substituted.

Benefits

This task will perform evaluations of ESP separation technologies for strontium and cesium removal from process waste water and contaminated groundwater. Successful tests of these processes may lead to full-scale demonstrations as part of the Underground Storage Tank Integrated Demonstration.

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 water.

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Mercury Separation from Mixed Wastes

Presenter: Tom Klasson, Oak Ridge National Laboratory

Description

Researchers at Oak Ridge National Laboratory (ORNL) are assessing state-of-the-art sorbent technologies for processing currently stored, mercury-containing aqueous waste streams at DOE sites. The work includes characterization of mercury-contaminated aqueous streams throughout DOE facilities and testing of selected technologies for treating those streams to remove mercury.

As a result of a technology assessment of methods for mercury removal from aqueous wastes (done in FY 1993), several mercury-selective and nonselective sorbents were identified. These sorbents include sulfur-impregnated, steam-activated carbon (nonselective); chelating resins with thiol functional group (selective); chelating resins with isothiorium functional group (selective); and molecular recognition resins (highly selective). Each sorbent will be evaluated by laboratory testing or literature review for its suitability for treating DOE aqueous waste.

The task is divided into three work elements:

1. Continue and extend assessment and characterization of mercury-contaminated aqueous streams at DOE facilities.
2. Investigate and test nonselective sulfur impregnated carbon adsorbents of three different DOE wastes.
3. Explore highly selective sorbents.

The desired result is engineering-scale data that can be used to design adsorption column processes for mercury-containing waste at DOE sites.

Technology Needs

EM Focus Area: mixed waste characterization, treatment, and disposal

New and improved separation methods are needed to treat a wide variety of mixed waste at many DOE facilities. Mixed waste contains sufficient radioactivity and toxic materials that must be handled both under the Atomic Energy Act and the Resource Conservation and Recovery Act. The volatile mercury must be removed from the aqueous stream before potential water evaporation and thermal treatment is implemented. For some solids, innovative methods such as selective leaching are being developed, and a need exists for secondary treatment or the regeneration of the leachate liquids.

The Idaho Chemical Processing Plant has more than 1.5 million gallons of sodium bearing acid waste stored, the Savannah River Plant has more than 30 million gallons of mercury-contaminated alkali aqueous waste, and ORNL has over 470,000 gallons of mercury-containing waste. Current mercury removal technology may be applied to these wastes; however, there is no detailed information on full-scale design and cost effectiveness. The proposed laboratory studies will produce equilibrium data and correlations, kinetic information, column testing, and information required to predict full-scale performance assessment and design of demonstrations or applications.

Accomplishments

Activities related to mercury removal from aqueous waste during FY 1993 and FY 1994 included a technology assessment for mercury removal from solid and aqueous waste, some characterization of DOE's mercury contaminated waste and selection of target wastes, and laboratory studies with a commercial sorbent and uncomplicated simulated aqueous waste. The results indicated that high levels of mercury in aqueous wastes can be removed to very low levels (<0.2 mg/L).

Benefits

The benefits of this activity include a DOE complex-wide inventory of mercury-containing waste and an assessment of available methods for mercury removal from aqueous liquids. This project will develop one or more advanced technologies for application to DOE aqueous wastes.

The objectives of this project are to provide detailed information to DOE to address the ESP's needs for Radionuclide and/or Toxic Component Removal and Aqueous Processing.

Technology applications developed and demonstrated in this task could be directly translated to private industry, because the work will involve the testing of commercial products. A subcontract will be initiated for the development of crown ether containing molecular recognition resins.

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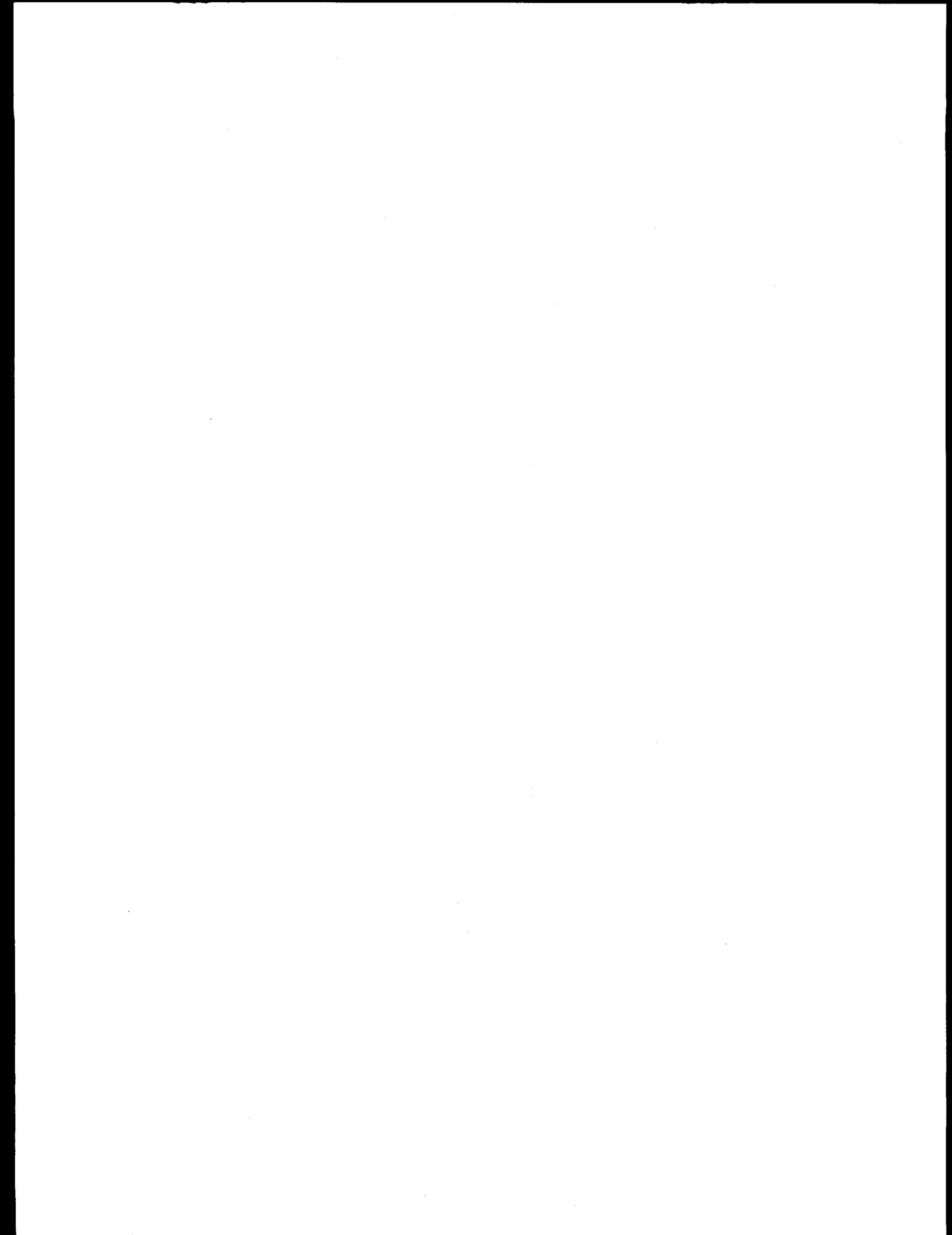
TTP Number OR153002-D

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Technetium Separation and Membrane Technologies

- ❑ Technetium and Nickel Ion Exchange Removal and Cobalt Dicarbollide Cesium Removal
- ❑ Selective Sorption of Technetium from Groundwater
- ❑ Alkaline-Side Technetium and Actinide Solvent Extraction Using Crown Ethers and Other Extractants
- ❑ Separation of Tritiated Water Using Composite Membranes
- ❑ Salt Splitting Using Ceramic Membranes



Technetium and Nickel Ion Exchange Removal and Cobalt Dicarbollide Cesium Removal

Presenter: Norm Schroeder, Los Alamos National Laboratory

Description

This work is divided into two subtasks: ion exchange for ^{99}Tc and nickel (both stable and ^{63}Ni) using conventional polymers, and development of new polymers based on cobalt dicarbollide for separating cesium and strontium.

For technetium separation, the approach being followed is development of a new baseline technology of ion exchange removal of technetium. For nickel removal the approach is to select readily available resins for the removal of nickel in a variety of waste streams.

We have investigated several anion-exchange resins. ReillexTM-HPQ resin, which contains the pyridinium functionality, has been shown to be superior in its stability towards radiation in acid media and nitric acid. It has very good sorption and selectivity properties for technetium. It has shown the most promise and is being tested as a replacement for the baseline DowexTM resin. A major technical hurdle for technetium separation technology is the development of a quick, safe eluent for the resin sorbed technetium. Such a new system would replace the standard eluent, 8 M nitric acid, which is viewed as unsafe for large processing and presents a large waste minimization problem.

A major objective for the nickel separation technology has been a screening of commercial resins for nickel removal in which the distribution coefficients of nickel on those resins are determined. The performance of the promising resins will be examined using simulants containing nickel.

The objective of investigating cobalt dicarbollide-based polymers is to develop a separations system for

removing cesium and strontium from alkaline and acidic high-level nuclear waste using derivatives of cobalt dicarbollide (CoB_2). Cobalt dicarbollide was first prepared in the United States in 1965, but its application as an extractant in nuclear waste treatment was investigated in the 1970s in the former Czechoslovakia and Soviet Union. Cobalt dicarbollide is an excellent hydrophobic anion for solvent extraction of cationic species from aqueous solutions; specifically, cesium and strontium can be extracted with very high selectivity and yield.

We are exploring the incorporation of cobalt dicarbollide (or its derivatives) into polymers to produce a material with the benefits of conventional ion exchange resins. This program builds on a considerable body of experimental and development work performed at the Nuclear Research Institute in R ez near Prague, Czech Republic, coupled with Los Alamos National Laboratory's expertise in the areas of radiochemistry and inorganic, organometallic, and polymer synthesis.

Technology Needs

EM Focus Area: high-level waste tank remediation

Technetium. Technetium is a major fission product resulting from nuclear reactors and by nuclear fission of plutonium. At the present rate of production, ^{99}Tc will reach 170,000 kg in nuclear waste form by the year 2000. Technetium, as TcO_4^- , is a very mobile species in the environment. Its long half-life (213,000 years) causes technetium to be a major contributor to a long-term risk assessment of stored nuclear waste. Additionally, incorporation of technetium into currently planned waste forms (glass) may pose chemical and engineering problems during vitrification.

Nickel. Certain tanks contain unusually high concentrations of nickel; ~178,000 kg of nickel containing about 300,000 Ci of ^{63}Ni . It may be necessary to remove nickel from the waste processing stream because of glass requirements.

Cobalt Dicarbolide. Because of the short half-lives of ^{137}Cs and ^{90}Sr (30.17 and 28.6 years, respectively), as well as their high yields from uranium or plutonium fission and high contribution to the radiation and thermal burden of defense and commercial nuclear waste, these isotopes constitute a major concern to the safety of stored bulk waste. Separation of these nuclides using a new polymer could provide new options for the immobilization, disposal, or use of cesium and strontium separated from tank waste.

Accomplishments

Technetium. The major accomplishment in FY 1994 was the development of a new technetium eluent for the ReillexTM-HPQ resin that is significantly more efficient than the standard eluent 8 M nitric acid. In addition, the reagent is safer and has a larger waste minimization factor. Where 8 M nitric acid required approximately 30 column volumes to remove the technetium from ReillexTM-HPQ resin, the new system only requires approximately ~3 column volumes (Figure 1).

We have now safely sorbed technetium containing simulant at $5 \times 10^{-5} \text{ M TcO}_4^-$ onto ReillexTM-HPQ resin, eluted the technetium from the column with the

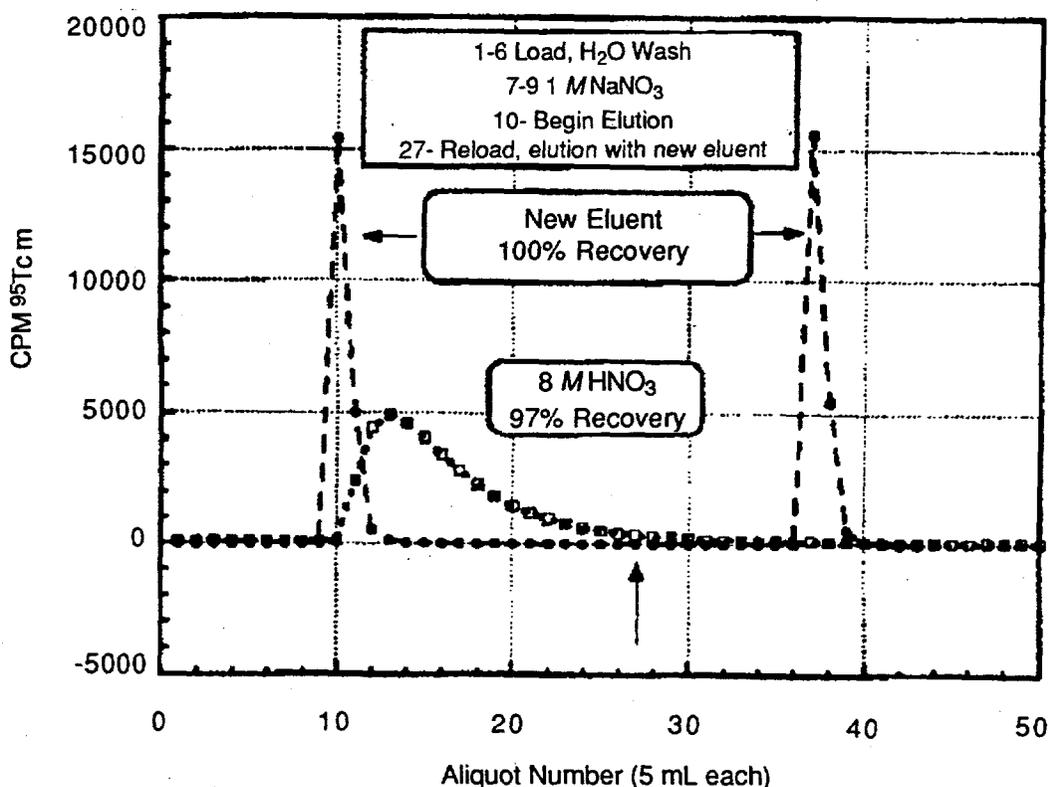


Figure 1. $7.5 \times 10^{-4} \text{ mmol TcO}_4^-$ loaded onto a 4.5-mL ReillexTM-HPQ column

new eluting system and repeated this cycle on the same column four times with no diminishing effects on resin performance for technetium.

Breakthrough experiments using a simulant containing $5 \times 10^{-5} M TcO_4^-$ indicate that the column (1 x 20 cm) will permit approximately 44 column volumes of this simulant before 1% of the technetium appears in the eluent. Technetium was eluted from this column with three column volumes of the new eluent.

Nickel. We have selected several resins that have indicated promise for nickel removal from studies in the open literature. These resins are commercially available. These resins have been evaluated by determining their K_d for nickel over a pH range where nickel remains in solution. A preliminary selection from among these resins has taken place.

Cobalt Dicarbollide. Cobalt dicarbollide has been grafted onto a variety of polymers, including poly-(chloromethyl)styrene (see Figure 2), and poly-benzimidazole (PBI). Preliminary measurements on the poly(sulfonato)styrene-cobalt dicarbollide are promising with respect to cesium and strontium uptake and selectivity (versus sodium), and we are proceeding with confirmatory measurements. We have also developed new synthetic methods for derivatizing cobalt dicarbollide by electrophilic and nucleophilic substitution routes. In this task, we have alkylated cobalt dicarbollide directly, producing complexes that are less soluble in base than the parent

dicarbollide. The reduced solubility of our derivatives improves their solvent separations performance by preventing loss of the dicarbollide extractant into the aqueous phase. We are exploiting this property by sorbing these derivatives into inorganic- and organic-based solid supports.

Both Czech and Russian groups report that B-chlorinated cobalt dicarbollides have better physical properties (i.e., radiation resistance) with equivalent or better separations capacity than the unsubstituted molecules; however chlorination has been difficult to achieve and control. We have prepared pure dichloro-cobalt dicarbollide via an easily scalable route and have found it to have comparable Cs^+ extraction properties to the unsubstituted species. Both the alkylated and chlorinated derivatives will be incorporated into poly(sulfonato) styrene for sequestering tests.

Benefits

The need for technetium to be removed from high-level waste and mixed waste arises from potential risk associated with currently proposed waste forms (i.e., glass). The reasons for partitioning technetium from high-level waste are that 1) the low-level waste storage form would have a lower long-term risk associated with it that would reduce the engineering requirements for containment, 2) technetium wouldn't add to the "noble metals problem," and would thereby

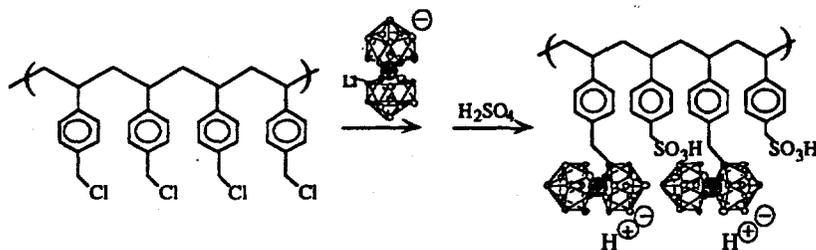


Figure 2. Incorporation of cobalt dicarbollide into 80% chloromethyl polystyrene/20% divinylbenzene with subsequent sulfonation to produce a hydrophilic cation exchange resin

reduce the number of melter failures and new melter purchases, and 3) efficient separation of technetium using a more stable resin or extractant would save nuclear waste processing by reducing downtime for resin or extractant replacement and would also enhance waste minimization efforts.

Development of a new polymer for cesium and strontium must removal could provide options for design of innovative separations processes.

Collaboration/Technology Transfer

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Selective Sorption of Technetium from Groundwater

Presenter: Gil Brown, Oak Ridge National Laboratory

Description

Researchers are developing an anion exchange resin that will selectively remove the radionuclide technetium, in the form of the pertechnetate anion (TcO_4^-), from groundwater, while leaving behind other interfering anions. A resin bed of this material will be used as part of a coupled treatment-recirculation system for the in situ treatment of technetium-contaminated groundwater.

The pertechnetate anion is strongly adsorbed on commercially available strong base ion exchange resins, but in view of the low concentration of technetium involved, enhanced selectivity is needed for the pertechnetate anion over other anions commonly found in groundwater, such as chloride, sulfate, and nitrate ions. New anion exchange resins are being prepared and evaluated that will be selective for the technetium species.

Technology Need

EM Focus Area: contaminant plume containment and remediation

Groundwater at DOE's Paducah and Portsmouth sites is contaminated by radionuclides. Regulations or permits do not allow the water to be removed from the ground, processed, and then returned to the ground; therefore, in situ contaminant removal methods are required. Technetium is the principal contaminant to be removed, and it is present at a concentration of about 25 ng/L.

The principal form of technetium in oxygenated groundwater is the TcO_4^- anion, which is quite mobile in underground aquifers. A related problem exists at other DOE sites where materials used to

process uranium or plutonium were disposed of or leaked out of containers into the ground. We will develop resins to adsorb technetium from groundwater that can be used with a remediation scheme involving recirculation of the water through a decontamination station within a contaminated aquifer.

Accomplishments

The resin will be made selective for technetium by using the basic principles of anion exchange. The pertechnetate anion is more organophilic than the other anions in groundwater, and a selective resin will be synthesized so that the strong base sites will prefer this anion. We will make modifications to the chemical and physical properties of existing polymeric resins to improve the ratio of distribution coefficients to favor TcO_4^- over other anions.

The resins will be synthesized at the University of Tennessee at Knoxville. During FY 1995, the resins will be synthesized and tested in an iterative fashion to produce a material that meets the requirements of the task. In following years we will test the selected resin in a bench-scale pilot plant using a treatment module that can be scaled up to practical flow rate. The technology will then be taken to a focus area.

Benefits

Commercially available anion exchange resins are not selective enough to remove the TcO_4^- ion in the presence of typical anions found in groundwater. The current baseline technology includes schemes that will reduce the technetium to a lower oxidation state that is insoluble or precipitates from solution. However, these method may not be effective if

oxygen in the aquifer or from other sources oxidizes the technetium back to the soluble TcO_4^- ion.

Using a resin to absorb the anion will have advantages over reductive schemes if the resin can be made selective. The general approach being employed here will use a module that takes technetium out of groundwater while maintaining the general concept of a treatment-recirculation scheme.

Collaboration/Technology Transfer

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TTP Number OR153002

Alkaline-Side Technetium and Actinide Solvent Extraction Using Crown Ethers and Other Extractants

Presenter: Bruce Moyer, Oak Ridge National Laboratory

Description

In this project, researchers are developing efficient solvent extraction and stripping processes using crown ethers or other extractants to remove radioactive contaminants from alkaline tank wastes. Two target radionuclides of concern during FY 1995 include ^{99}Tc and secondarily trivalent actinides.

Tank wastes at the Hanford Site, Oak Ridge National Laboratory (ORNL), and other DOE sites are typically strongly alkaline and contain actinides, technetium, and other fission products. Contaminants may be found in the aqueous supernatant under certain conditions, or they may be solubilized from the sludge during washing or leaching operations. Because they contain high concentrations of salts such as sodium nitrate, these waste streams pose special problems for current extraction technologies, which have historically focused mainly on acidic, low-salt aqueous streams.

Certain crown ethers are being investigated as potential solvent-extraction reagents for technetium removal because the high-salt condition promotes technetium extraction by these compounds and because an inexpensive water wash effects stripping of the technetium from the solvent.

Experimental efforts are currently driving toward tests with actual tank wastes, beginning with Melton Valley Storage Tank (MVST) waste at ORNL. Key issues of concern in FY 1995 include the most effective combination of solvent components, selectivity, and flowsheet design.

Tests are also being conducted to determine whether solvent-extraction methods can be used to remove

certain actinides from alkaline waste solutions containing complexants. Although most alkaline tank supernates contain negligible levels of actinides, complexants in the Hanford complexant concentrate (CC) wastes solubilize the actinides to significant levels. In the testing program, various classes of extractants are being surveyed, and promising candidate systems are being examined to determine the effect of various waste components (e.g., complexants) on extraction behavior.

Technology Needs

EM Focus Area: high-level waste tank remediation

Technetium in tank wastes at DOE sites poses long-term risks because of its long half-life and environmental mobility. In addition, its volatility during thermal treatment raises short-term safety issues connected with vitrification of the waste. Thus, processes are needed to remove technetium from the waste and to deal with its special handling and storage problems.

The actinide content in certain alkaline waste streams raises regulatory issues and will affect the fraction of the waste stream that must be directed to geologic storage. Economic concerns with the volume of waste committed to long-term storage thus require treatment options to reduce the actinide content of the alkaline waste.

Accomplishments

Results obtained to date demonstrate that certain crown ethers dissolved in a suitable diluent extract technetium as pertechnetate from high-nitrate-containing

alkaline waste simulants. Further, it has been demonstrated that the extracted technetium can be readily stripped with water. 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 best commercially available crown ether for technetium extraction and stripping was identified as 4',4'',(5'')di-t-butyl-dicyclohexane-18-crown-6 (abbreviated DtBuCH18C6). Several diluent/modifier combinations give good extraction and stripping performance in batch tests with DtBuCH18C6. Candidate solvents employing DtBuCH18C6 are ready for more critical tests involving actual waste in FY 1995. A number of new crown ethers have been synthesized to improve extraction efficiency and selectivity, one of which showed superior extraction and stripping ability to DtBuCH18C6.

Several classes of solvent-extraction systems were surveyed employing simple waste simulants containing europium(III) as a convenient surrogate for trivalent actinides. A class of extractants was identified as promising, and a particular commercial member of that class exhibits good performance, tolerating pH variation, high concentrations of poly(ethyleneamino)polycarboxylate complexants (e.g., EDTA, HEDTA, NTA), and the presence of aluminum and iron. In addition, it functions well at concentrations down to 0.01 M or less, while removing more than 95% of the Eu(III) in one contact, and can be employed in practical diluents.

Expected Progress

The knowledge gained thus far will be used to select the most promising candidate extraction systems and test them using actual tank waste. Tests with simulants will proceed toward multi-step extraction and stripping procedures, characterizing selectivity and stability under realistic conditions, and evaluating options for harvesting the extracted metals from the strip solutions.

Goals for improving the technetium solvent system include 1) achieving stronger technetium extraction, leading to a minimum required concentration of crown ether, 2) increasing selectivity over nitrate, leading to more effective stripping and ease of post-processing, 3) minimizing losses of solvent components to the aqueous phase, leading to improved economics and minimal effects on downstream operation, and 4) maximizing safety and environmental friendliness. The implementation strategy at this stage involves initiation of a possible future hot-cell demonstration of a counter-current system with Hanford tank waste and MVST under the Underground Storage Tank Integrated Demonstration.

As for actinide extraction, future progress will involve moving from the surrogate Eu(III) to Am(III) and Cm(III); tests with more realistic waste simulants and actual waste will be conducted to address many of the same issues in the technetium work.

Collaboration/Technology Transfer

An industrial partner could logically become involved in supplying crown ethers in large quantity at reasonable cost. Large-scale procedures for preparing the crown ethers may need to be worked out to bring costs down. In addition, industrial assistance may prove valuable in designing and fabricating the appropriate contacting equipment for pilot- and plant-scale use.

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TTP Number OR153002

Separation of Tritiated Water Using Composite Membranes

Presenters: Jim Duncan, Westinghouse Hanford Company; Dave Nelson, Pacific Northwest Laboratory

Description

Composite membranes are being developed that will remove tritium from contaminated water at DOE sites. Experience with membrane systems in industry indicates that they are inherently energy efficient. Furthermore, membrane technologies such as reverse-osmosis have been well developed for desalination and other industrial/municipal applications. Aromatic polyphosphazenes were chosen as the polymeric material for the membranes being investigated because they have excellent radiological, thermal, and chemical stability.

Technology Needs

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

Although processes are available to remove tritiated water (e.g., combined electrolysis-catalytic exchange), most require intensive capital or energy expenditures. Thus, the considered remediation of tritiated water (HTO) from DOE sites involves migration with time through geologic formations.

Although this is a logical approach because of tritium's short half-life (12.3 years), regulatory agencies have requested more emphasis on separation technology, because of the inherent uncertainties in geologic strata. Any defects would accelerate groundwater flow and allow a plume of tritiated water quicker access to a river and ultimately to human and animal ingestion.

Accomplishments

Poly(diphenoxy)phosphazene (PN_x) and the 10% carboxylated polymer $PN_x(10\% CO_2H)$ have been solvent cast on a nonwoven polyester support to form composite membranes. These membranes have shown promise with dead-end filtration (approximately 40% tritiated water depletion) in the permeate under laboratory conditions. In the laboratory, cross-flow experiments, using a small-scale cross-flow membrane module cell in a single-pass mode, with 10 pCi/mL HTO have currently obtained only 15% HTO depletion with the PN_x membranes.

The membrane test cell mimics the hydraulic flow regime of a spiral wound reverse-osmosis module. The pilot test cell and chiller/recirculator were moved and reassembled in the K-East Basin hot laboratory at the Hanford Site. The first two experiments were performed at room temperature (22°C) with both membrane types. Water in these experiments contained 2.8 $\mu\text{Ci/L}$ HTO. The PN_x provided 15% HTO depletion, while $PN_x(CO_2H)$ reduced the HTO content in the permeate by 27%.

The K-East Basin water was obtained after the new ion exchange module (IXM) was installed in the basin. However, there was enough ^{137}Cs present in the water samples to interfere with the ^3H scintillation count. Thus, the samples had to be distilled before tritium analysis. Although the presence of ^{137}Cs was not anticipated, it is interesting to note that the membrane decreased the ^{137}Cs by approximately 4.5 times (22% depletion).

The effect of membrane annealing was also investigated. Polyphosphazenes generally undergo a phase transition intermediate between the glass transition point and the true melting point. The phase transition point $T(l)$ apparently involves an ordering (straightening) of the polymer chain from its normal folded position. PN_x has a $T(l)$ near 160°C . However, we have found that exposure of the membrane to 110°C for 24 hours allows more consistent permeate depletion and increases the permeation rate.

Benefits

Water containing unacceptable tritium concentrations (above environmental release limits or drinking water standards) is released at DOE sites, including Hanford, Savannah River, and possibly Mound. One example involves the projected C-018H Treatment Facility at Hanford, 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 Hanford test wells contain tritium concentrations approaching $6 \times 10^7 \text{ pCi/L}$. The Tri-Party Agreement requires the tritiated water in the K-East Basin (spent nuclear fuel storage) be treated or relocated. No currently acceptable removal options exist for tritium remediation other than migration with time through geologic formations.

This research is the first step to develop a process that 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 at the Savannah River Site (SRS) 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 parts-per-million range as a result of neutron emission/capture (uranium fission). This technology would go far to mitigate tritiated water

as a point source pollutant for light water reactors. Also, there is a possibility that this membrane separation process would be of use in fusion development efforts.

The polyphosphazene membrane system may also be able to separate HTO from water in the mCi range, which could be of great benefit to the Tritium Aqueous Waste Recovery System developed by Mound Technologies and SRS, as well as other catalytic tritium recovery systems. The membrane system would concentrate HTO in streams too dilute for the catalytic system, this should provide an added amount of tritium for separation that would otherwise become part of a waste stream.

Future Work

Work in FY 1995 is focusing on materials and system development in continued collaboration with the Pacific Northwest Laboratory. Joint work during this phase will include preparation of larger amounts of the composite membrane, cross-flow tests at the K-East Basin, and material specifications for engineering design. Design and fabrication of a membrane module with ancillary tests at K-East Basin will be conducted in FY 1996 and FY 1997.

Collaboration/Technology Transfer

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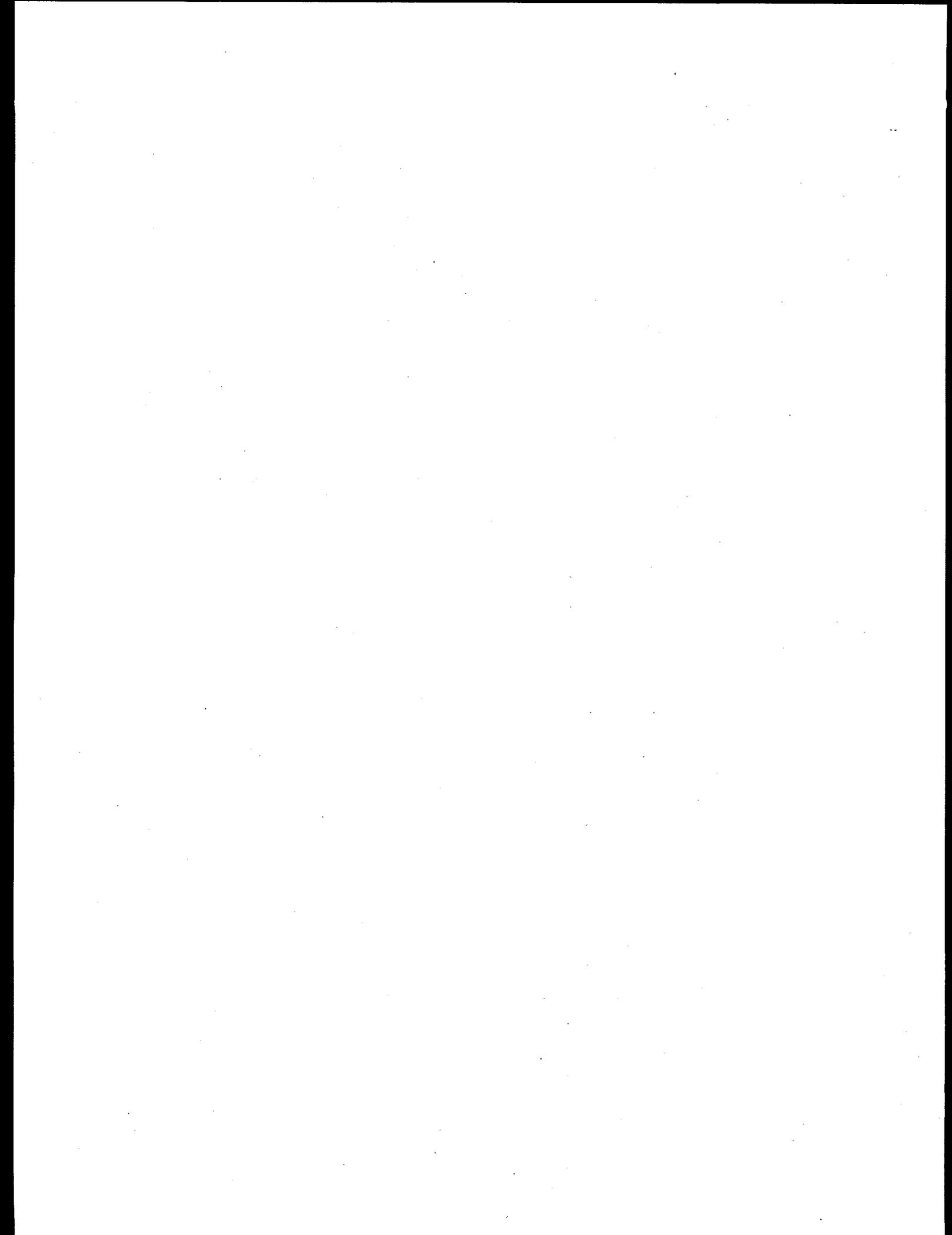
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Salt Splitting Using Ceramic Membranes

Presenter: Glenn Hollenberg, Pacific Northwest Laboratory

Description

The goal of this task is to develop and evaluate ceramic membranes for the electrochemical separation of sodium from solutions that also contain radioactive and nonradioactive elements. Near-term experimental work is focusing on the separation of sodium from caustic solutions containing aluminum ions.

Successful application of this technology to sodium-bearing supernates within tanks throughout the DOE complex is anticipated to 1) permit recycling of low-activity caustic soda, and 2) reduce the complexity of vitrification and disposal of the bulk of the tank waste.

The FY 1995 task consists of two major subtasks. The first task is to fabricate the ceramic membranes and electrochemical cells to demonstrate separation of sodium from aluminum ions in a caustic solution. The second task is to develop a technique for in situ demonstration of sodium/aluminum separation in FY 1996.

Technology Needs

EM Focus Area: high-level waste tank remediation

Researchers have been working toward separation of sodium from radioactive and nonradioactive sources for several years. The flow sheets for pretreatment of Hanford Site tank waste often included salt splitting as a method to recycle sodium and reduce low-level waste glass volume.

Recent trade studies indicate that the true value of caustic recycle is not in the reduced amount of chemicals purchased, but in the reduction of low-level waste glass that is produced. The amortized cost savings is predicted to be from \$425 million to \$595 million for

reducing low-level waste glass production as the result of recycling sodium during caustic washing.

Beyond these savings, even larger savings could be generated by separating sodium with low activity from the entire tank waste components. Without ^{99}Tc , ^{137}I , and ^{14}C , the offgas system for a low-level waste glass system could be reduced or eliminated, which could result in reducing as much as half of the plant costs. Without the high gamma emitters such as cesium, shielding requirements for the facility would also be reduced. The relatively small volume of low-sodium, low-level waste dominated by these radioactive species could be processed in a much smaller facility, reducing overall processing costs.

Accomplishments

This program began in FY 1995, and only preliminary work has been accomplished to date. A subcontract to the University of Utah was made to fabricate at least two NASICON membranes for insertion into electrochemical cells. In the cells, sodium will be separated from aluminum to form a sodium hydroxide mixture and a lower pH aluminum-bearing mixture. Chemical measurements as well as electrical measurements on the solution will be used to determine process performance and efficiency.

Benefits

The benefits of successfully implementing this technology include reduced or eliminated personnel exposure risk during recycle of sodium solutions during caustic leaching of tank sludges. In addition, significant cost reductions from recycling of this sodium

are possible. The potential for impacting the low-level waste vitrification process in terms of reduced radioactivity and offgas systems could present further reductions in the cost of tank waste disposal.

Collaboration/Technology Transfer

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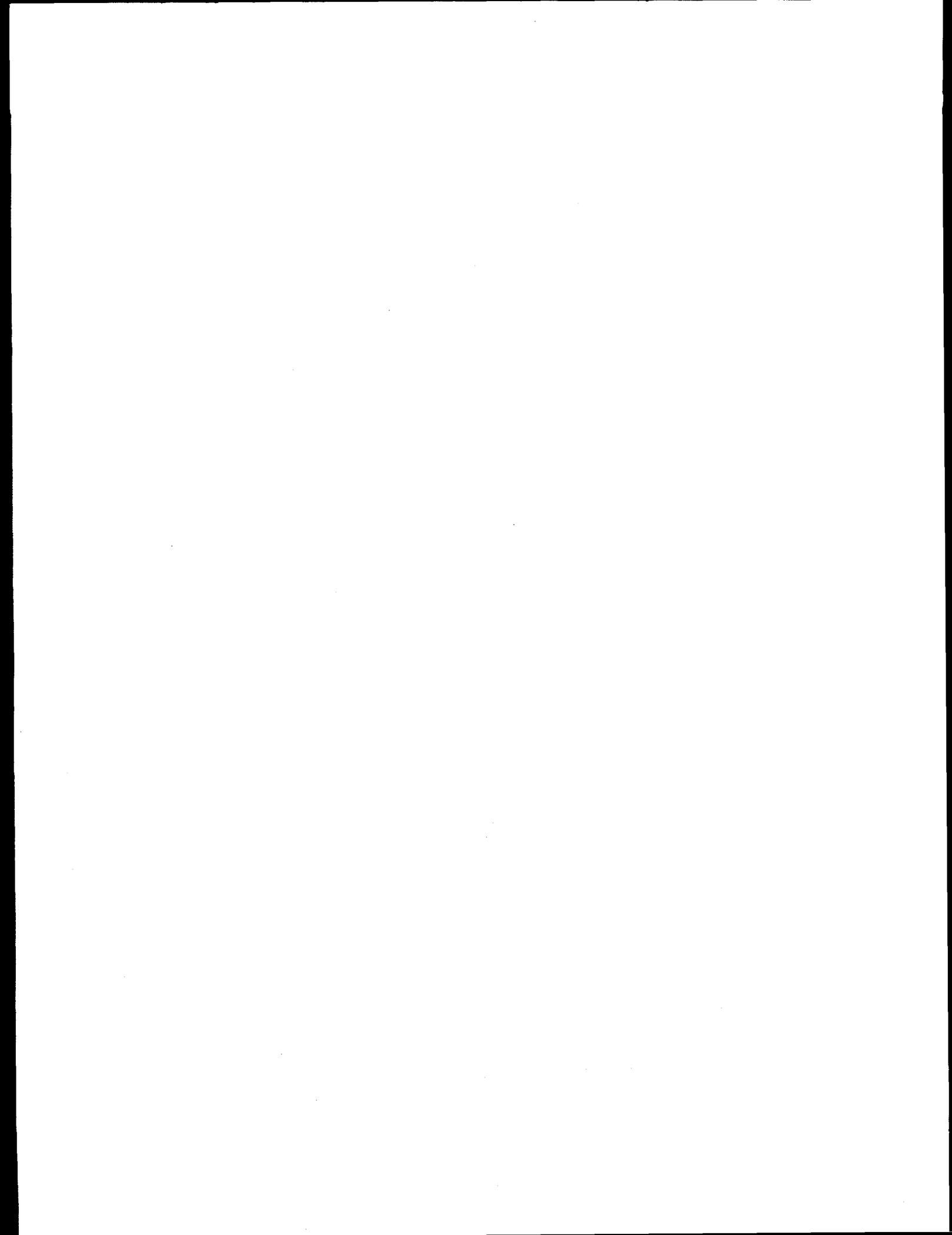
TTP Number RL353001

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"Salt Splitting of Sodium-Dominated Radioactive Waste Using Ceramic Membranes," presented at SPECTRUM 94, August 1994, Atlanta, Georgia, includes the basis for this effort.

Actinide Separations and New Polymers

- Advanced Integrated Solvent Extraction Systems
- Thermally Unstable Complexants/Phosphate Mineralization of Actinides
- Distillation Separation of Chloride Salts from Plutonium
- Water-Soluble Chelating Polymers for Removing Actinides from Waste Waters
- Derivatives of Natural Complexing Agents for Removing Plutonium from Waste Streams
- Removal and Recovery of Toxic Metal Ions from Aqueous Waste Streams Using Polymer Pendant Ligands



Advanced Integrated Solvent Extraction Systems

Presenter: Phil Horwitz, Argonne National Laboratory

Description

Advanced integrated solvent extraction (SX) systems are a series of novel solvent extraction 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. Each system is based on the use of new metal ion-specific extractants and aqueous complexants that are incorporated into new process flowsheets.

The purpose of the integrated SX processes is to minimize the quantity of waste that must be vitrified and buried in a deep geologic repository by producing raffinates and effluent streams that will meet the specifications of Class A low-level waste. By integrating or combining a number of SX processes into a single process, the number of times that the initial volume of waste must be handled and the amount of equipment and size of the facility required for chemical processing is significantly reduced.

The purpose of this task is twofold. The first portion is to develop and demonstrate a front-end, acid-side SX process to simultaneously extract cesium and strontium from acidic nitrate media. This involves the development of the process solvent, batch test on simulated waste solutions, and cold/hot tests performed in a continuous countercurrent mode using centrifugal contactors.

The Combined Cs-Sr Extraction Recovery Process has major advantages in a chemical processing scheme for high-level liquid waste treatment. Foremost among these is that by applying the process at the very beginning of chemical processing, the radiation level for all subsequent processing is significantly reduced. Another advantage is that the Cs-Sr fraction is non TRU. Therefore, this fraction will be low-level

waste after a few hundred years and may not have to be buried in a deep repository.

The second portion of this task is to develop a new actinide(III)/lanthanide(III) separation process using the TRUEX process solvent. This facet of the program involves the demonstration of the proof-of-principle and batch tests on simulated TRU-lanthanide fraction from the TRUEX process. The major advantage of this new process is that it does not introduce a new process solvent into a plant.

The sequence of processes is shown in Figure 1.

Several optional features of the separation sequence are shown in Figure 1. Uranium and sodium can be co-extracted with cesium and strontium or rejected to the raffinate and barium can be selectively scrubbed from the loaded Cs-Sr process solvent thus reducing weight of the Cs-Sr fraction.

Technology Needs

EM Focus Area: high-level waste tank remediation

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

Accomplishments

A new cesium-selective extractant has been developed that effectively removes cesium from acidic

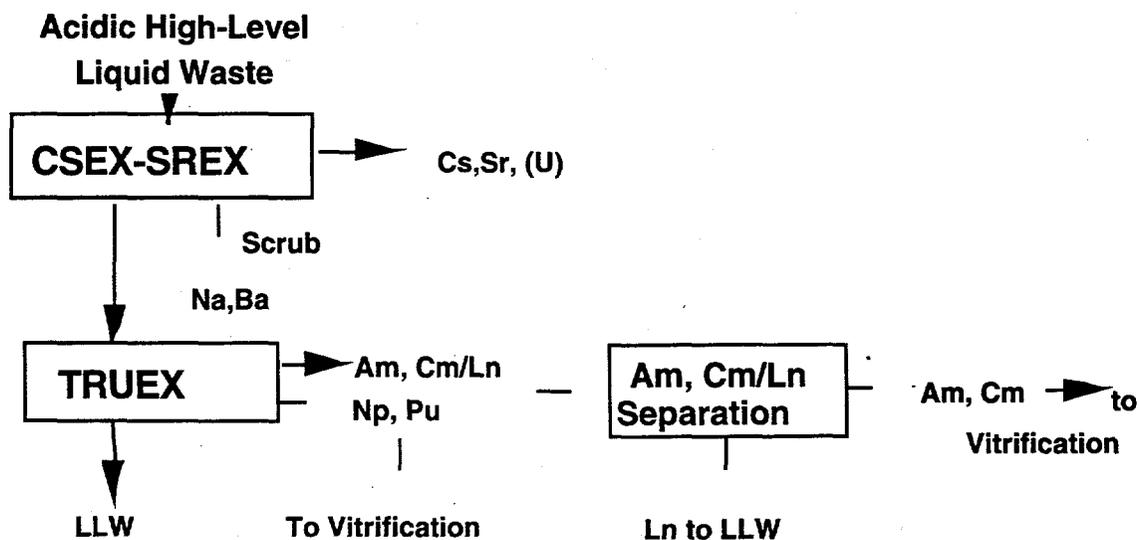


Figure 1. Advanced integrated solvent extraction systems

nitrate solutions containing HNO_3 concentrations in the range of 3 to 6 M. Cesium can be effectively back-extracted from the organic phase using 0.1 M HNO_3 . The CSEX process solvent has been combined with the SREX process solvent to form a Combined CSEX-SREX process solvent that can be used as a head-end treatment of acidic high-level nuclear waste streams. Both cesium and strontium are effectively stripped from the combined process solvent using dilute HNO_3 (e.g., 0.1 M).

A major feature of the Combined CSEX-SREX Process is that barium can be scrubbed from the organic phase and uranium can be co-extracted with strontium and cesium or rejected to the raffinate. Cold and hot test runs will be performed in a continuous mode using centrifugal contactors.

Benefits

The anticipated benefit of the advanced integrated solvent extraction systems is the minimization of high-

level waste that must be vitrified 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 systems should also reduce the cost of chemical pretreatment of waste by reducing the amount of equipment and size of the processing facility.

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TTP Number CH232005

Thermally Unstable Complexants (TUCS)/ Phosphate Mineralization of Actinides

Presenter: Ken Nash, Argonne National Laboratory

Description

The purpose of this project is to reduce the solubility of heavy metals (in particular, actinides) in groundwater and surface soils by adding a reagent designed to generate a precipitant (phosphate) that will enable formation of thermodynamically stable insoluble phosphate mineral phases. Converting the metal ion to a thermodynamically stable mineral form will reduce the ion's inherent solubility, and thus the potential for its environmental migration.

The objectives of this work are to 1) demonstrate the decomposition of a thermally unstable phosphonate complexant under representative groundwater conditions of E_h and pH, 2) demonstrate the formation of actinide phosphate solids under these conditions, 3) characterize the solids, 4) determine the leachability of actinides from the phosphate solids, and 5) perform preliminary testing with representative geomeedia.

A key component of this project is demonstration of decomposition of Thermally Unstable Complexants (TUCS) under groundwater conditions. TUCS, which constitute the preferred phosphate delivery system, are diphosphonic acid chelating agents designed to spontaneously decompose under suitable conditions. Because these reagents are strong complexers of polyvalent metal ions, they are expected to demonstrate high affinity for actinide ions, thus delivering the reagent selectively to the appropriate site.

Independent of the TUCS decomposition task, lanthanide and actinide phosphate solids will be prepared under conditions representative of the target environments. These materials will be characterized

by thermal analysis, X-ray diffraction, and EXAFS to determine their degree of crystallinity, state of hydration, and to identify the mineral form. This information is needed for accurate thermodynamic modeling of the system.

Actinide phosphate solids will then be tested for their leachability of the radioactive ions by contact with synthetic groundwater of appropriate pH, E_h , and chemical composition. Finally, solubility and crystallinity testing will be done on these solids on representative surfaces (mineral, organic, and metallic).

Technology Needs

EM Focus Area: contaminant plume containment and remediation

The phosphate mineralization concept has the potential to immobilize radioactive metal ions in the environment. It represents a safe, simple, and inexpensive alternative to pump-and-treat methods for groundwater decontamination or the installation of massive barriers to prevent nuclide migration (in situ grouting). The process could be applied to waste disposal sites (used either before or after burial), areas of accidental environmental contamination with radionuclides, or even to mill tailings piles.

Accomplishments

This is a new program for FY 1995; therefore, there are no accomplishments to report. Literature reports have described TUCS decomposition and phosphate mineralization.

Benefits

Because it involves only the application of inexpensive reagents, the method 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 contamination of the surrounding environment.

This process will eliminate the need for groundwater pumping or soil excavation to maximize the environmental (geochemical) stability of radionuclides in buried wastes. Immobilizing radionuclides in the subsurface environment can be accomplished by this method at low cost and without having to construct massive barriers to restrict groundwater flow (as would be done in underground grouting of wastes).

Because thermodynamically stable actinide phosphates will be formed, accurate prediction of radionuclide migration potential will be possible using 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.

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Distillation Separation of Chloride Salts from Plutonium

Presenter: Ed Garcia, Los Alamos National Laboratory

Description

Distillation separation of waste salts resulting from past pyrochemical processing of plutonium is being investigated by researchers at Los Alamos National Laboratory (LANL). This process has the potential of providing clean separation of the salt and the actinides with minimal amounts of secondary waste generation. The process could produce chloride salt that could be discarded as low-level waste and a concentrated actinide oxide powder that would be stored as special nuclear material 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 and oxychlorides. However, the plutonium content in these salts is usually in the 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 or oxychloride through an oxidation process.

A process developed at LANL that uses carbonate salts to act as an oxidant has proven very effective in converting all plutonium species into plutonium dioxide and can be ultimately combined with a distillation separation process.

Technology Needs

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

Residue and waste salts have resulted throughout the DOE complex from past pyrochemical processing of plutonium. The problem is especially acute at DOE's

Rocky Flats Plant, where ~20 metric tons of salt contain a large fraction of the plutonium inventory. These salts must be treated for disposal as waste.

Accomplishments

Testing of uncontaminated salts has established that sodium-potassium chloride salts can be distilled at a rate of hundreds of grams per hour. This meets the target rate of 3 kilograms of salt per 24-hour cycle. Information gained from these experiments was also used to design a prototype distillation apparatus that has been tested with uncontaminated salts and is ready to be installed in a plutonium glovebox.

Tests with plutonium-containing salts have established that the distillation process can purify salts down to the background contamination level of the glovebox. This background contamination level is coincidentally right at the low-level waste criterion. Most salts have been just slightly above the low-level waste cutoff, but some have qualified as low-level waste and proved the capability of the process to produce the desired product.

Benefits

The proposed salt distillation process, if successfully demonstrated, will be operationally simpler, generate less waste, and will be significantly lower in cost than the traditional baseline aqueous process. The high-payoff goal is the separation of the spent salts into actinide concentrates (special nuclear material-storable) and the chloride salts, which would be disposable as low-level waste.

By significantly reducing the amount of transuranic (TRU)-level waste produced, the salt distillation process would reduce offsite storage costs by a factor of

55:1, producing savings to DOE of about \$50 million. The costs of storing a drum of TRU-level waste at the Waste Isolation Pilot Plant are currently estimated to be \$10,000/drum. The wastes resulting from the salt distillation process are expected to be low-level waste, which has a disposal cost of about \$50/drum. The salt distillation process would also generate significantly fewer drums than would the aqueous process.

Consequently, the proposed process could reduce offsite disposal costs of the waste generated from processing the residues from the estimated \$55 million for the aqueous process to about \$1 million. It should be noted that these estimates assume that the

costs for the two processes are roughly equal; in fact, the aqueous process requires significantly more equipment.

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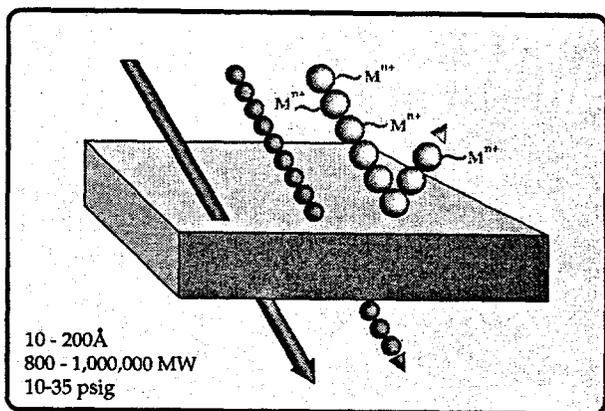
Water-Soluble Chelating Polymers for Removing Actinides from Waste Waters

Presenters: Gordon Jarvinen and Barb Smith, Los Alamos National Laboratory

Task Description

The application of water-soluble chelating polymers and ultrafiltration for the treatment of waste waters contaminated with low levels of Resource Conservation and Recovery Act (RCRA) and radioactive metal ions is a relatively new separations technology under development at Los Alamos National Laboratory (LANL).

The basis for metal ion separation, as shown in the figure, involves retaining metal ions bound to the chelating water-soluble polymer while smaller unbound species freely pass through the ultrafiltration membrane. The separation process allows the selective concentration of dilute solutions of metal ion contaminants. The reduced volume containing the polymer/metal ion complex can go directly to disposal or the metal ions can be recovered by pH adjustment and the polymer recycled for further metal ion recovery.



— Ions and Solvents ●● Micromolecules ○—Mⁿ⁺ Polymer Bound Metal Ions

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

An advantage of this separation technology for dilute metal ion solutions is in the rapid kinetics resulting from the homogeneity of the process. In addition, by careful selection of the water-soluble chelating polymer, selective metal ion complexation can be obtained. This project focuses on metal contaminants (especially plutonium and americium) in waste streams at the Plutonium Facility and the Waste Treatment Facility at LANL and at the Rocky Flats site. Applications at other DOE facilities are also apparent.

Reducing the concentration of a targeted metal ion to extremely low levels requires that the extraction system have a high binding strength for that ion. The system should also have a high selectivity for the target ion in the presence of competing metal ions. To this end, the work involves small-scale testing of the chelating polymer systems for the required selectivity and binding constants, followed by an engineering assessment at a larger scale to compare to competing separation technologies. Extraction systems under investigation include polyphosphonic acids, polyhydroxamic acids, and poly(acylpyrazolones).

Technology Needs

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

An urgent need exists for alternative technologies to treat radioactive waste water to meet regulatory limits, decrease disposal costs, and minimize waste. In particular, this technology would address the need to replace precipitation methods that generate large volumes of radioactive sludge at LANL and Rocky Flats, and reduce TRU wastes that will be generated from

processing the multitude of plutonium-contaminated residues that exist at DOE facilities.

More stringent discharge regulations are anticipated from DOE, the Environmental Protection Agency, and the states that will require considerably lower metal ion concentrations in the effluent water from facilities such as the LANL Waste Treatment Facility. This technology also applies to radionuclide-specific treatment of multiple aqueous waste streams at Hanford that would be generated by the cleanup of the storage tank wastes and various environmental contamination sites.

An important subset of the waste waters of concern are mixed wastes that contain radioisotopes and hazardous organics or toxic metals. Treatment of the mixed waste to reduce the amount of the toxic metals to levels below regulatory concern would generate separate waste streams that can be treated by other technologies better established from a regulatory viewpoint.

Accomplishments

A series of water-soluble polymers functionalized with phosphonic acid, acylpyrazolone, and hydroxamic acid chelating groups have been prepared for evaluation. The phosphonic acid and acylpyrazolone polymers were tested for metal ion retention at pH values from 1-6 and ionic strengths from 0.1 to 4.0 (sodium nitrate/nitric acid or sodium chloride/hydrochloric acid with tracer amounts of americium and plutonium).

The concentration of the polymer is generally in the range of 0.01 to 0.25 wt%, and the solution is filtered through an ultrafiltration membrane with a molecular weight cutoff of 10,000 daltons. Results of the studies indicate that both polymers have high retention (>99.9%) when working in the optimum pH range. Both polymers show higher retention as the nitrate concentrations are increased.

The phosphonic acid polymer has proven to be the best polymer for the complexation of americium and

plutonium with distribution values of 1 to 2 orders of magnitude higher than the acylpyrazolones. Preparation of the hydroxamic acid polymers is being optimized, and these materials have not been extensively evaluated for actinide retention.

The phosphonic acid polymer has been used in a series of polymer filtration runs with simulated and actual waste water representing the average composition of a major waste water stream treated at the LANL Waste Treatment Facility. Americium removal was measured after adjustment of the pH to 4 and addition of hydrofluoric acid to avoid silicate precipitation.

Americium retention was high even though the solution contains a variety of other metal ions and anions that could compete with the polymer, including iron, copper, calcium, magnesium, zinc, nickel, fluoride, phosphate, and chloride. Additions of ferric nitrate showed that iron(III) did not significantly depress the americium binding until the iron level reached about 1500 ppm. The high americium retention values indicate good selectivity for the target metal ion in the presence of a variety of potentially competing cations and anions that are commonly present in waste streams.

Additional projects at Los Alamos are evaluating the potential of the polymer filtration technology for other applications. As part of a project funded by the Industrial Waste Reduction Program of the DOE Office of Energy Efficiency and Renewable Energy, the polymer filtration technology is being evaluated for use in recycling metals from electroplating operations. A successful demonstration was conducted in May at Boeing Aerospace in Seattle to recover nickel and zinc from 150 gallons of plating bath rinse waters.

In October, staff involved in this ESP project took part in a polymer filtration workshop in Albuquerque for companies interested in commercializing this technology. The focus for this workshop was the metal finishing industry, particularly electroplating

waste waters, because that is the application where polymer filtration is closest to deployment. After the workshop, interested companies submitted a proposal for collaborating with Los Alamos on commercialization. These proposals are under review, and a partner or partners will be chosen in the near future. These companies will be potential partners in helping us apply the polymer filtration technology to the applications under development for ESP.

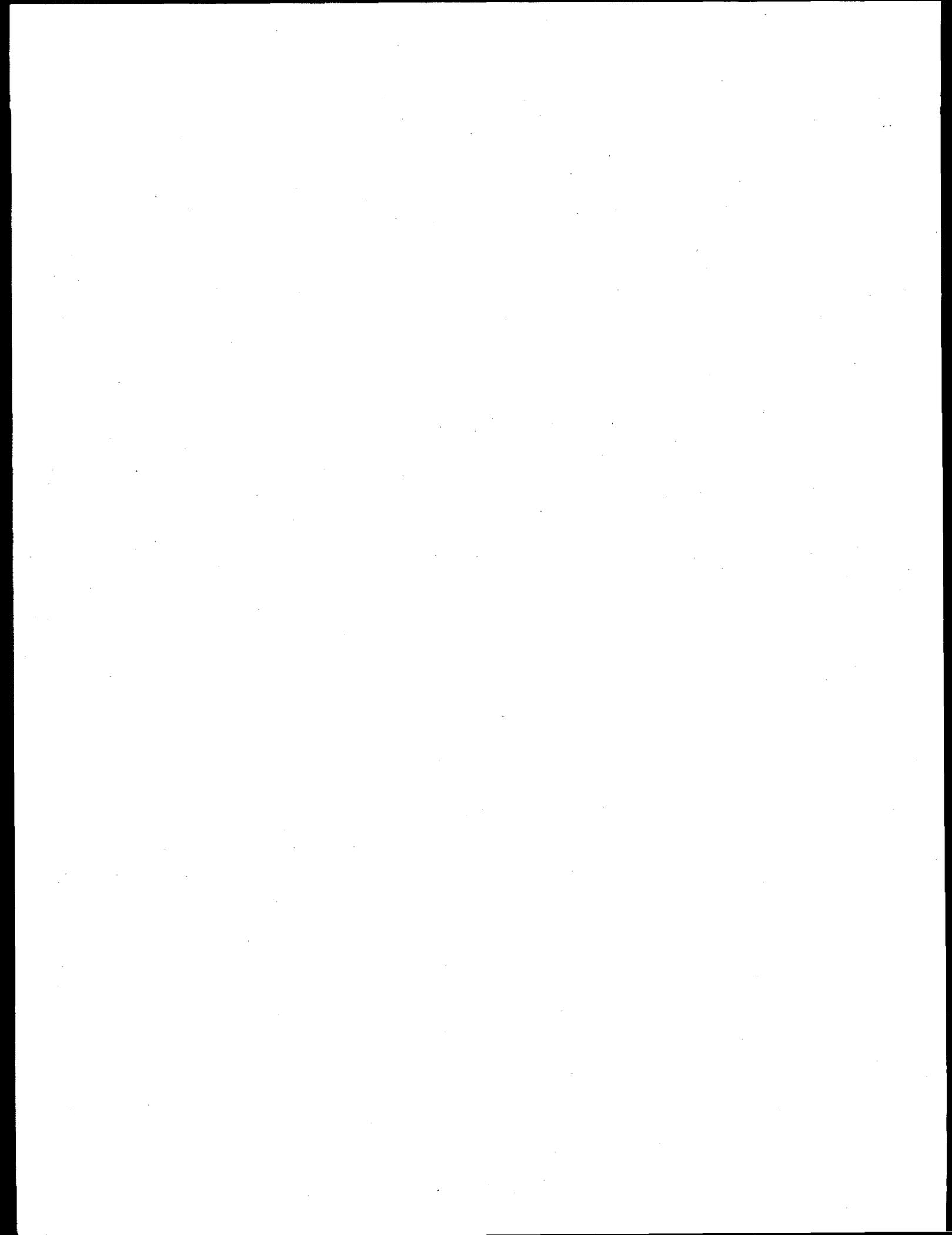
Work in the immediate future includes further evaluation of the polymers for americium and plutonium retention in the presence of other metal ions and anions to further refine the process parameters. Once made in large enough quantities, the hydroxamic acid polymer will undergo the same systematic evaluation.

The longer term goal is to set up an ultrafiltration unit at the LANL Plutonium Facility to demonstrate and

evaluate this technology for the removal of americium and plutonium that is currently sent to the waste treatment facility. This could result in large savings in capital and operating costs for the planned upgrade of the LANL Waste Treatment Facility.

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Derivatives of Natural Complexing Agents for Removing Plutonium from Waste Streams

Presenter: Don Whisenhunt, Lawrence Livermore National Laboratory

Description

Scientists are developing a separation system that uses a highly selective complexing agent derived from natural materials to remove plutonium (IV) (and perhaps other TRUs) from dilute solutions. The target solutions may vary in ionic strength, pH and competing ions depending on the exact flowsheet or waste stream.

In nature, bacteria and other microorganisms produce siderophores, low-molecular-weight multidentate iron chelators, to scavenge ferric ion from their environments. The main binding groups employed by siderophores are shown in Figure 1. These bidentate chelating groups are strong Lewis bases and show remarkable selectivity for Lewis acidic metal ions including Pu(IV) and Th(IV). Very selective sequestering agents can be synthesized by incorporating these chelating groups into multidentate ligands. These chelating groups can also be incorporated into molecules appropriate for use as liquid/liquid extractants or into insoluble polymers for use as solid/liquid extractants.

In this task, work is being conducted to

- synthesize liquid/liquid and solid/liquid extractants for the selective removal of actinide (IV) ions from dilute solution under varying conditions
- evaluate liquid/liquid and solid/liquid extractants for their ability to remove actinide (IV) ions from

simple solutions at various pH values, ionic strengths, and in the presence of competing ions

- test the engineered materials on actual waste and determine the economic feasibility of using such materials.

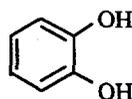
Technology Needs

EM Focus Areas: mixed-waste characterization, treatment, and disposal; landfill stabilization; facility transitioning, decommissioning, and final disposition

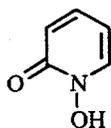
Efficient chemical processes for the selective removal of actinide elements from large volumes of dilute solutions are needed for the treatment and minimization of wastes at DOE sites. Before this objective can be accomplished, new metal complexing agents must first be developed and then modified for use in practical separation systems.

Accomplishments

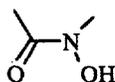
The solid/liquid extracting agents shown in Figure 2 have been synthesized and quickly remove Th(IV) from solution. Currently, the mmoles/g of sulfonic acid sites and mmoles/g of chelating group sites are being determined. The liquid/liquid extracting agents shown in Figure 3 have been synthesized. These materials, as well as others, will be tested for their efficiency in extracting actinide (IV) ions into organic solvents.



Catechol



1,2-Hydroxypyridinone



Hydroxamate

Figure 1. Binding groups employed by siderophores

Benefits

Development of highly selective and efficient ligands capable of complexing plutonium selectively from dilute solutions over a wide range of solution composition have the potential for drastically reducing the

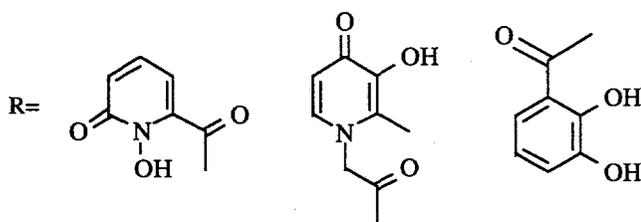
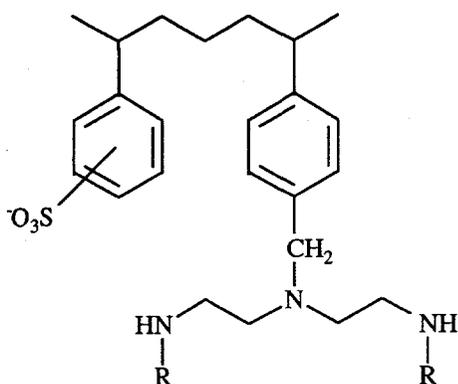
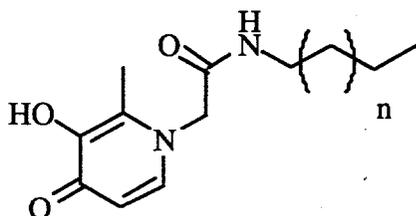


Figure 2. Chelating ion-exchange resins



$$n = 3, 5, 7, 15$$

Figure 3. Liquid/liquid extracting agents

volume of certain waste streams and thus reducing the cost of treatment or disposal. A cost reduction could be realized if the ligands 1) could be manufactured inexpensively, 2) exhibit resistance to harsh chemical and radiation environments, and 3) show high selectivity in the presence of large quantities of other metal ions.

Collaboration/Technology Transfer

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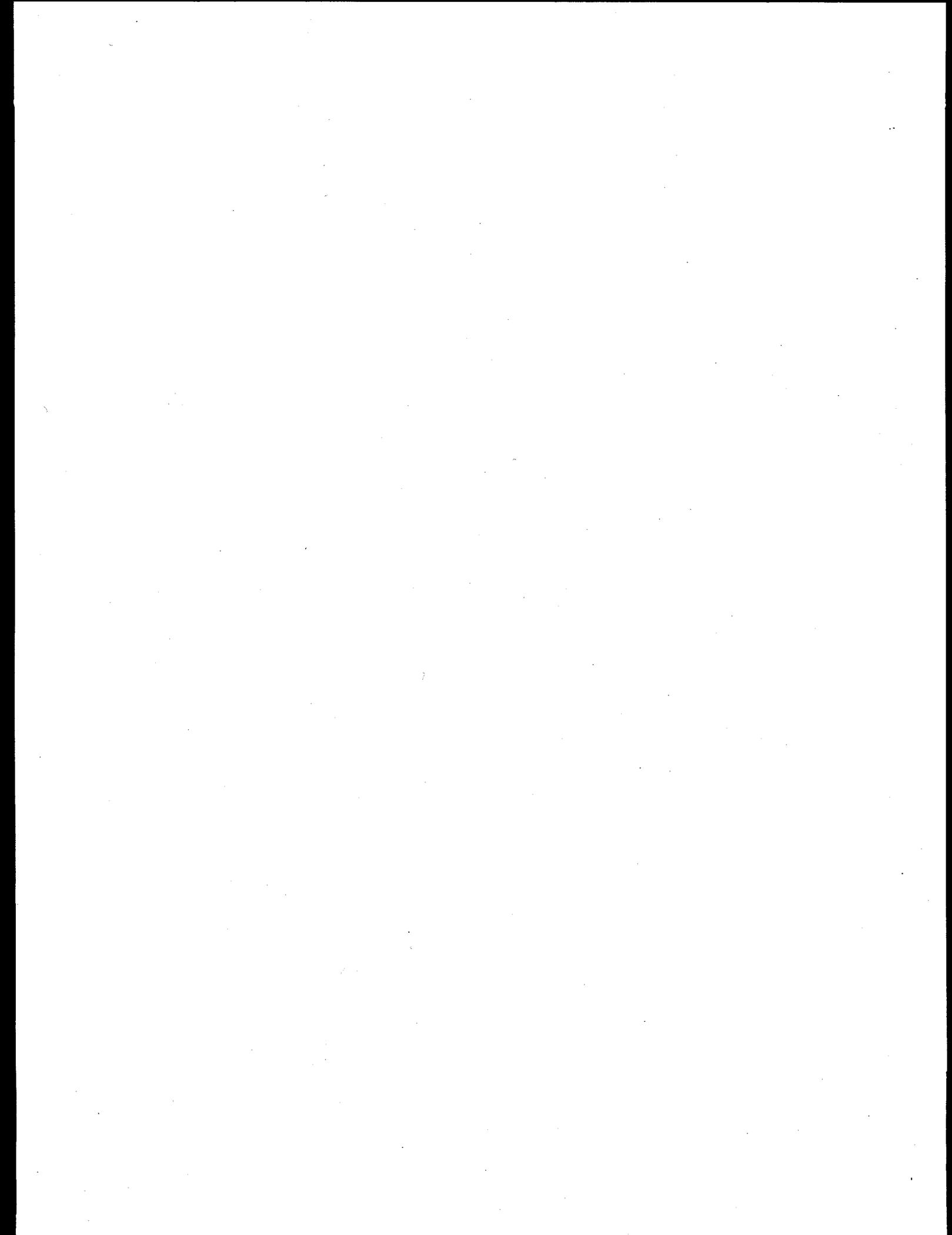
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Removal and Recovery of Toxic Metal Ions from Aqueous Waste Streams Using Polymer Pendant Ligands

Presenter: Dick Fish, Lawrence Berkeley Laboratory

Description

Researchers are investigating the use of polymer pendant ligand technology to remove and recover valuable or toxic metal ions from DOE waste streams. Polymer pendant ligands are organic ligands, bound to cross-linked, modified divinylbenzene-polystyrene beads, that can selectively complex metal ions. The metal ion removal step usually occurs through a complexation or ion exchange phenomena; therefore, the metal ions can be recovered readily and the beads reused.

The research objectives, which were achieved in FY 1995, include synthesizing selective polymer pendant ligands for removal and recovery of the metal ions of interest to the ESP goals, determining rates of both removal and recovery of these metal ions, and gaining industrial partners to implement the polymer pendant ligand technology that has been generated.

The studies have initially focused on the waste waters of the Berkeley Pit (pH = ~2.5) located in Butte, Montana, with emphasis on the following metal ions: Fe^{3+} , Al^{3+} , Cr^{3+} , Cu^{2+} , Zn^{2+} , Mn^{2+} , Mg^{2+} , Ni^{2+} , and Ag^+ . Because Fe^{3+} was dominant in the Berkeley Pit waste waters, special attention was placed on devising Fe^{3+} -selective polymer pendant ligands. Once iron is removed from solution, we will focus on removing and recovering the other economically important metal ions, such as Cu^{2+} , Zn^{2+} , Mn^{2+} , Mg^{2+} , and Al^{3+} .

Technology Needs

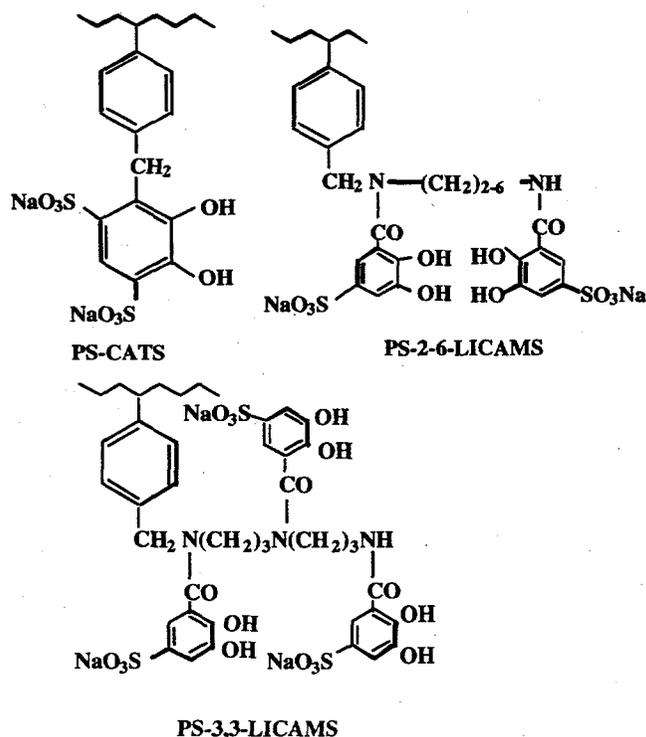
EM Focus Areas: contaminant plume containment and remediation; mixed-waste characterization, treatment, and disposal; facility transitioning, decommissioning, and final disposition

Removal and recovery of metal ions from aqueous waste streams will demand a considerable amount of

technology development. The cost effectiveness of the polymer pendant ligand technology would make it an excellent alternative to precipitation techniques.

Accomplishments

The first priority for this task is to develop selective polymer pendant ligands for iron (Fe^{3+}) removal and recovery, which was successfully accomplished at Lawrence Berkeley Laboratory through experimental studies. The polymer pendant catechol ligand derivatives, sulfonated catechol, sulfonated 2-6-LICAMS, and sulfonated 3,3-LICAMS were ideal biomimetic candidates for an Fe^{3+} -selective polymer pendant ligand, because they are structurally similar to biological ligands that selectively sequester Fe^{3+} (see structures for CATS, 2-6-LICAMS, and 3,3-LICAMS).



We have, therefore, been able to synthesize and evaluate the Fe^{3+} selectivity for the above-designated polymer pendant ligands. From pH values of 0.5 to 2.5, the following order for removal of Fe^{3+} from aqueous solution is as follows: **3,3-LICAMS >>>> CATS >> 2-6-LICAMS** with high capacities (0.8 to 1 mmol/g beads) and excellent removal kinetic rates ($2-4 \times 10^{-4} \text{ sec}^{-1}$). Recovery of Fe^{3+} from the beads and then reuse of the beads was readily accomplished using a 2N H_2SO_4 solution.

These important Fe^{3+} results show that divalent metal ions such as Cu^{2+} , Zn^{2+} , Mn^{2+} , Mg^{2+} , and Ni^{2+} can be removed using the **2-6-LICAMS** polymer pendant ligands; unfortunately, without selectivity to any particular divalent metal ion. In addition, the above-designated polymer pendant ligands also may be useful in addressing other DOE remediation problems; for example, selectively removing radionuclides such as Cs^+ and Sr^{2+} , and environmentally important metal ions such as Hg^{2+} and Pb^{2+} from aqueous solutions. Data are available on several new polymer pendant ligands that are highly selective to Ag^+ and Al^{3+} ; both of which are high economic value in any resource recovery process to be designed for remediation of the Berkeley Pit.

Finally, novel molecular recognition polymers for metal ions have been synthesized for selective removal and recovery of metal ions from aqueous waste solutions.

Collaboration/Technology Transfer

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TTP Number SF132001

Publications

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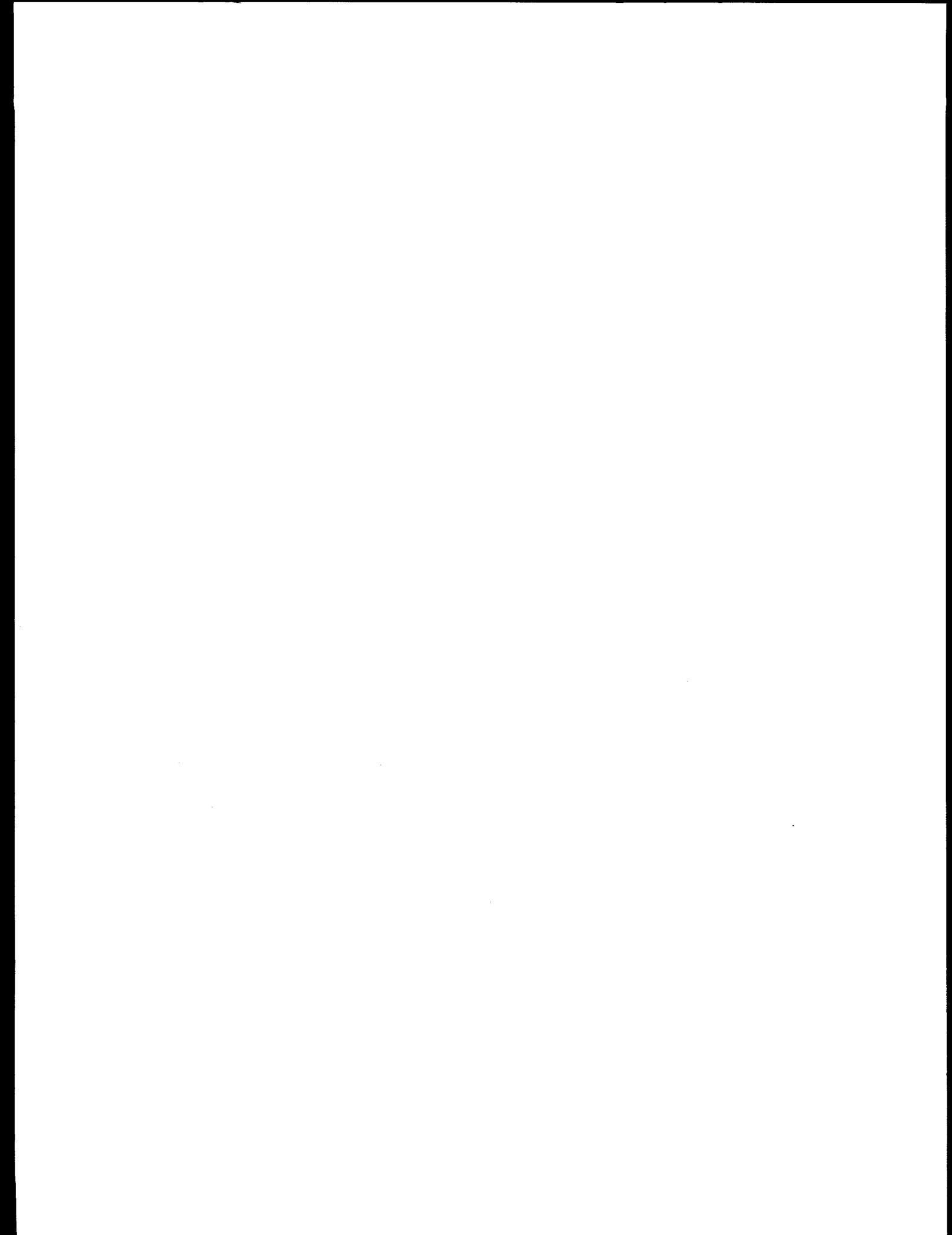
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Tank Waste Processing

- Sludge Washing and Dissolution of Melton Valley Storage Tank Waste
- Aluminum Removal from Washed Sludge
- Colloid Formation in Sludge Washing
- Institute of Physical Chemistry (Russian Academy of Sciences) Liaison and Chemistry of Calcination/Dissolution
- Selective Leaching of Tank Sludge by the ACT*DE*CON™ Waste
- Electrochemical Destruction of Nitrates and Organics



Sludge Washing and Dissolution of Melton Valley Storage Tank Waste

Presenter: Ed Beahm, Oak Ridge National Laboratory

Description

Researchers at Oak Ridge National Laboratory (ORNL) are conducting experimental and modeling research and development to support the comprehensive sludge/supernatant processing flowsheet work conducted for EM-50's Underground Storage Tank Integrated Demonstration.

A major emphasis here is on Hanford tank waste disposal involving dissolution of the sludge before pre-treatment. Understanding the compositions of the dissolving solutions is important for planning further treatment strategies, such as the various extraction options and vitrification. Actual wastes from the Melton Valley Storage Tanks (MVST) at ORNL are used for experiments on sludge washing and dissolution.

Technology Needs

EM Focus Area: high-level waste tank remediation

This work will help delineate and predict 1) the distribution of chemical species between aqueous solutions and solids, and 2) potential problems resulting from chemical interactions that could result in process difficulties or safety concerns.

One possible treatment of tank waste sludge could involve leaching or dissolution using acid. The chemical interactions both within the sludge and between the sludge and process chemicals must be better understood to plan subsequent treatment strategies, such as vitrification, TRUEX, or any of the other high-level waste separation technologies.

Accomplishments

The combination of tests on actual MVST sludge, tests on sludge simulants, and modeling of sludge chemistry provides a broad evaluation of sludge and supernatant processing useful for both MVST and Hanford tank wastes. Frequent discussions between ORNL and Pacific Northwest Laboratory staff help ensure that results of these studies apply to sludge treatment at both sites. Two letter reports on thermodynamic modeling and initial sludge tests have been issued.

Treatment of waste tank sludge will most likely begin with washing, followed by basic or acidic leaching. Both acidic and basic leaching of MVST sludge are being evaluated by actual sludge tests and by modeling. Acidic leaching tests have shown that the distribution of species between the aqueous phase and solids can be altered by changing the pH of the leachate. However, some species, notably cesium and plutonium, are difficult to dissolve, even in acid concentrations up to 6 M. In addition, the acid leaching studies have demonstrated that gels or particulate solids form in leachates that are left undisturbed for time periods of up to several months.

Caustic leaching at room temperature with 3 M NaOH and 6 M NaOH was not very effective in removing metals from the sludge solids. Only ~5% of the aluminum was leached, and very little phosphate dissolved in caustic solution. MVST sludge contains relatively high concentrations of calcium that likely played a part in retarding dissolution of aluminum and phosphate.

Benefits

The management of approximately 400,000 gallons of highly radioactive alkaline nitrate wastes at ORNL can benefit from washing to partition fission products (e.g., cesium and strontium) from the resulting wastes. This smaller volume of partitioned actinides could be transferred to existing waste processing facilities at other sites for vitrification, thus eliminating the need for MVST transuranic fixation at ORNL. The resulting low-level waste can then be handled either onsite or in a low-level waste repository instead of having to go to the Waste Isolation Pilot Plant.

The technologies tested in this project can potentially benefit all DOE sites that must manage alkaline nitrate waste liquids/sludges. A key example of this is Hanford tank wastes. If vitrified without separation, approximately 200,000 canisters of waste would be generated at great cost. Separations technology can reduce the number of canisters substantially, with

most of the waste volume becoming low-level waste that is more easily and inexpensively managed via onsite disposal. This could reduce the amount of waste sent to a repository. This technology also applies to meeting regulatory commitments at Hanford.

Collaboration/Technology Transfer

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Aluminum Removal from Washed Sludge

Presenter: Zane Egan, Oak Ridge National Laboratory

Description

In this project, methods are being developed to reduce the volume of storage tank sludge to be treated by removing the aluminum and other nonradioactive components. Successful caustic dissolution and separation of aluminum and other components from solid tank waste could result in a simple process for substantially reducing the amount of waste requiring valuable repository space.

Specific tasks include 1) preparation and testing of surrogate sludges; 2) measurement of the caustic dissolution behavior of selected sludge components; 3) optimization of the time, temperature, and NaOH concentration for dissolution of selected sludge components; 4) testing the caustic dissolution behavior of an actual sludge sample; and 5) evaluation of the feasibility of recovering the soluble components and recycling the caustic solution.

Because of the difficulties in obtaining and working with actual radioactive waste sludge, several Hanford sludge surrogates are used in these studies. Samples of dried synthetic sludges are washed at different temperatures and for varying times with NaOH solutions ranging from 0.1 M to 6.0 M. Samples are analyzed for various elements, including aluminum, chromium, zinc, bismuth, cerium, strontium, zirconium, iron, uranium, and thorium.

Technology Needs

EM Focus Area: high-level waste tank remediation

Storage tank sludge generally contains mixtures of hydrated metal oxides, hydroxides, and phosphates. Separation technology is the primary means to reduce

the large volumes of storage tank waste to smaller volumes of more concentrated and well-defined waste.

Aluminum and several other waste constituents are amphoteric. Consequently, in addition to forming insoluble hydroxides and oxides, these materials also have the potential of forming soluble chemical species under highly caustic conditions. There is increasing emphasis on removing these materials through "enhanced sludge washing." If these materials could be preferentially solubilized, then the volume of the remaining radioactive waste to be treated and/or stored would be significantly reduced.

Accomplishments

In initial sludge surrogate studies, aluminum, chromium, and zinc showed the highest solubility in NaOH solutions. Cerium and zirconium were the least soluble of the elements tested. The removal of iron and bismuth approached 2%, but the rest of the elements studied showed <1% removal. The amount of aluminum removed from the sludge surrogates increased as the NaOH concentration increased from 0.1 to 6.0 M. Sequential washing of the sludge surrogate with 3.0 M NaOH removed 84% of the aluminum, 39% of the chromium, and 65% of the zinc.

Surrogate sludges containing uranium and thorium were also prepared, and their dissolution behavior was characterized. In one of the sludges the uranium was precipitated as a hydrous oxide. In another sludge, the uranium, along with calcium and magnesium, were precipitated as both hydrous oxides and phosphates. In addition, samples of the sludges were "aged" by refluxing them at 100°C for several days in an aqueous solution at pH 10.

Kinetic data at 70°C showed that the dissolution of chromium, iron, uranium, bismuth, and calcium increased with time. Larger amounts of each of these elements, as well as aluminum, were removed at 70°C compared to room temperature.

Initial results were obtained on the caustic dissolution of an actual sludge sample from Oak Ridge National Laboratory Melton Valley Storage Tank (MVST) W-25. As with the Hanford surrogate sludges, the most leachable elements were aluminum, chromium, and zinc. However, the percentage removal was much less from the MVST W-25 sample.

Preparation and testing of additional sludge surrogates is continuing. These tests will be used to measure the dissolution behavior of additional components such as silicon and phosphates. Studies on MVST W-25 sludge will be extended, and efforts are also being made to obtain samples of Hanford sludge for testing.

Benefits

The technology developed in this project would be of potential benefit to several DOE sites. Separating the nonradioactive elements would result in a much smaller amount of solid tank waste to be managed or handled in downstream processing, and in a substantial reduction in the amount of waste requiring valuable repository space.

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Colloid Formation in Sludge Washing

Presenter: Walt Bond, Oak Ridge National Laboratory

Description

Experimental research and development is under way to assess the potential for formation and stabilization of the bulk sludge materials as colloids during sludge washing of Hanford Site and Melton Valley Storage Tank (MVST) waste. Colloidal dispersions of the bulk sludge materials will carry plutonium and americium as their hydrous oxides by sorption on or aggregation with the major hydrous oxide (aluminum, chromium, zirconium, bismuth, etc.) constituents of the sludge. Therefore, a potential exists for formation of additional transuranic (TRU) wastes.

Minor components in the tank wastes such as silicic acid and organics will be evaluated by experiment because they can act as stabilizers for hydrous oxides. The aim of the washing is to minimize the amount of TRU wastes by displacing the interstitial aqueous salt solution from the sludge and by dissolving the inert components such as aluminum hydroxide. Experimental tests are currently conducted with "cold" surrogate waste. Hot-cell tests with actual waste sludges from MVST and from currently generated TRU wastes at Oak Ridge National Laboratory's (ORNL's) Radiochemical Engineering and Development Center are planned for FY 1995.

Technology Needs

EM Focus Area: high-level waste tank remediation

Sludge washing is required to minimize the volume of TRU wastes. It is necessary to determine factors that promote stability of sludge colloids so that these conditions can be avoided in processing tank sludges. Colloids, if formed, could contaminate supernates

with TRU elements because colloids are often not easily filterable nor easily coagulated.

Accomplishments

Cold laboratory investigations were carried out at ORNL and at Georgia Institute of Technology on the preparation of hydrous alumina colloidal particles by precipitation techniques. The type of hydrous, gelatinous aluminas that form as a function of pH and sodium salt concentrations were investigated. Scoping tests are being completed to determine the most important parameters which include pH, temperature, aging time, and type and concentration of sodium salts present.

Characterization of the hydrous aluminas produced include visual observation of their appearance, relative volumes, pH and conductivity of precipitate mother liquors, particle size, surface charge, and their flocculation and filtration behavior.

Stable colloidal solutions could be produced after precipitates were washed with as few as 5 equal volume portions of demineralized water. The colloids have remained dispersed in the liquid phase for several days. Electrolyte concentrations at which the colloids formed were determined by chemical analysis.

Initial studies indicate the rare earth element, neodymium, will serve nicely as an actinide "stand in" for americium and that thorium serves to emulate plutonium in cold studies. Neodymium is readily detected by spectrophotometric means whereas thorium is determined radiometrically. We have demonstrated the codispersion of neodymium and aluminum oxide and the codispersion of thorium and aluminum oxide.

Benefits

Benefits of this technology include gathering data that will aid in design of a successful process for washing tank sludges. Formation of colloids during washing could be avoided and eliminate the necessity of add-on systems to coagulate and collect them as solids.

Proposed Future Activities

Future work will emphasize hot tests with actual MVST and spiked surrogate wastes that are based on sludge washing parameters established in previous cold tests with surrogates. We also expect to conduct tests on aluminum decladding wastes, and acid dissolution residues from operations at ORNL's Radiological Development and Engineering Center. These wastes closely mimic those generated at Hanford in their fuel reprocessing and plutonium recovery in terms of possible silicic acid stabilization of colloids and in the nature of the hydrous aluminum hydroxide precipitates produced.

Collectively, the tests with the various types of wastes will permit defining operational windows and/or pretreatment options that will eliminate colloidal losses of actinides. Some cold studies continue in support of these hot tests to more firmly define the chemical and physical mechanisms involved in colloidal formation and its avoidance. Most of the cold work in support of the hot cell efforts will be conducted at Georgia Tech by subcontract.

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TTP Number OR132012

Institute of Physical Chemistry (Russian Academy of Sciences) Liaison and Chemistry of Calcination/Dissolution

Presenter: Cal Delegard, Westinghouse Hanford Company

Description

This program has two facets: it 1) provides a technical liaison for research being conducted at the Institute of Physical Chemistry, Russian Academy of Sciences, (IPC/RAS), and 2) conducts laboratory investigations of the chemistry of calcination/dissolution pretreatment of Hanford Site tank waste.

The IPC/RAS is supported by ESP international programs efforts to investigate the chemistry of transuranic (TRU) elements; primarily neptunium, plutonium, and americium) and technetium in alkaline media. This work is important because the radioactive wastes present in the tank wastes at DOE sites (Hanford, Savannah River and Oak Ridge National Laboratory) are stored in alkali, and the chemistry of TRU and technetium in this system is not well developed. Four areas are currently under investigation:

- solubilities of neptunium, plutonium, americium, and technetium as functions of oxidation states and hydroxide concentration
- reactions and reagents suitable for co-precipitating neptunium, plutonium, and americium
- alpha and gamma radiolysis reactions of neptunium, plutonium, americium, and technetium under the influence of nitrate and nitrite
- redox reactions and reagents for neptunium, plutonium, americium, and technetium.

The technical liaison provides information to the IPC/RAS on the Hanford Site waste system, helps define and refine the work scope, and communicates the IPC/RAS results to scientists and engineers in the DOE complex.

Calcination/dissolution (C/D) treatment of Hanford Site tank waste is being investigated as an alternative to the reference in-tank dissolution and sludge washing pretreatment approach. The program of C/D process chemistry development involves lab-scale tests of C/D with genuine Hanford Site wastes, comparison of C/D test results with corresponding results from tests on the reference (alkaline washing) process approach, investigation of neptunium and plutonium speciation under C/D processing, determination of techniques for neptunium and plutonium removal from solution, and support of engineering laboratory-scale plasma calcination tests conducted under Tank Waste Remediation System (TWRS) support at the University of Idaho.

Technology Needs

EM Focus Area: high-level waste tank remediation

Current knowledge of the chemistry of the TRU and technetium in alkaline media does not reliably predict the behavior and distribution (to solid or solution phases) of the TRU and technetium under existing tank conditions and particularly under projected alkaline waste processing options.

This knowledge is vital because isolation of the TRU and technetium to a low-volume high-level waste fraction is the goal of Hanford Site waste retrieval, processing, and immobilization. The technical liaison will focus the investigations towards areas of application in the DOE complex and disseminate the data from the studies of the fundamental chemistry of TRU and technetium in alkaline media being conducted by the IPC/RAS.

Wastes retrieved from Hanford Site waste tanks will need to be pretreated before their immobilization as separate low- and high-level forms. In-tank water and alkaline washing (using added sodium hydroxide) is the reference method to achieve the desired low- and high-level partition. Calcination/dissolution is a waste pretreatment strategy that is attractive and provides an alternative should the reference technology be found inadequate or unacceptable. In contrast to the reference approach, the C/D process achieves an efficient low- and high-level waste partition that requires no additional sodium hydroxide. The C/D approach also eliminates the separate steps for organic, nitrate, and nitrite destruction that will likely be required for pretreatment and immobilization.

Accomplishments

With modest ESP support, the IPC/RAS provided an extensive technical literature review of the chemistry of TRU and technetium chemistry in alkaline media in FY 1994. The liaison funded the visit of Professor V. F. Peretrukhin to the Hanford Site in March 1994 to describe the results of the technical review.

Laboratory and engineering investigations of C/D pretreatment have been conducted with ESP, TWRS, and Underground Storage Tank Integrated Demonstration support since FY 1992. Early work was motivated by tank safety concerns and focused on organic destruction for the Initial Pretreatment Module. Subsequent work revealed the utility of C/D as a comprehensive pretreatment technology.

Chemistry and engineering development included extensive lab testing of C/D using both simulant and genuine Hanford Site tank waste, performance testing of materials of construction, development of a C/D residue treatment technology (supported by ESP in FY 1993 and FY 1994), two 20%-scale demonstrations of plasma-arc calcination, and preparation of a preliminary C/D process flowsheet.

Benefits

A strong technical liaison is being established with the IPC/RAS to maximize the benefit of the IPC/RAS research for DOE site applications. The technical liaison helps focus and prioritize the work in light of the evolving DOE complex needs. The liaison disseminates the research results to the technical community through contractor and DOE publications and aids in administrative tasks, freeing the IPC/RAS for the essential investigations.

The C/D process is an alternative to the reference pretreatment processing technology, water- and alkaline-washing. In addition to the intrinsic merits of C/D processing with respect to the reference technology, further development of C/D chemistry maintains a viable alternative should the reference technology be proven inadequate or unacceptable to meet performance goals.

To date, laboratory investigations with genuine wastes have shown C/D achieves the desired solubilization of aluminum, chromium, and phosphate phases. Processing by C/D also destroys organic components (that compromise strontium and americium partitioning to the high-level fraction, cause gassing problems in glass melters, and contribute to tank safety concerns) and eliminates foaming and NO_x abatement problems at the glass melter by decomposing nitrate and nitrite to benign nitrogen and oxygen offgases before melting.

Collaboration/Technology Transfer

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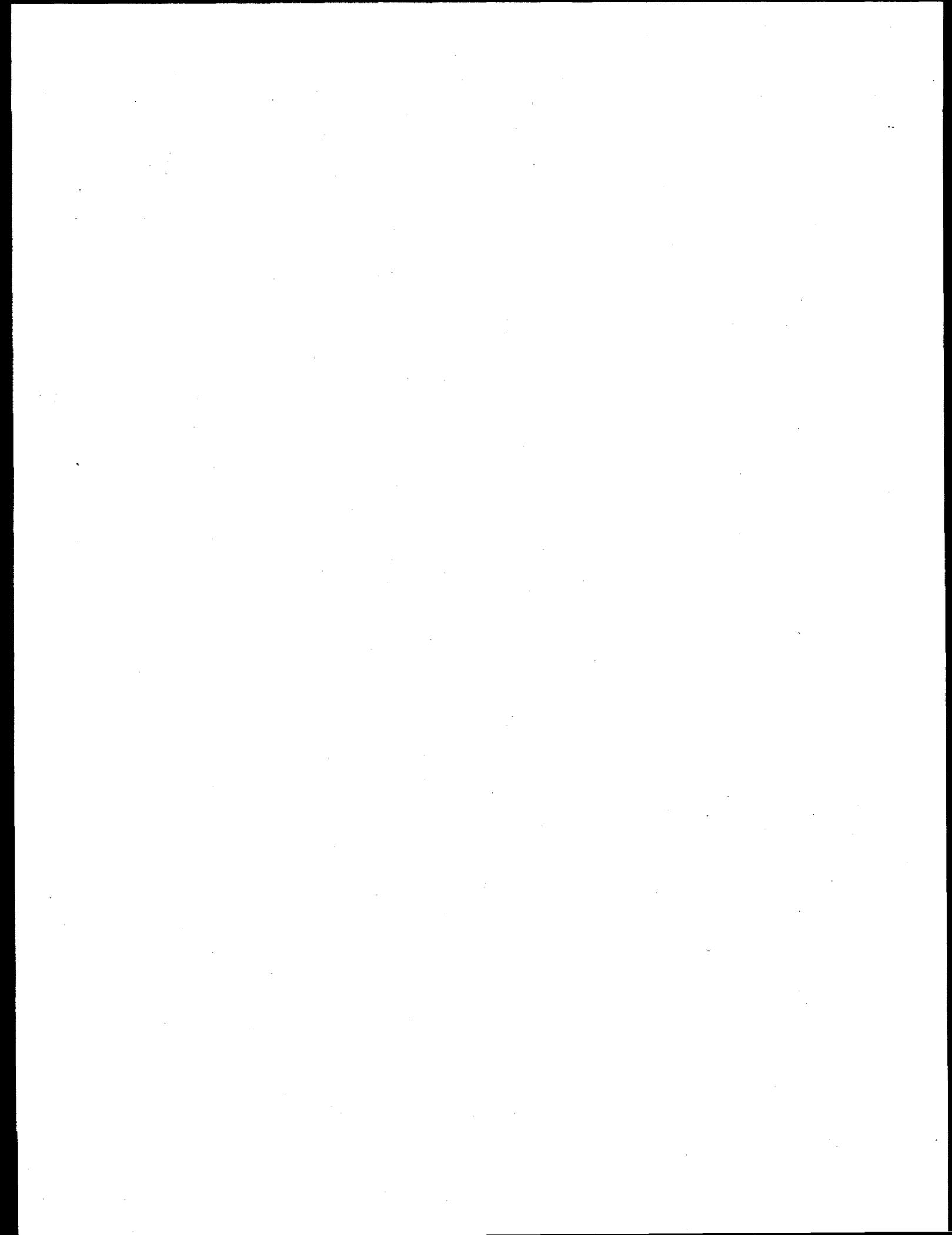
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Selective Leaching of Tank Sludge Using the ACT*DE*CON™ Process

Presenter: Mike Dunn, Bradtec

Description

Pacific Northwest Laboratory researchers are assessing the ability of Bradtec's proprietary ACT*DE*CON™ process to treat and recover various radionuclides from the waste sludge of the single-shell tanks (SST) at Hanford, thus leaving a material less costly to dispose of.

The ACT*DE*CON™ process is unique in that it combines dissolution of the contaminants with nonhazardous and noncorrosive dilute selective solvents, recovery of contaminants, and regeneration of solvents for a continuous recirculating treatment process. The ACT*DE*CON™ solvent chemistry uses well-established carbonate recovery chemistry, a chelant (EDTA), and an oxidant (hydrogen peroxide).

The process has worked well for treatment of soil contaminated with uranium or plutonium. Under separately funded DOE programs, ACT*DE*CON™ has been tested on uranium-contaminated Fernald soils, plutonium-contaminated Mound soil, and at the pilot stage at Idaho National Engineering Laboratory pit-9.

A three-phase approach is being used in this project: lab-scale testing with spiked-waste simulants, lab-scale testing with actual waste, and pilot-scale testing with waste simulants and actual waste. One approach to be tested will be the ability to dissolve sludge directly in a tank. The solvent, dissolved materials, and entrained solids will then be separated to recover nondissolved sludge materials.

If these sludge materials meet low-level radioactive waste criteria, they can be disposed of as low-level waste. If the sludges contain levels of transuranic (TRU) waste greater than 10 nCi/g, they can be treated in a contactor with the ACT*DE*CON™

process and mechanical action to further break up the sludge and dissolve the TRU waste. Furthermore, the liquid stream could be converted to a low-level waste by anion exchange recovery of uranium, technetium, iodine, and TRU and cation exchange recovery of cesium and strontium. Alternately, the ACT*DE*CON™ solution stream could be evaporated and sent directly to vitrification.

Technology Needs

EM Focus Area: high-level waste tank remediation

Actinides are constituents of major importance in Hanford tank sludge. Vitrifying the washed sludge with no pretreatment could be prohibitively expensive, so a method that can remove the contaminants of greatest concern from the sludge is of significant economic benefit.

There is currently a dearth of technologies dealing with the treatment of sludges and solids that also might be amenable to in-tank application. Technologies at a level of development that would allow timely implementation are also at a premium. The ACT*DE*CON™ process is viewed as having a low probability for success in treating Hanford single-shell tank waste, but, if successful, it may reduce high-level waste significantly.

This high-risk, moderate-to-high benefit, pretreatment alternative merits study for three primary reasons: 1) it is an alkaline-side recovery process and thus would not require addition of large amounts of nitric acid to the waste; 2) it operates under benign conditions (near-ambient temperature and atmospheric pressure); and 3) the process could likely be performed in-tank and, thus would avoid costs associated with having a separate facility.

Accomplishments

Phase I testing was completed on a spiked sludge simulant, and a final report was issued.

Benefits

The development of an alkaline-side process to separate TRUs from the nonradioactive components of high-level tank wastes would have the following benefits:

- Eliminate the need to add large quantities of acid (nitric, hydrofluoric, oxalic, etc.) to the wastes to dissolve the TRUs for acid-side processing; e.g.; TRUEX. Thus, alkaline-side processing could result in smaller volumes of low-level waste being generated in the pretreatment of tank wastes.
- Require a smaller processing facility than that required for acid-side processing, because the leaching step could likely be done directly in the underground storage tanks. Thus, the need for dissolvers in the processing facility would be eliminated.
- Provide an alternative to enhanced sludge washing. The benefit is that, if successful, the ACT*DE*CON™ process renders the sludge solids low-level waste. Thus, high-level waste volume is reduced.

Collaboration/Technology Transfer

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Electrochemical Destruction of Nitrates and Organics

Presenters: David Hobbs, Savannah River Technology Center; Jeff Surma, Pacific Northwest Laboratory; Ralph White, University of South Carolina

Description

The goal of this task is to develop and evaluate the various electrochemical methods for 1) destroying nitrates, nitrites and organic compounds in high-level waste and low-level waste and 2) removing radionuclides and hazardous metals from alkaline waste solutions (see figure). In an electrochemical cell, nitrate and nitrite can be reduced to nitrogen, ammonia, and nitrous oxide; these gases have very low solubilities in alkaline solutions and so are effectively separated from the waste. Metal ions can be reduced producing solid phases or deposits on the electrodes that can also be separated from the liquid waste.

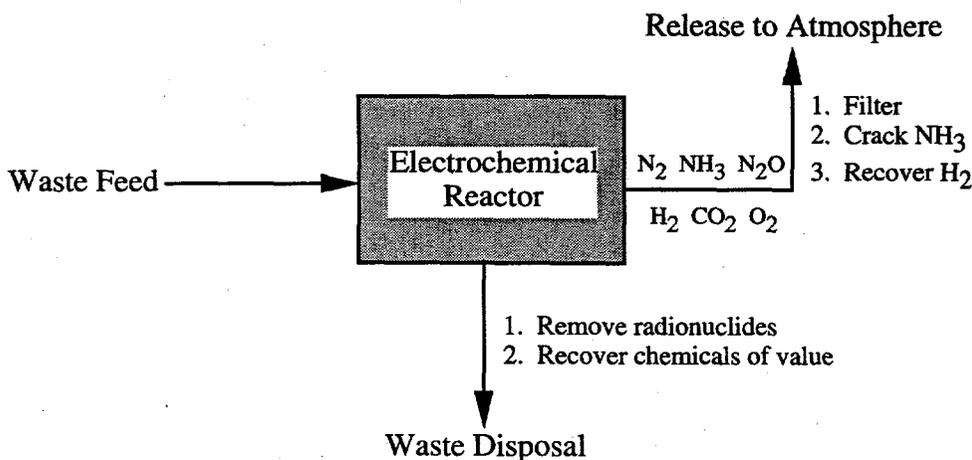
In addition to electrochemical reduction, anodic electrochemical reactions can be brought about to oxidize organic compounds to carbon dioxide and water. In this work, researchers are examining divided and undivided parallel-plate, porous metal, packed bed, and fluidized bed electrochemical cells, and identifying electrocatalysts for these destruction reactions.

The task consists of five major subtasks. The first is to determine optimum reactor conditions for the destruction and removal of hazardous waste components. The second is to develop engineering process models. The third is laboratory-scale tests with radioactive materials. The fourth is the pilot-scale tests, and the fifth is analysis and evaluation of the testing data.

Technology Needs

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

Organic compounds such as EDTA significantly impact radionuclide separation processes and the safe storage of high-level waste. Performance assessments of low-level waste forms indicate that nitrate and nitrite are among the major contributors to potential environmental release and personnel exposure risk.



Separation of nitrates/organics in high-level waste by electrolysis

Electrochemical treatment is one possible technology that could destroy nitrates, nitrites, and organics and remove radionuclides and hazardous metals from waste solutions. The electrolytic process is robust, operates at low temperature and pressure, can be highly selective in controlling reaction chemistry, does not require the use of additional chemical reagents, and produces little secondary waste. Considerable reduction (possibly up to 75%) in the waste volume requiring disposal could be realized by recovery and recycle of valuable chemicals after electrolytic treatment.

Accomplishments

Electrolytic destruction of nitrate and nitrite was demonstrated in an engineering-scale flow reactor using actual waste from the Savannah River Site. Engineering models for the parallel-plate reactor and a dynamic flowsheet model incorporating the electrochemical reactor and an evaporator for the destruction of nitrate and nitrite have been developed at the University of South Carolina.

Parametric studies for the oxidation of organic compounds that are present in Hanford Site high-level waste have been conducted in an engineering-scale flow reactor at Pacific Northwest Laboratory. Evaluation of fluidized-bed and packed-bed electrochemical reactors was initiated at Texas A&M University for the destruction of nitrate and nitrite and the removal of hazardous metals. Evaluation of porous-metal cathodes, gas-diffusion anodes, and kinetic studies are in progress at the University of South Carolina.

Benefits

The benefits of successfully implementing this technology include the removal of organic complexants that reduce radionuclide separation efficiencies and the reduction or elimination of environmental, safety,

and personnel exposure risks from the presence of nitrate, nitrite, organics, and hazardous metals in the waste as currently stored and in the low-level waste forms produced for permanent disposal.

Recovery and recycling of the sodium hydroxide produced by this type of process would significantly decrease the volume of waste requiring disposal, resulting in significant cost savings for disposal of low-level waste.

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