



Office of Environmental Management  
Technology Development

EFFICIENT  
SEPARATIONS AND PROCESSING  
CROSSCUTTING PROGRAM

Technology Summary

June 1995

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# EFFICIENT SEPARATIONS AND PROCESSING CROSSCUTTING PROGRAM

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## TABLE OF CONTENTS

Introduction .....	iii
Efficient Separations and Processing Crosscutting Program Overview .....	xi
<b>1.0 NOVEL ION EXCHANGE MATERIALS .....</b>	<b>3</b>
1.1 High-Capacity, Selective Solid Sequestrants for Innovative Chemical Separation: Inorganic Ion-Exchange Approach .....	4
1.2 Waste Separation and Pretreatment Using Titanate Ion-Exchangers .....	6
1.3 Fission Product Chemistry .....	10
1.4 Separation of Cesium and Strontium from High-Level Radioactive Waste .....	13
1.5 Development of Magnetically-Assisted Chemical Separation Processes .....	16
1.6 Evaluation of Improved Techniques for Removal of Strontium and Cesium from Process Waste Water and Ground Water .....	19
1.7 Continuous Annular Chromatography .....	21
1.8 "Carbollide"/Cobalt Dicarborane Anion Process Development for <sup>137</sup> Cs Decontamination .....	23
<b>2.0 ADVANCED SOLVENT EXTRACTION .....</b>	<b>27</b>
2.1 Advanced Integrated Solvent Extraction .....	28
2.2 Alkaline-Side Extraction of Technetium from Tank Waste Using Crown Ethers and Other Extractants .....	31
2.3 "TALSPEAK" Chemistry .....	33
2.4 Aqueous Biphasic Systems for Radioactive Waste Pretreatment .....	35
<b>3.0 WASTE SOLIDS TREATMENT .....</b>	<b>39</b>
3.1 Distillation Separation of Chloride Salts from Plutonium .....	40
3.2 Calcine Residue Treatment: Volume Reduction for High-Level Waste Sludges .....	42
3.3 Pyrochemical Treatment and Immobilization of Idaho Chemical Processing Plant High-Level Waste Calcine .....	45
3.4 Sludge Washing and Dissolution of Melton Valley Storage Tank Waste .....	47
3.5 Aluminum Removal from Washed Sludge .....	49
3.6 Colloid Formation in Sludge Washing .....	51
3.7 Selective Leaching of Tank Sludge by the ACT*DE*CON™ Process .....	53

4.0	SELECTIVE SORBENTS/LIGANDS .....	57
4.1	High-Capacity, Selective Solid Sequestrants for Innovative Chemical Separations: Membrane-Supported, Bound-Particle Approach .....	58
4.2	Derivatives of Natural Complexing Agents for the Removal of Plutonium from Waste Streams .....	60
4.3	Removal and Recovery of Toxic Metal Ions from Aqueous Waste Streams by Utilization of Polymer Pendant Ligands .....	62
4.4	Sequestering Agents for the Removal of Transuranics from Radioactive Waste .....	65
5.0	OTHER SEPARATIONS AREAS .....	71
5.1	Development and Evaluation of Electrochemical Methods of Destroying Nitrates and Nitrites in High-Level Waste and Low-Level Waste .....	72
5.2	Separation of Tritiated Water from Water Using Composite Membranes .....	75
5.3	Significant Volume Reduction of Tank Waste by Selective Crystallization .....	77
5.4	Aqueous Phase Catalytic Exchange for Detritiation of Water .....	80
5.5	Technology Evaluation and Process Definition: Unit Process Level and Global Level .....	82
6.0	DOE BUSINESS OPPORTUNITIES .....	87
7.0	ACRONYM LISTING .....	93
8.0	APPENDIX .....	99

### Figures

A.	The EM Organizational Structure as of May 1, 1994 .....	vii
B.	The OTD Organizational Structure as of May 1, 1994.....	viii
1.2a	Transmission Electron Micrograph of TAM-5 Phase Particle of the Crystalline Silicotitanates .....	6
1.2b	Cesium Distribution Coefficients as a Function of Equilibrium pH .....	7
1.3	Comparison of Technetium Removal Using Nitric Acid and Reductant/Complexant on a 4.5ml HPQ Column Load with $4.5 \times 10^{-4}$ mmol Tc <sup>04</sup> .....	11
1.4	Incorporation of Cobalt Dicarbollide into 80% Chloromethyl Polystyrene/20% Divinylbenzene with Subsequent Sulfonation to Produce a Hydrophilic Cation Exchange Resin .....	14
1.8	Cobalt Dicarbollide [Co(C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> ) <sub>2</sub> ] <sup>-</sup> .....	23
2.1	A Total Radionuclide Extraction (TOREX) Process Flowsheet .....	29
4.2	Solid/Liquid Extractants .....	60
4.3	Biomimetic Candidates for Selective Polymer Pendant Ligands .....	63
5.1	Removal of Nitrates/Organics from High-Level Waste by Electrolysis. ....	72

# INTRODUCTION

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## THE NEW APPROACH

### PURPOSE

Although positive steps have been taken during the past three decades to remedy the world's environmental problems, the nation's ability to respond to many current and future environmental and economic challenges depends on technological advances produced by a well-organized and productive federal research and development program.

To ensure that such programs focus on the most pressing environmental restoration and waste management problems at the U.S. Department of Energy (DOE), the Assistant Secretary for the Office of Environmental Management (EM) established a Working Group in August 1993 to implement a new approach to environmental research and technology development. The goal of DOE's new approach is to conduct a research and technology development program that will 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 developers of technological solutions.

The key features of the new approach are:

- establishing five focus areas to address DOE's most pressing problems;
- teaming with the customers in EM to identify, develop, and implement needed technology;
- focusing technology development activities on major environmental management problems;
- coordinating management of scientific and development activities in support of EM;
- focusing resources in national laboratories more effectively;
- involving industry in developing and implementing solutions, including technology transfer into DOE and from DOE to the private sector;
- coordinating basic research by involving academia and other research organizations to stimulate technological breakthroughs; and
- enhancing involvement of regulators and stakeholders in implementation of technology development.

DOE has established a framework and strategy for coordinating efforts among DOE organizations, Management and Operations (M&O) contractors, the national laboratories, other government agencies, the scientific community, industry, academia, and the affected public. Full implementation of the new approach is planned for the FY 95/96 timeframe. The new strategy will build upon existing programs and will seek continual improvement of all EM operations and processes.

Prior to implementation of the new approach, EM's Office of Technology Development (OTD) 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 (IP) and Integrated Demonstrations (ID). These concepts, introduced in 1989, were engineered to

manage the research, development, demonstration, testing and evaluation (RDDT&E) activities within EM.

An IP was the cost-effective mechanism which assembled a group of related and synergistic technologies to evaluate their performance to solve a specific aspect of a waste management or environmental problem. The problem can be unique to a site or common to many sites. An IP supports applied research to develop innovative technologies in key application areas organized around specific activities required in each stage of the remediation process (e.g., characterization, treatment, and disposal).

An ID was the cost-effective mechanism that assembled a group of related and synergistic technologies to evaluate their performance individually or as a complete system to correct waste management and environmental problems from cradle to grave.

## BENEFITS

A keystone for implementation of the new approach is to encourage development of technologies that are better, faster, safer and more cost-effective than those currently available. More importantly, the new approach has been adopted to foster implementation of new and innovative environmental technologies, facilitating the national commitment to long-term environmental, energy, and economic goals.

An important benefit of the new approach is the creation of investment returns for developing new technologies — technology dividends. These technology dividends result from partnerships and leveraging within government and between government and the private sector. The partnerships can consist of technology developers, technology users, problem holders, and problem solvers.

EM technology dividends will include:

- Employment opportunities with new businesses and existing businesses;
- Cleanup of sites posing the greatest threats to human health, safety, and the environment;
- Materials reused and recycled, instead of thrown away or freshly contaminated;
- Pollution prevented;
- More effective and efficient industrial processes, leading to greater U.S. competitiveness globally; and
- Technology transfer to other countries.

By implementing the new approach for the unique environmental problems associated with DOE sites, EM/OTD, scientists, and engineers at the national laboratories stand at the threshold of opportunity to develop new technologies. This work will enhance quality of life through a cleaner environment, improved global competitiveness, and ensure job opportunities for American workers.

## FOCUS AREAS

Five major remediation and waste management problem areas within the DOE Complex have been targeted for action on the basis of risk, prevalence, or need for technology development to meet environmental requirements and regulations. Other areas may be added or currently identified areas further partitioned to ensure that research and technology development programs remain focused on EM's most pressing remediation and waste management needs. These major problem areas, termed "Focus Areas," are described below.

**Contaminant Plume Containment and Remediation.** Uncontained hazardous and radioactive contaminants in soil and ground water exist throughout the DOE Complex. There is insufficient information at most sites on the contaminants' distribution and concentration. The migration of some contaminants threatens water resources and, in some cases, has already had an adverse impact on the off-site environment. Many current characterization, containment, and treatment technologies are ineffective or too costly. Improvements are needed in characterization and data interpretation methods, containment systems, and in situ treatment.

**Mixed Waste Characterization, Treatment, and Disposal.** DOE faces major technical challenges in the management of low-level radioactive mixed waste. Several conflicting regulations, together with a lack of definitive mixed waste treatment standards hamper mixed waste treatment and disposal. Disposal capacity for mixed waste is also expensive and severely limited. DOE now spends millions of dollars annually to store mixed waste because of the lack of accepted treatment technology and disposal capacity. In addition, currently available waste management practices require extensive, and hence costly waste characterization before disposal. Therefore, DOE must pursue technology that leads to better and less expensive characterization, retrieval, handling, treatment, and disposal of mixed waste.

**High-Level Waste Tank Remediation.** Across the DOE Complex, hundreds of large storage tanks contain hundreds of thousands of cubic meters of high-level mixed waste. Primary areas of concern are deteriorating tank structures and consequent leakage of their contents. Research and technology development activities must focus on the development of safe, reliable, cost-effective methods for characterization, retrieval, treatment, and final disposal of the wastes.

**Landfill Stabilization.** Numerous DOE landfills pose significant remediation challenges. Some existing landfills have contaminants that are migrating, thus requiring interim containment prior to final remediation. Materials buried in retrievable storage pose another problem. Retrieval systems must be developed to reduce worker exposure and secondary waste quantities. Another high-priority need is in situ methods for containment and treatment.

**Decontamination and Decommissioning.** The aging of DOE's weapons facilities, along with the reduction in nuclear weapons production, has resulted in a need to transition, decommission, deactivate, and dispose of numerous facilities contaminated with radionuclides and hazardous materials. While building and scrap materials at the sites are a potential resource, with a significant economic value, current regulations lack clear release standards. This indirectly discourages the recovery, recycling, and/or reuse of these resources. The development of enhanced technologies for

the decontamination of these materials, and effective communication of the low relative risks involved, will facilitate the recovery, recycle, and/or reuse of these resources. Improved material removal, handling, and processing technologies will enhance worker safety and reduce cost.

## CROSSCUTTING TECHNOLOGIES

Crosscutting technologies are those which overlap the boundaries of the focus areas while providing simultaneous benefits. These technologies may be used in several or all focus area testing and evaluation programs, and include:

**Characterization, Monitoring, and Sensor Technology.** DOE is required to characterize more than 3,700 contaminated sites, 1.5 million barrels of stored waste, 385,000 m<sup>3</sup> of high-level waste in tanks, and from 1,700 to 7,000 facilities before remediation, treatment, and facility transitioning commence. During remediation, treatment, and site closure, monitoring technologies are needed to ensure worker safety and effective cleanup. Cost-effective technologies are needed for all EM characterization requirements.

**Efficient Separations and Processing.** Separation and treatment technologies are needed to treat and immobilize a broad range of radioactive wastes. In some cases, separations technologies do not exist. In others, improvements are needed to reduce costs, reduce secondary waste volumes, and improve waste form quality. Separations technologies are also needed for environmental restoration of DOE sites, for groundwater and soils cleanup, and for decontamination and decommissioning of facilities. Many separations agents developed for waste treatment can be adapted for environmental restoration needs.

**Robotics.** DOE's waste disposal efforts have particular issues—access, safety, final disposal, and cost efficiency. Due to hazardous radiation, massive waste loads, and restricted entry ways, many sites are inaccessible for human labor. It is unsafe to expose humans to radiation, harmful chemicals, and injurious mechanical objects. Human labor requires higher compensation, the need for expensive protective clothing, and stringent decontamination procedures. Robotics systems are safe, efficient, and cost-effective means to automate the handling and processing of mixed waste and characterizing and/or retrieving storage tank waste. Systems can also be designed for surveillance, characterization, cleanup, and decommissioning of retired DOE facilities.

**Innovative Investment Area.** DOE has set aside funding to foster research and development partnerships within the public and private sector, and to introduce innovative technologies into OTD programs. The Innovative Investment Area supports two types of technologies: (1) technologies that show promise to address specific EM needs, but require proof-of-principle experimentation, and (2) proven technologies in other fields that require critical path experimentation to demonstrate feasibility for adaptation to specific EM needs.

**Pollution Prevention.** DOE and the Department of Defense (DoD) have similar waste stream pollution problems and common environmental concerns. By combining their resources, these agencies can develop a coordinated interagency environmental research and technology development program that produces cost-effective technological solutions, particularly in the areas of process change or in-process recycling.

## TECHNICAL TASK PLANS

Technical Task Plans (TTPs) are used to identify and to summarize work funded and managed by OTD at headquarters, the field, and the national laboratories. These plans include a project summary, technical task description, budget schedule, and milestone schedule. The EM-50 FY 1994 Program Summary (DOE/EM-0216) lists TTPs current as of the date of this document.

All tasks require a TTP number. Each TTP number contains information on the fiscal year in which the task is first funded, the DOE Operations Office funding allotment code, and the laboratory/contractor/university designator. See appendix for further details.

## EM ORGANIZATIONAL STRUCTURE

The Office of Environmental Management (EM) is responsible for managing the cleanup of DOE wastes from past nuclear weapons production and current operations. The EM mission is to bring DOE sites into compliance with all environmental regulations while minimizing risks to the environment, human health and safety posed by the generation, handling, treatment, storage, transportation, and disposal of DOE waste. The EM organization was established to provide focus, accountability, and visibility for DOE's waste management and remediation efforts. See Figure A.

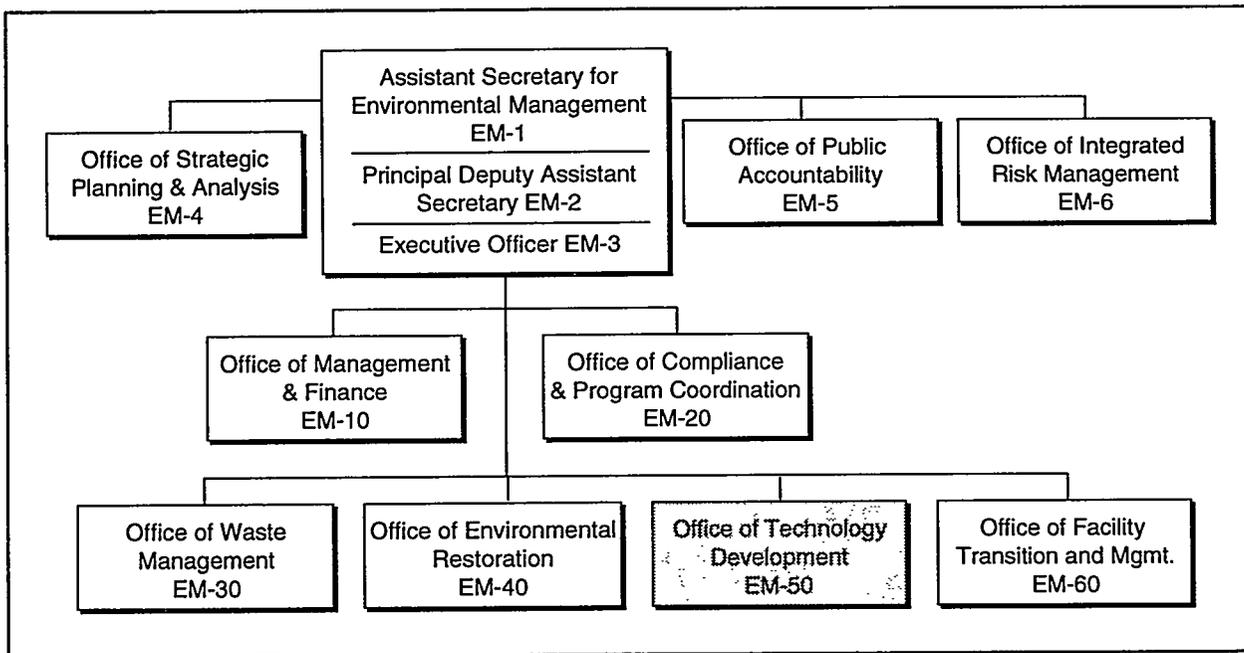


Figure A. The EM Organizational Structure as of May 1, 1994.

## OFFICE OF TECHNOLOGY DEVELOPMENT

The Office of Technology Development (EM-50) has the overall responsibility to develop technologies to meet DOE's goals for environmental restoration. OTD works closely with EM-30, -40, and -60 in identifying, developing, and implementing innovative and cost-effective technologies. Activities within EM-50 include applied research and development, demonstration, testing, and evaluation (RDDT&E), technology integration, technology transfer, and program support. See Figure B.

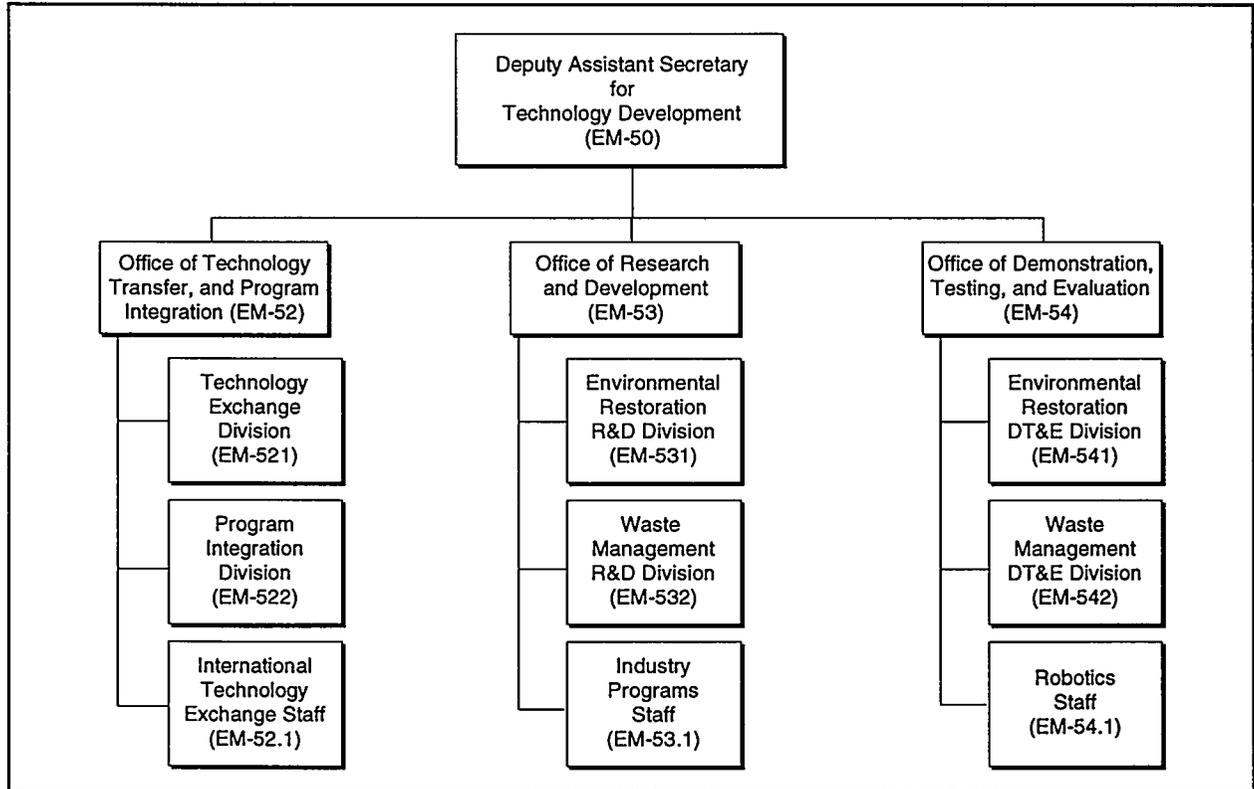


Figure B. The OTD Organizational Structure as of May 1, 1994.

### EM-50 ORGANIZATION

The Office of Technology Transfer and Program Integration (EM-52) provides management, financial, and internal program support to line organizations that comprise EM-50. It also provides efforts to encourage and to facilitate the infusion and diffusion of innovative environmental technologies for internal and domestic application through collaborative partnerships with U.S. and foreign industry or organizations, the national laboratories, other federal agencies, and universities. Technology transfer and technology leveraging are important program components. Enhanced communication to internal and external stakeholders is a goal of this Office.

The Office of Research and Development (EM-53) is responsible for establishing applied research and development (R&D) program at DOE sites nationwide. Programs are designed to identify operational needs in environmental restoration, waste operations, and corrective activities, and to

provide solutions to key technical issues that, if not solved in a timely manner, would adversely affect DOE's ability to meet its cleanup goal.

**The Office of Demonstration, Testing, and Evaluation (EM-54)** is responsible for identifying environmental management technologies in the research and development stage that are ready for transition to the demonstration arena. Those technologies are complete systems to demonstrate a solution to a specific problem area. Programs are conducted to advance selected technologies so they can be utilized by DOE to meet its cleanup goal in a cost-effective manner.

## **OTHER EM ORGANIZATIONS**

**The Office of Waste Management (EM-30)** has program responsibilities for managing waste generated at all DOE sites during weapons processing and manufacturing, research activities, and site cleanup activities. This includes the treatment, storage, transportation, and disposal of several types of waste: transuranic, low-level radioactive, mixed, and solid sanitary wastes. EM-30 is also responsible for the storage, treatment, and processing of defense high-level radioactive waste (HLW), waste minimization efforts, and corrective activities at waste management facilities.

**The Office of Environmental Restoration (EM-40)** has program responsibilities for assessment and cleanup of inactive hazardous and radioactive facilities and waste sites at all DOE installations and some non-DOE sites. EM-40 oversees program activities to reduce or eliminate risks to human health and the environment.

**The Office of Facility Transition and Management (EM-60)** has the responsibility to ensure that shut-down facilities are brought to a deactivated state, are properly maintained, and are eventually decontaminated and/or decommissioned or released for other uses.



# THE EFFICIENT SEPARATIONS AND PROCESSING CROSSCUTTING PROGRAM OVERVIEW

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The Efficient Separations and Processing (ESP) Crosscutting Program 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 multi-year 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.

## 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 Program 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 downgrading to a waste form less difficult and expensive to dispose of.

Initially, ESP R&D efforts focused on treatment of high-level waste (HLW) from underground storage tanks (USTs) because of the potential for large reductions in disposal costs and hazards. As further separations needs emerge and as waste management and environmental restoration priorities change, the program has evolved to encompass the breadth of waste management and environmental remediation problems.

## MISSION AND SCOPE

The mission of the ESP Program 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 within DOE-EM;
- Foster future expertise in separations technologies by encouraging university participation; and
- Transfer separations technologies between DOE and the U.S. industrial sector to facilitate competitiveness of U.S. technology and industry in the world market.

The ESP Program 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 solids);
- Removal of bulk constituents from waste streams to recover chemicals for recycle and waste minimization;
- Solid/liquid separation; and
- Destruction of complexants and bulk anions.

## CURRENT PROGRAM

The ESP Program conducts applied laboratory research to create new or to improve existing chemical separations technologies and processes. The scope of research sponsored by ESP is further detailed here. The most important category is the development of new separations processes, which involves:

- Novel ion exchange materials;
- Advanced solvent extraction;
- Waste solids treatment;
- Selective sorbents/ligands; and
- Other separations areas.

FY 1994 tasks supported by ESP and presented in this document are separated into these categories.

The ESP Program 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. 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, ESP sponsors research on processes such as organic destruction and leaching and dissolution of tank waste sludges to enable liquid-based separation technologies.

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**NOVEL ION  
EXCHANGE MATERIALS**

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**Section 1.0**

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The ESP Program is funding novel materials for ion exchange separation of cesium, strontium, and technetium from alkaline, acid, and neutral wastes, with emphasis on cesium and strontium separation from alkaline wastes. Treating alkaline tank wastes at several DOE sites requires the separation of fission products such as cesium (as  $^{137}\text{Cs}$ ) from the wastes.

Cesium removal is traditionally done using ion exchange materials such as CS-100 (an organic resin) or zeolites (inorganic). Such separations can generate substantial secondary waste because of the limited affinity or selectivity for cesium (compared to, e.g., sodium and potassium).

The ESP Program is improving inorganic ion exchange materials that can be implemented in a typical packed-bed or column configuration and therefore essentially substitute for existing materials in cesium separation processes. The resulting novel materials should increase both the affinity and selectivity, but they must endure the severe chemical (e.g., pH approximately 14) and radiation (approximately  $10^9$  rads) environment encountered during many radionuclide separations from typical alkaline tank wastes. Engineered forms (i.e., granules suitable for packed beds) of the ion exchange materials must be developed that can survive these environments. This can be as great a challenge as providing the ion exchange.

Finally, integrated processes that include sorption, stripping, washing, conditioning steps, and disposition of spent ion exchange materials and secondary wastes must be developed and tested before novel processes are accepted by designers of radionuclide separation facilities.

ESP supported the following tasks in this category during FY94:

- High-Capacity, Selective Solid Sequestrants for Innovative Chemical Separation: Inorganic Ion Exchange approach;
- Waste Separation and Pretreatment Using Titanate Ion Exchangers;
- Fission Product Chemistry;
- Separation of Cesium and Strontium from High-Level Radioactive Waste;
- Development of Magnetically Assisted Chemical Separation Processes;
- Evaluation of Improved Techniques for Removal of Strontium and Cesium from Process Waste Water and Ground Water;
- Continuous Chromatography; and
- "Carbollide"/Cobalt Dicarborane Anion Process Development for  $^{137}\text{Cs}$  Decontamination.

# 1.1 HIGH-CAPACITY, SELECTIVE SOLID SEQUESTRANTS FOR INNOVATIVE CHEMICAL SEPARATION: INORGANIC ION-EXCHANGE APPROACH

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## TASK DESCRIPTION

The purpose of this task is 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, Pacific Northwest Laboratory (PNL) is collaborating with industry and university participants to develop high capacity, selective, solid ion exchangers for the removal of specific contaminants from nuclear waste streams. This work is one of two parallel projects. Contracts were awarded in 1992 to the AlliedSignal Corporation in partnership with Texas A&M University. During 1993, three classes of exchangers were screened and developed; 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  $\text{NaNO}_3$ . 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 with cesium in the presence of potassium is being studied to enhance the selectivity of the 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 showed that the majority of binders were incompatible with the highly alkaline feed. However, an excellent candidate for use with sodium titanate powders was identified.

## TECHNOLOGY NEEDS

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 would address a variety of problems in the DOE Complex, specific applications to high-level tank wastes have been targeted. A major goal for AlliedSignal/Texas A&M for FY94 is to continue to obtain necessary scientific and engineering information required to remove cesium and strontium from highly alkaline wastes at the Hanford site.

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## 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 greater than 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 have been replaced with synthetic micas, which have 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.

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## BENEFITS

Because the cost of nuclear waste treatment depends in part on the ability to selectively remove certain troublesome radionuclides, these advanced ion exchange materials could result in substantial cost reductions in nuclear waste treatment.

The cost of waste treatment depends on the efficient and selective removal of elements that complicate waste disposal. This technology emphasizes removal of the heat-emitting isotopes  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ , which will reduce both the amount of activity in low-level waste (LLW) and the volume of HLW forms.

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 a variety of waste streams.

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## EM FOCUS AREA

High-Level Waste Tank Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

A solicitation of interest and capabilities was issued in FY92 through the Commerce Business Daily (CBD). The purpose was to identify candidate advanced separation materials and processes to be investigated and candidate industry/university teams to collaborate with PNL in the proposed studies. A Request for Proposals (RFP) was issued to qualified respondents from the CBD notice, from which the contract with AlliedSignal Corporation in Des Plaines, IL and Texas A&M University was awarded. AlliedSignal has a subcontract in place with Texas A&M, specifically with Prof. A. Clearfield and his team. Texas A&M develops the ion exchange materials and sends them to AlliedSignal for further testing, commercialization and characterization. All actual waste and radioactive testing will be done at Hanford by PNL or at one of the other national laboratories.

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## 1.2 WASTE SEPARATION AND PRETREATMENT USING TITANATE ION EXCHANGERS

### TASK DESCRIPTION

The objective of this project is to develop and evaluate inorganic crystalline silicotitanate (CST) ion-exchange materials to selectively remove  $^{137}\text{Cs}$  and other radionuclides from a wide spectrum of radioactive defense wastes. CSTs comprise several phases and were jointly invented by Sandia National Laboratories (SNL) and Texas A&M 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 has been shown to be highly selective for cesium separation, even in waste streams containing high concentrations (5 to 10 M) of sodium. See Figure 1.2a.

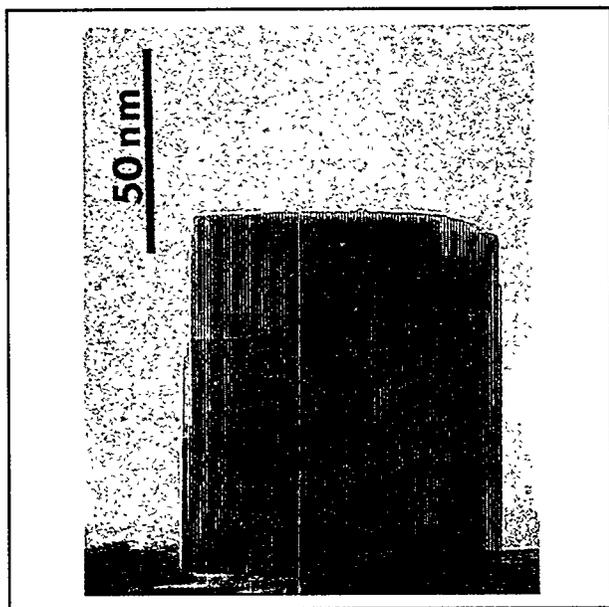


Figure 1.2a. Transmission Electron Micrograph of TAM-5 Phase Particle of the Crystalline Silicotitanates.

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 will be accomplished through four primary activities:

- Evaluation of the ion exchange properties of the TAM-5 powder, especially the effects of pH and solution composition on cesium selectivity;
- Stability of the TAM-5 powder in both acidic and basic solutions as well as the stability under exposure to radiation at levels of 109 Rads (Si) or greater;
- Assessment of the feasibility of regenerating the CST ion-exchangers; and
- Evaluation of the performance of the TAM-5 material for radionuclide removal at DOE facilities, specifically for the Hanford site, Oak Ridge National Laboratories (ORNL), Savannah River site (SRS), and Idaho National Engineering Laboratory (INEL).

### TECHNOLOGY NEEDS

Across the DOE Complex, there are currently more than 200 tanks for storing radioactive waste by-products generated by weapons materials production facilities. These tanks contain tens of millions of gallons of highly radioactive supernate, 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, titanate ion-exchange materials and

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

## 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 with a yield of 750 grams. 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. In September 1994 UOP molecular sieves successfully scaled up production of CST powder to the 1,800 pound batch level.

Cesium and strontium distribution coefficients were measured across a pH range from less than 0 to greater than 14. See Figure 1.2b. The TAM-5 material has high cesium selectivity over the entire pH

range, but is selective for strontium (distribution coefficients greater than 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 more than 100 days and in low pH solutions (up to 6 M HNO<sub>3</sub>) for at least several days. The material ion exchange performance is also stable after exposure to 109 Rads (Si).

The feasibility of regeneration was investigated using up to 1.0 M HNO<sub>3</sub> and water to elute cesium-loaded TAM-5 powder. Neither solution showed potential for regenerating the material, as expected because of the high cesium selectivity exhibited by the TAM-5 powder.

Tests have been performed on a variety of waste compositions, both acidic and alkaline. Hanford Site, INEL, SRS, and ORNL waste simulants have been tested as well as actual wastes at ORNL and INEL. The 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 greater

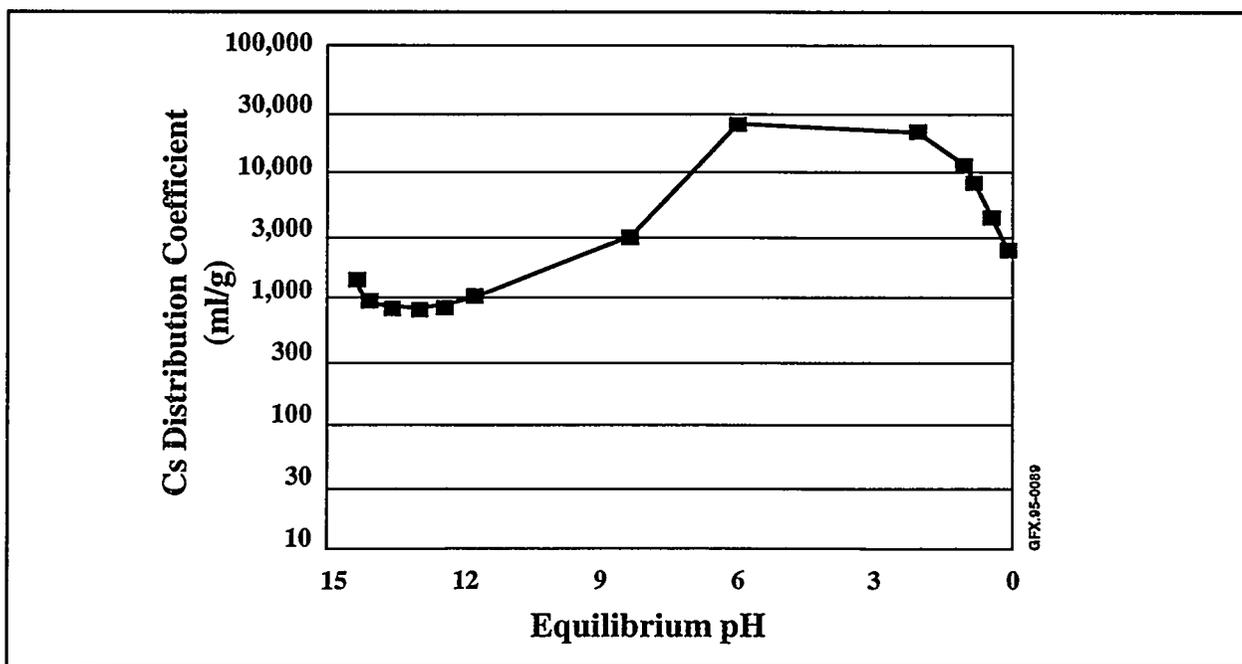


Figure 1.2b. Cesium Distribution Coefficients as a Function of Equilibrium pH.

than 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.

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## BENEFITS

No technology currently exists that will selectively remove cesium and strontium from highly alkaline, defense radioactive wastes without additional reprocessing. CSTs are inorganic ion exchangers that are being developed for a single-use removal of cesium, strontium, and possibly other radionuclides from highly alkaline radioactive wastes with little or no pretreatment. A once-through process will eliminate the need for equipment and facilities necessary for regeneration, handling, and storage of the cesium-loaded eluant.

Studies have shown that CSTs are stable in the chemical solutions required for treatment, and the CST lattice is not degraded by  $^{60}\text{Co}$  doses of  $10^9$  Rads. Studies have also indicated that the capacity of CST for cesium is sufficiently high that the quantity of CST is compatible with the allowable limit for  $\text{TiO}_2$  in HLW glass.

In addition to their excellent performance in highly alkaline solutions, CSTs have high selectivity for cesium from highly acidic solutions and extremely high capacity from neutral solutions.

The high specificity for cesium from pH 0 to 14 indicates that CST will have a range of potential applications, including treatment of solutions resulting from acidic and basic sludge processing and the clean salt process. It is also probable that CSTs will have application for facility decontamination and decommissioning (D&D) within DOE and commercial nuclear operations.

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## EM FOCUS AREA

High-Level Waste Tanks Remediation, Contaminant Plume Containment and Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

This project has culminated in a collaboration between SNL, Texas A&M University, and most recently UOP Molecular Sieves. The CST materials were invented by SNL and Texas A&M University in 1992. A Cooperative Research and Development Agreement (CRADA) was signed with UOP Molecular Sieves on March 2, 1994. The 18-month CRADA will result in development of a commercial supply of CST powder, conversion of the CST powder to an engineered form, and a commercial source of CST in engineered form. The engineered form of the material, suitable for use in ion-exchange columns, is expected to be commercially available in mid-1995.

Evaluation the CST powder and eventually the engineered form for radionuclide removal is ongoing at a number of DOE facilities including: the Hanford Site, ORNL, SRS, INEL, and West Valley Nuclear Services.

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### TASK DESCRIPTION

This task is divided into two initiatives compatible with existing separation strategies and flowsheets addressing the separation of technetium-99 ( $^{99}\text{Tc}$ ) and nickel-63 ( $^{63}\text{Ni}$ ) from HLW. For technetium separation, a new baseline technology of ion-exchange removal is being developed. For nickel removal, the approach is to select readily available resins for the removal of nickel in a variety of waste streams. The separation technologies are designed to be robust, safe, and flexible for the Hanford tank waste and other nuclear waste streams.

Several anion-exchange resins have been investigated. Reillex<sup>TM</sup>-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 Dowex<sup>TM</sup> 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.

The approach to nickel separation 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.

### TECHNOLOGY NEEDS

Technetium is a major fission product resulting from fission of plutonium in nuclear reactors. At the present rate of production,  $^{99}\text{Tc}$  will reach 170,000 kg in nuclear waste form by the year 2000.

Technetium, as the pertechnetate ion ( $\text{TcO}_4^-$ ), 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 unusual chemical and engineering problems during vitrification. Glass frit formulations may contain components that are capable of reducing technetium to  $\text{TcO}_2$ . During vitrification,  $\text{TcO}_2$  can disproportionate into metal, which could precipitate as a conducting layer and short out melter electrodes and  $\text{Tc}_2\text{O}_7$ , which could volatilize into the offgas system—two undesirable situations.

Certain tanks contain unusually high concentrations of nickel. The single-shell tank inventory indicates that there are 178,000 kg of nickel containing about 300,000 Ci of  $^{63}\text{Ni}$ . It may be necessary to remove nickel from the waste processing stream because of glass requirements. The  $^{63}\text{Ni}$ , which is an extremely weak beta emitter, has a 100-year half-life.

Development of both of these separation and removal technologies may have other applications such as the environmental restoration of natural waters that may require technetium or nickel removal.

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### ACCOMPLISHMENTS

Technetium. The major accomplishment in FY94 has been the development of a new technetium eluent for the Reillex<sup>TM</sup>-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 Reillex<sup>TM</sup>-HPQ resin, the new system only requires approximately 3 column volumes. See Figure 1.3.

Testing has indicated that technetium containing simulant at  $5 \times 10^{-5} \text{ M TcO}_4^-$  has safely sorbed onto Reillex™-HPQ resin. The technetium eluted from the column with the new eluting system. This cycle was repeated on the same column four times with no diminishing effects on resin performance for technetium.

Breakthrough experiments using a simulant containing  $5 \times 10^{-5} \text{ M TcO}_4^-$  indicate that the column (1 x 20 cm) will permit approximately 44 column volumes of this simulant before 1 percent of the technetium appears in the eluent. Technetium was eluted from this column with three column volumes of the new eluent.

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

## BENEFITS

The need for technetium to be removed from HLW and mixed waste arises from potential risk associated with currently proposed waste forms (i.e., glass or grout). The reasons for separating technetium from HLW are 1) the LLW storage form (grout) would have a lower long-term risk, reducing the engineering requirements for containment, 2) technetium would not add to the "noble metals problem," and would thereby reduce the number of melter failures and new melter purchases, and 3) efficient separation of technetium with a more stable resin or extractant would reduce downtime for resin or extractant replacement in nuclear waste processing and would enhance waste minimization efforts.

## EM FOCUS AREA

High-Level Tank Waste Remediation

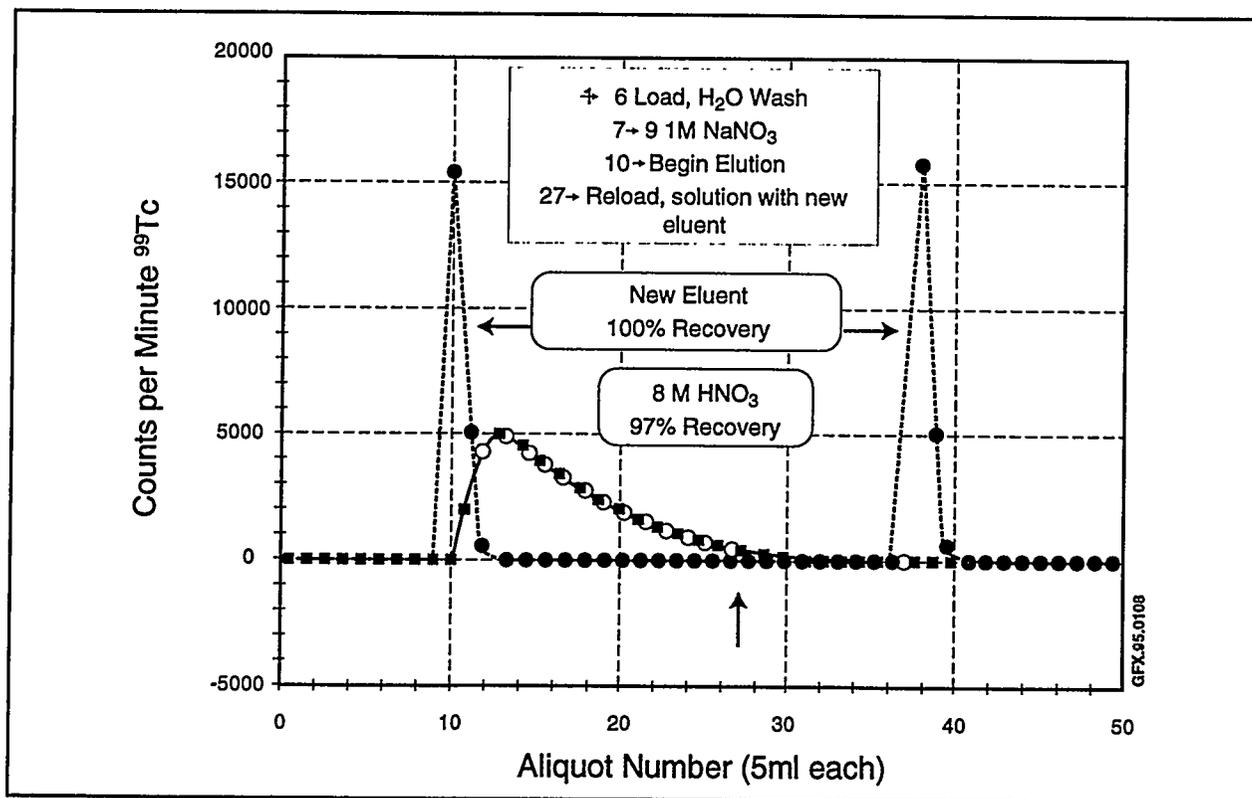


Figure 1.3. Comparison of Technetium Removal Using Nitric Acid and Reductant/Complexant on a 4.5ml HPQ column loaded with  $4.5 \times 10^{-4} \text{ mmol TcO}_4^-$ .

## COLLABORATION/TECHNOLOGY TRANSFER

The task that studies the separation of  $^{99}\text{Tc}$  from HLW at Los Alamos National Laboratory (LANL) has benefited from the counsel of two university participants, Prof. K.R. Ashley at East Texas State University and Prof. S. H. Strauss at Colorado State University. In support of this activity, discussions have also been initiated with Reilly Industries, the supplier of the resins used in the sorption studies. Initial interest in collaboration has been expressed.

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## 1.4 SEPARATION OF CESIUM AND STRONTIUM FROM HIGH-LEVEL RADIOACTIVE WASTE

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### TASK DESCRIPTION

The objective of this investigation is to develop a separations system for removing cesium and strontium from alkaline and acidic high-level nuclear waste using derivatives of cobalt dicarbollide. 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 the former Soviet Union. Cobalt dicarbollide is a nearly ideal hydrophobic anion, is almost ideal for solvent extraction of cationic species from aqueous solutions; specifically, cesium and strontium can be extracted with very high selectivity and yield. In addition, cobalt dicarbollide possesses excellent radiation stability. Much of the earlier work focused on the use of this molecule in solvent extraction systems with highly toxic solvents such as nitrobenzene.

The thrust of the task is to explore 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 Rez near Prague, Czech Republic, coupled with LANL's expertise in the areas of radiochemistry and inorganic, organometallic, and polymer synthesis.

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### TECHNOLOGY NEEDS

Because of the short half-lives of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  (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. During the first 30 years after removal from the reactor, these two nuclides account for more than 90 percent of the thermal energy and penetrating radiation of the waste. Separation of these nuclides for engineered surface stor-

age or vitrification will reduce the immediate safety concerns of the waste storage tanks, allow isolation of these nuclides for potential future use, and reduce the structural concerns arising from the incorporation of high thermal loads on borosilicate glass. The borosilicate glass is the proposed HLW and LLW storage form.

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### ACCOMPLISHMENTS

Cobalt dicarbollide has been grafted onto a variety of polymers, including poly(chloromethyl)styrene and polybenzimidazole (PBI). See Figure 1.4. Preliminary measurements on the poly (sulfonato) styrene-cobalt dicarbollide are promising with respect to cesium and strontium uptake and selectivity (versus sodium), and confirmatory measurements are proceeding. Also developed are new synthetic methods for derivatizing cobalt dicarbollide by electrophilic and nucleophilic substitution routes. In this task, cobalt dicarbollide has been directly alkylated, producing complexes that are less soluble in base than the parent dicarbollide. The reduced solubility of the derivatives improves their solvent separations performance by preventing loss of the dicarbollide extractant into the aqueous phase. This property is being exploited 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. Pure dichloro-cobalt dicarbollide has been prepared via an easily scalable route and has been found to have comparable  $\text{Cs}^+$  extraction properties to the unsubstituted species. Both the alkylated and chlorinated derivatives will be incorporated into poly(sulfonato) styrene for sequestering tests.

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## BENEFITS

Radioactive cesium and strontium must be removed from Hanford tank wastes. These two elements generate excessive radiation and heat loads to the final waste material both in handling and storage. In addition, removing cesium radionuclides eliminates one of the most mobile elements from the final proposed waste forms: grout and/or glass. Because the Group 1A elements are highly soluble and consequently, can be highly mobile in aqueous systems, the risks associated with these waste forms can be great. Furthermore, cesium and strontium removal technologies are not as reliable or robust as desired. In most separation strategies, removing cesium and strontium radionuclides is essential for radiation and thermal loading considerations.

## EM FOCUS AREA

High-Level Waste Tank Remediation

## COLLABORATION/TECHNOLOGY TRANSFER

Cobalt dicarbollide, although originally prepared in the United States, was first applied as an extractant in nuclear waste treatment in the former Czechoslovakia. Since this pioneering work in the 1970s, the Czechs have furthered the development of cobalt dicarbollide usage in radioanalytical application as

well as the possibility of use for larger scale applications. The collaboration with Prof. Jiri Rais at the Nuclear Research Institute in the Czech Republic is an extension of this earlier work to U.S. applications. This international collaboration has been expanded with Dr. Rais' trip to LANL in the summer of 1995 to work with U.S. scientists on the project.

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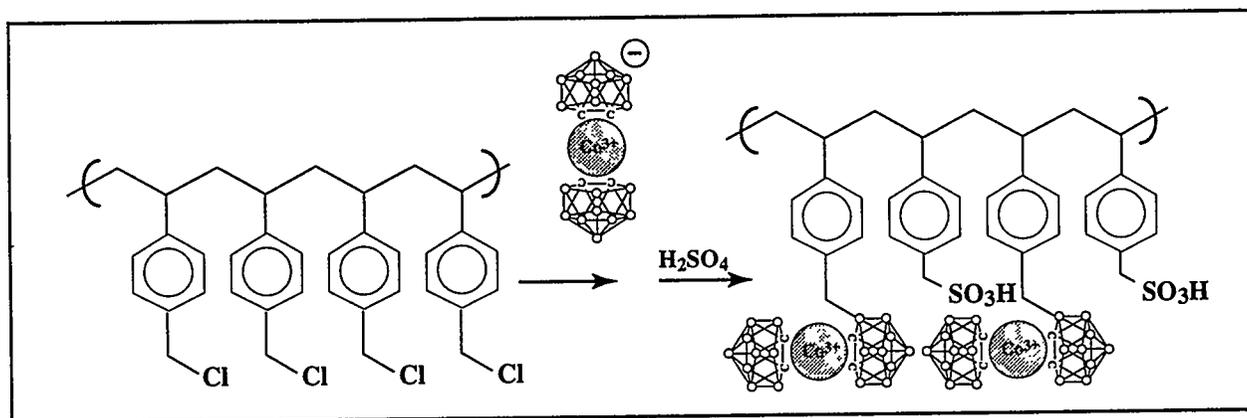


Figure 1.4. Incorporation of Cobalt Dicarbollide into 80% Chloromethyl Polystyrene/20% Divinylbenzene with Subsequent Sulfonation to Produce a Hydrophilic Cation Exchange Resin.

TTP Number: AL132010

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## 1.5 DEVELOPMENT OF MAGNETICALLY-ASSISTED CHEMICAL SEPARATION PROCESSES

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### TASK DESCRIPTION

This task is developing a magnetically assisted chemical separation (MACS) technology that can be applied to a wide variety of remediation efforts within DOE. The MACS technology uses ferromagnetic particles coated with chemically selective reagents to separate and recover specific radionuclides and heavy metals from contaminated solutions. Specifically, ferromagnetic beads are coated with either 1) a selective ion exchange material or an organic complexant-containing solvent for cesium and strontium, or 2) solvents for selective separation of transuranic (TRU) elements. This project combines the research and development (R&D) efforts of industry (Bradtec-US), academia (Northern Illinois University and the University of Illinois), and Argonne National Laboratory (ANL).

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### TECHNOLOGY NEEDS

Compact, economic, in-tank or near-tank processes are needed for the removal of contaminants from waste solutions at Hanford and other DOE sites. The greatest benefit of this technology is the simple separation of radionuclides from liquid waste by use of a cost-efficient and compact process without the production of large secondary waste streams. Opportunities exist for the application of this process to many DOE waste remediation activities.

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### ACCOMPLISHMENTS

Magnetic particles have been coated with several composition of octyl(phenyl)-N, N-diisobutylcarbamoyl-methylphosphine oxide/tributyl phosphate (CMPO/TBP)<sup>1</sup> mixtures to optimize the coating composition and coating process. These coated particles have been tested for their ability to remove americium from 2 M nitric acid solutions.

A drop in americium concentration by a factor of 7 was achieved using 3 to 10 g of the CMPO/TBP-coated magnetic beads per liter of solution [distribution coefficients ( $K_d$ ) values in the 300 to 5000 range]. These coated particles were also tested for their ability to remove plutonium from 2 M nitric acid solutions. Preliminary results were extremely encouraging. A drop in plutonium concentration by a factor of 50 to 120 was achieved using 3 to 10 g of the CMPO solvent-coated magnetic beads per liter of solution ( $K_d$  values in the 5500 to 15,000 range).

Tests on the same magnetic particle series for stripping using alcohol and stripping agents were conducted. Both the alcohol and one of the stripping agents were able to reduce  $K_d$  values of plutonium to less than 0.1. The waste volume was reduced by a factor of 400, and greater than 95 percent of the TRU was stripped in a single batch operation. Further tests of equal success include separation of TRU elements from simulated waste of the Plutonium Finishing Plant and from different compositions of dissolved tank sludge simulant.

These extractants are diluted with dodecane to make up the TRUEX solvent. The MACS process uses a higher concentration of these extractants than normally employed in the solvent extraction application.

A laboratory-scale design of a fluidized-bed column for a semicontinuous MACS process has been completed. The bed combines fluidization and a pulsing column with magnetic fields to minimize the equipment necessary for the separation. Following cold testing to optimize hydraulic performance (the column design has a 10L capacity), experiments with actinide-containing waste will be performed in a glovebox. Flowsheets for treating Hanford tank waste have been composed around this compact unit design.

Micrographs of noncoated, commercially available magnetic particles were prepared. These micrographs show that the differences in  $K_d$  values for americium tracer in 2 M  $\text{HNO}_3$  can be correlated to the sorption capabilities of the extractants.

Studies on coated and noncoated magnetic particles as well as gamma-irradiated particles have been initiated. The results show that irradiation (from  $10^1$  rad to  $10^6$  rad) has negligible effects on the magnetic properties of coated or noncoated particles. The irradiation studies also showed that the separation capabilities of the particles will be reduced by at least 30 percent at  $10^6$  rad (equivalent to 1000 cycles of use), partially due to nitric acid degradation.

Studies using cesium-extracting particles irradiated with a cobalt-60 gamma source show that the polymer core of the particle unravels as dose increases from  $10^1$  rad to  $10^6$  rad. Bradtec has begun testing cesium removal from simulated tank supernatants and has studied polymer particle for cesium separation. Marginal separation capabilities compared with traditional ion exchange material have been found.

Northern Illinois University has coated strontium-selective extractant onto magnetic particles and has tested them with a Hanford tank supernatant having high sodium and hydroxide concentrations, 8 M and 6 M, respectively. They obtained  $K_d$  values in the range of 100-450. These studies will continue.

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## BENEFITS

By implementation of this technology at various sites, DOE can seek large cost savings by 1) recovering and concentrating TRU, thus reducing the volume of waste that must be disposed of as glass, 2) recovering and concentrating species that are deleterious to low-level waste forms (cesium and strontium), and 3) reducing public and occupational risk.

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## EM FOCUS AREA

High-Level Waste Tank Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

This project is a collaboration involving representatives from the national laboratories, universities, and industry. Collaborating parties include ANL, Bradtec-US, Northern Illinois University, and the University of Illinois. The University of Illinois is working with ANL to develop a system for TRU removal from dissolved sludge; Northern Illinois University is responsible for work on a strontium selective extractant. The TRU and the strontium system will then be tested on actual Hanford supernatant and sludge. Initial evaluation and feasibility studies are being done by Bradtec-US. ANL will evaluate the Bradtec system with the initial pretreatment module (IPM) applications at Hanford.

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## 1.6 EVALUATION OF IMPROVED TECHNIQUES FOR REMOVAL OF STRONTIUM AND CESIUM FROM PROCESS WASTE WATER AND GROUND WATER

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### TASK DESCRIPTION

This project will test new sorbent materials, ion-exchange materials, or other processes for waste water decontamination that might be more selective for the removal of strontium and cesium than standard treatment methods. These materials will be tested in the laboratory with 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.

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### TECHNOLOGY NEEDS

Most DOE sites manage very large volumes of dilute liquid wastes that must be treated before discharge to the environment. The waste is mainly composed of contaminated ground water and cooling water. Waste water generated from research operations, reactors, and radiochemical production facilities also contributes to the overall waste inventory. The principal contaminants of the waste are  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ , 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 radioactive wastes is very expensive, and new processes are needed to minimize the volume of secondary waste produced.

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### ACCOMPLISHMENTS

The work for this project will focus on the use of crown ether based sorbents for the removal of strontium and cesium from process waste water. The materials are developed by IBC Advanced Technologies under the SuperLig<sup>®</sup> trademark and are available on solid supports, such as silica gel. In cooperation with 3M Corporation, the SuperLig<sup>®</sup> sorbents have been immobilized on membranes that will permit the application of the crown ether separations in process column applications. The work plan for FY94 includes acquiring samples of SuperLig<sup>®</sup>607 and developing the critical kinetic and equilibrium data for the removal of  $^{137}\text{Cs}$  from process wastewater simulant. Results will be compared with those obtained using the more standard chabazite zeolite treatment.

A process water simulant is currently being defined, based on recently acquired analytical data describing the composition of the process waste water going into the ORNL Process Waste water Treatment Plant. A stock quantity of TSM 300 chabazite zeolite, purchased from Steelhead Specialty Minerals, has been sized and completely converted to sodium form. Batch sorption studies using the treated zeolite will begin shortly in the waste water simulant to provide a basis for comparison with the SuperLig<sup>®</sup>607 material.

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## BENEFITS

Successful tests of separation technologies for strontium and cesium removal from process waste water and contaminated ground water may lead to large-scale demonstrations. These technologies may eventually be deployed on similar waste remediation operations at Hanford, SRS, ORNL, INEL, or other DOE sites that may generate large volumes of secondary, slightly contaminated process/ground/or surface waters.

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## EM FOCUS AREA

Contaminant Plume Containment and Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

This project is being done at ORNL in collaboration with PNL, 3M Corporation, and IBC Advanced Technologies. The SuperLig® technology developed by IBC Corporation under contract from PNL was originally intended for use in HLW tank remediation. The technology is now being adapted for the removal of strontium and cesium from process wastewater. The initial testing will be done at ORNL with potential for use across the DOE Complex.

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TTP Number: OR132012

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## 1.7 CONTINUOUS ANNULAR CHROMATOGRAPHY

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### TASK DESCRIPTION

This task addresses application of a variation of the continuous annular chromatograph (CAC) to achieve continuous ion exchange or sorption. A continuous ion exchanger (CIEX) and extraction chromatography are concepts developed at ORNL to separate dissolved metal species from supernatant fluids associated with tank sludges.

Fixed-bed units employed in tandem for pseudo-continuous services are typically oversized to provide convenient cycle times. In the past, research at ORNL has focused on continuous chromatography, where the feed stream is completely resolved into its separate components by the action of a relatively large flow of carrier. However, recent research has shifted toward efficient use of the resin bed and elution stream by developing the CIEX.

A minimal quantity of resin is required and a minimal inventory of sorbed material is produced by CIEX. The aim is to make efficient use of the resin bed and elution streams. Both the limited inventory of sorbate and annular geometry of the CIEX offer considerable advantages for the control of criticality and radiation exposure. Another advantage for radiochemical work is the comparatively short residence time of material on the column. CIEX is readily automated and requires a minimal commitment of manpower. In addition, CIEX offers the unique opportunity for continuous multicomponent separations on a single column.

CIEX uses a slowly rotating annular bed of particles to continuously contact the sorbent with feed and eluant streams. CIEX has by far the best performance of the continuous sorption concepts proposed. It is free from the related resin attrition problems associated with the other moving bed processes and large fixed-bed operations.

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### TECHNOLOGY NEEDS

Continuous sorption is an innovative process with broad application to the many separation technologies that rely on solid sorbents. A major drawback of the present fixed-bed technology is that it is a batch operation process requiring considerable cyclic startup costs and dead time. A truly continuous process offers superior performance by improving column efficiency, reliability, and safety.

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### ACCOMPLISHMENTS

This new concept was successfully demonstrated at the end of FY93 by efficiently removing and concentrating rare earths from an aqueous nitric acid stream on a strong-acid cation resin. The basic loading and elution characteristics were readily predicted from fixed-bed tests and showed essentially the same degree of separation as achieved during the analogous fixed-bed test. Present work includes CIEX experiments aimed at refining operations for improved performance, development of a predictive model for CIEX performance, and a pilot-scale test of CIEX on a "real" waste stream.

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### BENEFITS

This work will result in a broadly applicable separations technology that is superior to other concepts of continuous ion exchange and fixed-bed processes.

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### FUTURE WORK

Future goals include the development of a multi-component separations capability (i.e., by step/gradient elution), addition of improved instrumentation and controls for radiochemical work, and remote (modular) handling features. The ultimate goal is to develop continuous sorption as an impor-

tant tool for efficient separations in radiochemical processing and cleanup.

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TTP Number: OR132012

## BIBLIOGRAPHY OF KEY PUBLICATIONS

None at this time.

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## EM FOCUS AREA

High-Level Waste Tank Remediation

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## 1.8

# “CARBOLLIDE”/COBALT DICARBORANE ANION PROCESS DEVELOPMENT FOR <sup>137</sup>Cs DECONTAMINATION

## TASK DESCRIPTION

This project seeks to evaluate, test, and develop the use of cobalt dicarbollide and related reagents for the extraction of cesium from alkaline supernatant solutions and salt cake at SRS. A solution is needed to processing problems that have arisen at the facility as a result of using the tetraphenylborate precipitation process. This task is designed to identify possible alternatives. Elements of the task include acquisition of the precipitating reagent, radioactive and nonradioactive testing of its physical properties, and its effects on borosilicate glass. See Figure 1.8. They also include reproducible demonstration of the decontamination factors for cesium removal from radioactive and nonradioactive wastes and the examination of the factors controlling the achievable decontamination factor. Demonstration of direct feed of the precipitate to borosilicate glass, evaluation of the glass properties, and the long-term stability of the compound are also included. The purpose of these elements is to provide an accurate comparison of the key technical viability factors between tetraphenylborate and other possible contenders for the cesium removal process.

## TECHNOLOGY NEEDS

This technology addresses a specific problem within part of the DOE Complex. It will be examined as a substitute for the tetraphenylborate precipitation used in the In-Tank Precipitation Process at SRS. The tetraphenylborate precipitation has encountered difficulties because it contains four benzene functionalities per molecule. A replacement is desired.

## ACCOMPLISHMENTS

The decomposition of the cobalt dicarbollide anion in sodium hydroxide solution has been shown to be apparent first order with a half-life of 94 days in 1.0 M NaOH at 40°C and 7.3 days at 60°C. Continuous monitoring and control of temperature would be required to minimize cobalt dicarbollide loss and byproduct formation in process applications, rendering it unsuitable as a direct replacement for tetraphenylborate at the SRS. The solubility of cesium cobalt dicarbollide in 4 M NaOH<sub>3</sub> and 1 M NaOH solution ( $K_{sp}$  about  $5 \times 10^{-6} M^2$  at 40°C) is higher than cesium tetraphenylborate, contributing to the unsuitability of the cobalt dicarbollide anion

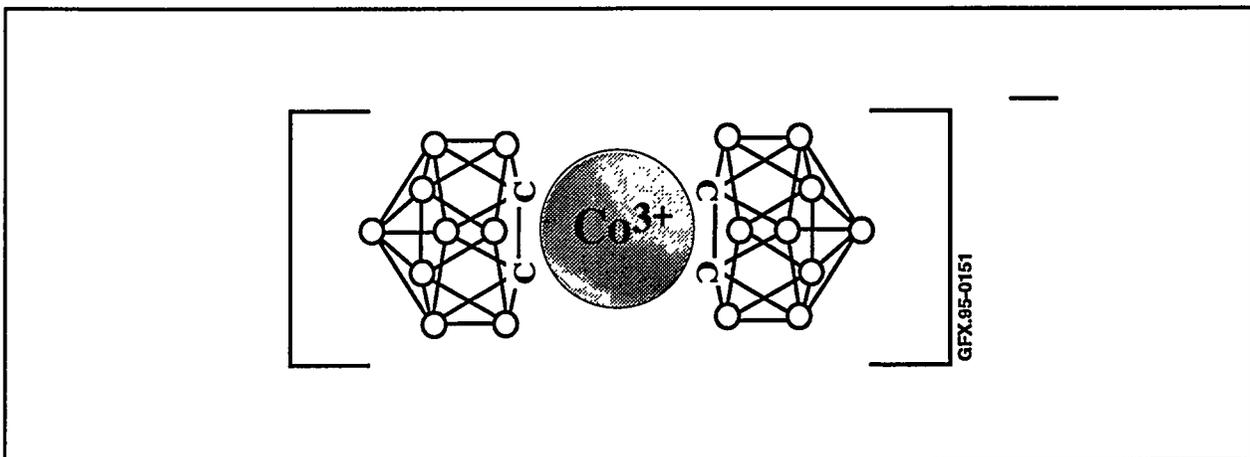


Figure 1.8. Cobalt Dicarbollide  $[Co(C_2B_9H_{11})_2]^-$ .

as a replacement for tetraphenylborate. The cobalt dicarbollide anion appears to precipitate with sodium at ambient temperature (greater than 30°C) and high sodium concentration (5 M). Synthesis and evaluation of ten cobalt dicarbollide derivatives and related boranes as precipitating reagents have been completed. None of the compounds studied have proven to be suitable derivatives due to higher solubility. Further testing of additional compounds is under way.

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## BENEFITS

This technology has the potential to significantly simplify the current tetraphenylborate flowsheet for radioactive <sup>137</sup>Cs decontamination, eliminate benzene handling and incineration, and simplify the process by eliminating hydrolysis.

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## EM FOCUS AREA

High-Level Waste Tank Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

This work is being done as a collaborative effort between Savannah River Technology Center (SRTC) and Clemson University. Prof. James Fanning from the Department of Chemistry at Clemson University is working on finding alternatives for tetraphenylborate. All of the radioactive or "hot" testing is being done at the SRTC.

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TTP Number: SR132007

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# ADVANCED SOLVENT EXTRACTION

Section 2.0



## 2.0

## ADVANCED SOLVENT EXTRACTION

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Many separation processes achieve selectivity through the use of complex organic compounds. Any organic compound can be degraded by nuclear radiation; the energy of the radiation is large compared to the bond strengths in organic compounds. Solvent-extraction separation processes are particularly attractive for processing nuclear waste because the organic materials involved can be continuously washed of radiolysis products.

The countercurrent design of processes such as plutonium-uranium extraction (PUREX), which involves tributylphosphate (TBP) in a kerosene-like solvent provides thorough separation of certain targeted sets of radionuclides. Such processes have been tested and used at ORNL and Hanford sites, resulting in considerable experience in solvent extraction separations in the nuclear industry. New solvent extraction processes, involving complex ligands in the solvent that can significantly expand the number of radionuclides which can be separated from complex waste streams are being developed.

The ESP Program is funding work on integrated, composite solvent extraction systems that separate cesium, strontium, actinides, and some other species from acid waste streams. Work is also being funded on a novel extraction system separating technetium from complex alkaline waste streams. The ESP program supported the following tasks in this category during FY94:

- Advanced Integrated Solvent Extraction;
- Alkaline-Side Extraction of Technetium from Tank Waste Using Crown Ethers and Other Extractants;
- "TALSPEAK" Chemistry; and
- Aqueous Biphasic Systems for Radioactive Waste Pretreatment.

## 2.1 ADVANCED INTEGRATED SOLVENT EXTRACTION

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### TASK DESCRIPTION

The purpose of this work is to develop new advanced solvent extraction and recovery processes in support of an extensive separations strategy that can reduce the complexity and cost of the chemical pretreatment of dissolved sludge to produce raffinates and effluent streams to meet specifications of Class A LLW.

This task has three objectives: 1) minimize the number of processes needed to implement extensive separations, 2) minimize the number of times that the initial volume of dissolved sludge must be handled, and 3) concentrate the product streams to reduce the scale of the operation to the smallest possible level. The requirements for an advanced chemical separations system to meet this goal are achievement of the required decontamination factors, feasibility of engineering scale-up, and stability in chemical and radiolytic properties. A decrease in the use of hazardous substances and a reduction in waste volume are also part of the requirements.

The new separation scheme comprises a series of novel processes designed to extract and recover thorium, uranium, TRUs (neptunium, plutonium, americium, curium),  $^{90}\text{Sr}$  and  $^{99}\text{Tc}$  from dissolved sludge waste in the Hanford storage tanks. See Figure 2.1. For example, a combined Strontium Extraction/Transuranic Element Extraction Process (SREX-TRU-EX) is being examined to extract strontium, technetium, uranium, and TRUs and to partition uranium and technetium from strontium and TRUs. A SREX Process is being examined to separate strontium from TRUs, lanthanides, and barium. An actinide/lanthanide resin is being examined to separate americium from lanthanide.

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### TECHNOLOGY NEEDS

The advanced chemical separation processes for a Total Radionuclide Extraction Process (TOREX flowsheet) will be applicable in the chemical pretreatment of waste retrieved from storage tanks at DOE sites (e.g., Hanford, SRS). The objective of using 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  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ , and  $^{99}\text{Tc}$  in the dissolved sludge waste.

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### ACCOMPLISHMENTS

A process solvent has been developed that can remove, in a single process, thorium, uranium, neptunium, plutonium, americium, the lanthanides, strontium, and technetium from synthetic dissolved sludge waste in the Hanford single- and double-shell storage tanks. The TRU elements (neptunium, plutonium, and americium) and strontium are then selectively stripped from the uranium and technetium. The latter point is of interest because it is not then necessary to vitrify uranium. A technetium-specific resin has been developed to remove technetium from uranium; thus, the uranium fraction is suitable for recycle. The concentrated TRU-strontium product stream is then treated by the SREX process.

A process solvent has been developed that is similar to the front-end process solvent that separates strontium, neptunium, and plutonium from barium, the lanthanides, and americium. A major feature of this process is that barium can now be separated from strontium, which could reduce the number of waste glass canisters going to the geologic repository. The raffinate (barium, the lanthanides and TRU fraction) is now a suitable feed for the lanthanide separation system.

Cold and hot test runs are being performed in a continuous mode using centrifugal contactors.

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## BENEFITS

The anticipated benefit of the TOREX flowsheet is the minimization of HLW that must be vitrified and the recovery of valuable TRUs (e.g.  $^{237}\text{Np}$ ) and uranium that could have beneficial uses or be recycled. The TOREX flowsheet should also reduce the cost of chemical pretreatment of waste.

## EM FOCUS AREA

High-Level Waste Tank Remediation

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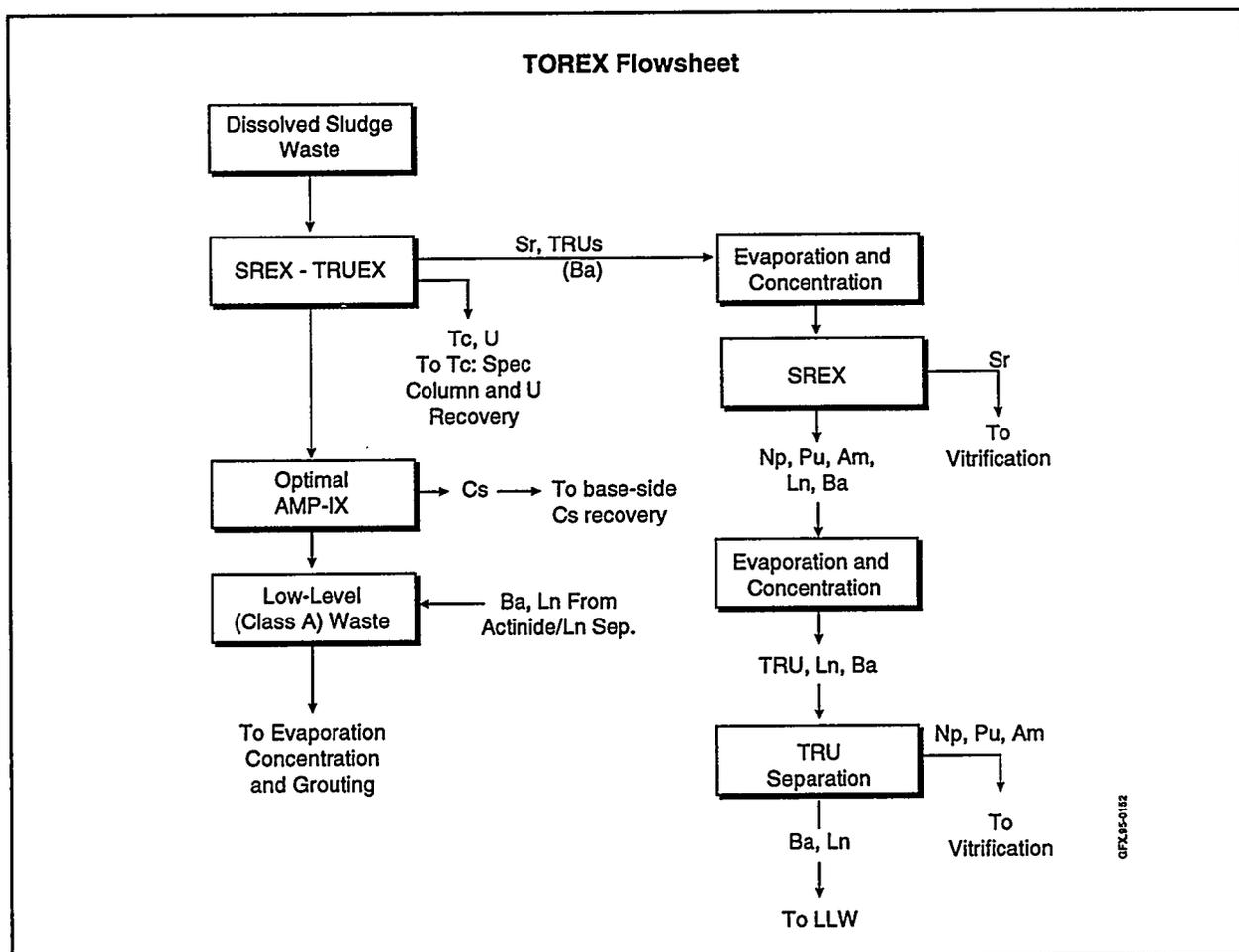


Figure 2.1. A Total Radionuclide Extraction (TOREX) Process Flowsheet.

TTP Number: CH232005

## BIBLIOGRAPHY OF KEY PUBLICATIONS

None at this time.

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## 2.2 ALKALINE-SIDE EXTRACTION OF TECHNETIUM FROM TANK WASTE USING CROWN ETHERS AND OTHER EXTRACTANTS

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### TASK DESCRIPTION

The primary objective of this project is to develop an efficient solvent extraction and stripping process using crown ethers or other extractants to remove technetium from alkaline tank wastes. The tank wastes at the Hanford site and other locations (e.g., Melton Valley Storage Tanks (MVST) at ORNL) are typically strongly alkaline and contain technetium, actinides, and other radioactive contaminants. These contaminants may be found in the aqueous supernates under certain conditions, or they may be solubilized from the sludge during washing or leaching operations.

Waste streams with high concentrations of salts such as sodium nitrate pose special problems for current extractive technology. Certain crown ethers are being investigated as potential solvent extraction reagents for technetium removal because the high-salt condition actually promotes technetium extraction and because an inexpensive water wash effects stripping of the technetium from the solvent. Experimental efforts are currently focused on evaluating the most effective combination of solvent components, including crown ether, diluent, and modifier. New crown ethers are being synthesized and compared with commercially available crown ethers for their effectiveness in technetium extraction and stripping.

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### TECHNOLOGY NEEDS

Technetium found in tank wastes primarily at Hanford and ORNL poses long-term risks due to its long half-life and environmental mobility. In addition, its volatility upon thermal treatment raises short-term safety issues connected with vitrification of the waste. Thus, a need has arisen to develop processes for the removal of technetium from the waste and to deal with its special handling and storage problems.

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### ACCOMPLISHMENTS

The results obtained to date demonstrate that certain crown ethers dissolved in a suitable diluent extract technetium as pertechnetate, the expected form in waste, from high-nitrate-containing alkaline waste simulants. Furthermore, it has been demonstrated that the extracted technetium can readily be stripped with water. Extraction and stripping efficiencies of 98 percent or better are attainable with two-stage extraction and two-stage stripping at unit phase ratio using waste simulants. One of the new crown ethers exhibited superior extraction and stripping ability compared with the best commercial crown ether. In general, the extraction and stripping properties depend markedly on the type of diluent and modifiers employed. Certain modifiers, in fact, have been shown to enhance extraction, permitting lower effective concentrations of the crown ether. A patent application for a process for removal of technetium from tank wastes using crown ethers has been completed.

Future work will use the knowledge gained recently to select the most promising extraction systems and test them using actual tank waste. Tests with simulants will proceed toward multi-step extraction and stripping procedures, characterization of selectivity and stability under realistic conditions, and evaluation of options for harvesting the technetium from the strip solution. Goals to improve the 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 aspects. Results to date point to the likelihood that a highly effective, versatile, and environmentally friendly extraction system can be developed.

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## BENEFITS

Removing actinides and key fission products from certain tank wastes can allow relatively inexpensive disposal as LLW. This practice can significantly reduce the volume of waste that must be stored in a geologic repository. Significant cost savings are anticipated if pretreatment processes add little or nothing to the waste volume. Direct extraction from alkaline tank waste avoids expensive acidification and consequent waste-volume increase.

Proposed extraction systems apply to complexant concentrate HLW stored at the Hanford Site and thus target a major safety concern. Developed solvent extraction methods may be applicable to technetium removal from several types of alkaline solutions likely to be generated in a complex flow sheet.

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## EM FOCUS AREA

High-Level Waste Tank Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

In this project, there is a role for an industrial partner to become involved as a supplier of crown ethers in large quantity at reasonable costs. 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: OR132012

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**TASK DESCRIPTION**

The Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Complexes ("TALSPEAK") process separates the trivalent actinides from the lanthanides. The method is based on the preferential complexation of the trivalent actinides by an aminopolyacetic acid. At the same time, the lanthanides are more strongly extracted by a monoacidic organophosphate or phosphonate. Single-stage separation factors between neodymium (the least extractable lanthanide) and americium, or curium, are about 50.

This task is a continuation of research and development on the TALSPEAK chemistry to resolve potential problems with the deleterious effects of impurity ions such as zirconium on the lanthanide extraction and loading. Methods of purifying the extractants from the radiolytic degradation products for recycling and reuse will also be examined.

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**TECHNOLOGY NEEDS**

The production of nuclear energy generates highly radioactive spent fuel that must be stored safely. The potential hazard posed to future generations by long-lived radionuclides (thousands of years), such as actinides and some fission products, is being addressed by the development of new technology.

If the long-lived isotopes are recycled, reused, and/or destroyed, the only potential hazard remaining would be from short-lived fission products that will disappear after a few hundred years of storage. Under such a program, there is no significant legacy of radioactive wastes, and the radioactive waste hazard can fall below that of the original uranium ore after a relatively short period.

The different groups of radionuclides can be partitioned using a variety of methods. One crucial aspect of partitioning is the separation of the long-lived, highly radioactive actinides from the rather similar, short-lived, or nonradioactive, lan-

thanides. Because of their almost identical chemical behavior, the separation between actinide and lanthanide elements is a difficult process. One of the very few methods that can successfully and efficiently accomplish this difficult separation is the TALSPEAK separation process.

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**ACCOMPLISHMENTS**

The experiments showed that some of the perceived problems in the TALSPEAK separation process, such as the deleterious effects of some impurity ions, the need to control pH and reagent concentrations within a narrow range, and the potential loss of the organic extractant, can be eliminated or minimized by replacing the conventionally used carboxylic-acid-buffers, lactic or glycolic, by citric acid. The cold experiments showed that replacing the glycolic or lactic acid by citric acid eliminates or greatly reduces the deleterious effects produced by impurities such as zirconium. Zirconium concentrations as high as  $10^{-3}$  M to  $10^{-2}$  M will not produce a "third phase" (higher pH can tolerate even higher zirconium concentrations).

The citrate-based TALSPEAK can tolerate appreciable changes in pH and reagent concentrations, maintaining an adequate lanthanide extraction. The relatively slower kinetics observed for the heavy lanthanides is balanced by their significantly higher extraction. Visual observation of relative volumes did not show any significant loss of organic phase under a wide variety of conditions.

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**BENEFITS**

This work should provide invaluable results necessary to evaluate lanthanide/actinide separations for waste minimization.

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## PROPOSED FUTURE ACTIVITIES

The cold test results using a citrate-based TALSPEAK, along with information accumulated during the testing, indicate that this technology can be effectively deployed after completion of further hot developmental work. Proposed future work includes the use of americium and curium tracers ( $^{243}\text{Am}$ ,  $^{247}\text{Cm}$ , or  $^{248}\text{Cm}$ ) first in batch tests followed by multistage processing to evaluate the actinide-lanthanide separation by a citrate-based TALSPEAK.

The behavior of uranium, plutonium, and neptunium species has to be determined. The interface of separative schemes such as the TRUEX process with TALSPEAK should also be analyzed. The combination TRUEX-TALSPEAK can potentially generate relatively pure lanthanide and actinide fractions with exclusion of almost any other impurity. Radiation effects also must be completely evaluated.

All available information indicates the process is robust with respect to radiolytic damage. The warm tests with tracer levels of americium and curium should be followed by small-scale multistage treatment of actual wastes.

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## EM FOCUS AREA

High-Level Waste Tank Remediation

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TTP Number: OR132012

## BIBLIOGRAPHY OF KEY PUBLICATIONS

None at this time.

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## 2.4 AQUEOUS BIPHASIC SYSTEMS FOR RADIOACTIVE WASTE PRETREATMENT

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### TASK DESCRIPTION

This project seeks to develop aqueous biphasic separation (ABS) systems for the pretreatment of supernatant solutions from USTs. The aqueous biphasic separations permit the extraction and recovery of dissolved inorganic ions from high ionic strength acid or alkaline electrolyte solutions. The ABS systems can be generated by the addition of polyethylene glycols and polypropylene glycols to high ionic strength electrolyte solutions.

The primary objective is to remove long lived radionuclides such as  $^{99}\text{Tc}$ ,  $^{129}\text{I}$ , and  $^{79}\text{Se}$  from alkaline solutions. Selective removal of these species by aqueous biphasic separation could be coupled with ion exchange processes to remove cationic species, such as  $^{137}\text{Cs}$  and TRUs, from alkaline solution. This would permit near surface disposal of the bulk of the alkaline supernatants and dissolved salt cake from USTs. The extractions could be carried out without pH adjustment. The only reagent added to the waste stream would be a minimum amount of water to ensure dissolution of the salt cake.

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### TECHNOLOGY NEEDS

Near-surface disposal of single-shell tank supernatants, after conversion to grout, requires that long-lived isotopes such as  $^{137}\text{Cs}$ ,  $^{129}\text{I}$ ,  $^{99}\text{Tc}$ , and  $^{79}\text{Se}$  be removed. Ion exchange technology for removal of Cs from alkaline solutions is well developed, while little or no technology is available for recovery of iodine, technetium, or selenium from high ionic strength alkaline solutions. Acidifying the supernatants would be required for recovery of technetium and cesium by the TRUEx or SREX processes, resulting in significant increases in waste volume. The process effluents would then have to be made alkaline again before conversion to grout. In addition, technetium, iodine, and selenium are not extracted well by the TRUEx process. Cesium recovery requires the use of a crown ether extractant in the SREX solvent.

### ACCOMPLISHMENTS

The goal has been to develop highly selective extraction systems that produce minimal amounts of secondary wastes. In working toward this goal, it was found that biphasic extraction systems based on polypropylene glycols (PPGs) offer certain advantages over polyethylene glycol (PEG) based systems. The PPGs are good candidates for biphasic separations because of their lower water solubility, which reduces polymer losses through dissolution into the aqueous waste stream.

Extraction of  $\text{TcO}_4^-$  from simulated tank waste supernatants by PPGs is rapid. Extraction selectivities are significantly improved over those obtained with PEGs. Partition coefficients of  $\text{TcO}_4^-$  range between 10 to 100, while the partition coefficients of many tank waste constituents (e.g.,  $\text{Al}^{3+}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{F}^-$ ) are below  $10^{-3}$ . Extraction of  $\text{TcO}_4^-$  as a function of PPG molecular weight shows an inverse relationship between  $D_{\text{Tc}}$  and PPG molecular weight. This extraction behavior is related to the degree of hydration of the polymer. Interestingly, extraction selectivity for  $\text{TcO}_4^-$  over  $\text{Na}^+/\text{NO}_3^-/\text{NO}_2^-$  increases dramatically in going from PPG-425 to PPG-725. The separation of  $\text{TcO}_4^-$  from  $\text{NO}_3^-$  has traditionally been difficult.

With PPG-725, single-stage separation factors greater than 3000 between  $\text{TcO}_4^-$  and  $\text{Na}^+/\text{NO}_3^-$  were obtained. Additionally, secondary waste production is minimized by the fact that deionized water can be used to strip  $\text{TcO}_4^-$  from the loaded polymer phase. Thus, PPG-725 could be used to extract technetium from high ionic strength tank supernatants and then regenerated by stripping with deionized water. Currently, waste surrogates are used in evaluating the performance of a membrane extraction system that uses the PPG chemistry.

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## BENEFITS

An ABS system to remove long-lived isotopes from tank waste supernatants could reduce the costs associated with the disposal of this waste stream. An extraction technique capable of handling alkaline or caustic waste streams would also significantly reduce the volume of material going to LLW and significantly reduce the costs of pretreatment.

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## EM FOCUS AREA

High-Level Waste Tank Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

In addition to ANL, this project involves the efforts of researchers at Northern Illinois University. The technology will be disseminated to the various sites that are burdened with volumes of caustic solutions containing high concentrations of nitrate, nitrite, and carbonate, and allow for the removal of iodine, selenium, and technetium from these waste streams. In addition, the work may be expanded to allow for the recovery of RCRA metals such as mercury, chromium, and lead from HLW.

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TTP Number: CH232006

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**WASTE  
SOLIDS TREATMENT**

**Section 3.0**



## 3.0

# WASTE SOLIDS TREATMENT

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Chemical separations mechanisms such as ion exchange, sorption, and solvent extraction act on mobile species in fluid phases. Many important waste streams are solid or include solids. If the species to be separated are bound in the solids, the solids must first be dissolved, leached, or otherwise treated to provide mobile species. The ESP Program supports work in pyrochemical processing. Both solid-vapor and solid-melt processes are investigated. An example of the solid-vapor process is the halogenation of plutonium waste and volatilization of essentially plutonium-free salts leaving a plutonium waste stream of reduced volume. An example of the solid-melt process is calcination of tank HLW, resulting in the decomposition of nitrate, nitrite, and organics to generate a sodium hydroxide melt into which various oxides dissolve; i.e., fusion. Some solids remain when the fused material is cooled and dissolved in water, constituting a separation step. These solids can be treated separately.

The ESP Program also supports work on leaching or dissolving HLW tank sludges, with emphasis on sludges at Hanford. Most of the sludge in the MVSTs at ORNL resulted from pilot-scale testing of the same processes that have resulted in the generation of large quantities of tank sludge at Hanford.

Because of the similarity of MVST and Hanford sludges, and because MVST sludge is currently more accessible than Hanford sludge, ESP is collaborating with the High-Level Waste Tank Remediation Focus Area to determine the behavior of the sludges when reacted with dilute and concentrated alkali and acid. The ESP Program is also trying to determine the nature of the resulting alkaline or acid solutions that would become the feed for chemical separations processes. In addition, ESP is funding work on leaching transuranic species from sludges using organic sequestrants and oxidizing agents.

The ESP supported the following tasks in this category during FY94:

- Distillation Separation of Chloride Salts from Plutonium;
- Calcine Residue Treatment: Volume Reduction for High-Level Waste Sludges;
- Pyrochemical Treatment and Immobilization of Idaho Chemical Processing Plant HLW Calcine;
- Sludge Washing and Dissolution of Melton Valley Storage Tank Waste;
- Aluminum Removal from Washed Sludge;
- Colloid Formation in Sludge Washing; and
- Selective Leaching of Tank Sludge by the ACT\*DE\*CON™ Process.

## 3.1 DISTILLATION SEPARATION OF CHLORIDE SALTS FROM PLUTONIUM

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### TASK DESCRIPTION

In this task, distillation separation of waste salts from past pyrochemical processing of plutonium is investigated. This process has the potential to provide clean separation between the salt and the actinides with minimum amounts of secondary waste generation. The process could produce chloride salt that could be discarded as LLW and a concentrated actinide oxide powder that would be stored as special nuclear material.

Distillation separation is based on the large difference in vapor pressures 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 achieve a good separation. Therefore,  $\text{PuCl}_3$  must be converted to an oxide or oxychloride through an oxidation process. An oxygen sparge process developed at LANL has proven to be effective in accomplishing the conversion. It can be ultimately combined with a distillation separation process.

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### TECHNOLOGY NEEDS

Residue and waste salts have resulted across the DOE Complex from past pyrochemical processing of plutonium. The problem is especially acute at DOE's Rocky Flats Plant (RFP), where approximately 20 metric tons of salt contain the largest fraction of DOE's plutonium inventory.

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### ACCOMPLISHMENTS

Initial experiments performed with plutonium salts thus far have shown distillation is viable. The plutonium content has been reduced from tens of percent to the ppm range. Clean separation of the salt from plutonium oxide powder has been achieved.

It is expected that as improved equipment and processing is developed, the plutonium content of the distilled salt will be lowered below the target level of 1 ppm  $^{239}\text{Pu}$ . This will allow disposal of the salt as LLW. The theoretically achievable level is many orders of magnitude below 1 ppm.

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### BENEFITS

The proposed salt distillation process, if successfully demonstrated, will be operationally simpler, generate less waste, and 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 disposed of as LLW.

By significantly reducing the amount of TRU-level waste produced, the salt distillation process would reduce off-site storage costs by a factor of 55:1, producing savings to DOE of about \$50 million. The off-site costs of storing a drum of TRU-level waste at the Waste Isolation Pilot Plant (WIPP) are currently estimated to be \$10,000/drum. The wastes resulting from the salt distillation process are expected to be LLW, which has a disposal cost of about \$50/drum. The salt distillation process would also generate 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.

The salt distillation process could also produce other savings. For example, the process could treat an additional 6105 kg of TRU-level salt (below the economic discard limit) that is classified as waste rather than residue. It should be noted that these estimates conservatively assume that the costs for the two processes are roughly equal; in fact, the aqueous process is significantly more equipment intensive.

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## EM FOCUS AREA

Facility Transitioning, Decommissioning, and Final Disposition

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## COLLABORATION/TECHNOLOGY TRANSFER

This is a joint project involving collaboration of LANL and RFP. In addition to the contamination at Rocky Flats, both Lawrence Livermore National Laboratory (LLNL) and LANL have an inventory of waste salts that can be treated by salt distillation. There is also a possibility that vacuum distillation can be used to treat some of the fluoride tank sludges at Hanford.

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## 3.2 CALCINE RESIDUE TREATMENT: VOLUME REDUCTION FOR HIGH-LEVEL WASTE SLUDGES

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### TASK DESCRIPTION

The objective of this task is to reduce the volume of residue remaining from calcination/dissolution (C/D) treatment of Hanford site tank waste. Literature studies and laboratory tests with simulated and actual Hanford tank waste have shown that calcination destroys organic constituents, transforming nitrates and nitrites to hydroxide with the release of off-gases. The production of a hydroxide melt in the calcination step transforms major components of the tank waste sludge (such as aluminum hydroxide, chromium hydroxide and phosphate) to water-soluble salts. A water-insoluble residue remains following C/D treatment. The residue consists of transition metal, bismuth hydroxides, alkaline earth salts (such as carbonates, sulfates, and phosphates), and sodium aluminosilicates.

Iron, nickel, and bismuth were identified as elements that will control the volume of HLW glass produced from C/D residue. With this evaluation, ten candidate processing technologies were identified and evaluated. Laboratory experiments were conducted with the most promising technologies — magnetic separation, electrostatic separation, electrodeposition, and carbonylation. Also identified and defined were five prototypical Hanford tank waste types. The thermodynamic response to calcination of each defined waste type was determined.

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### TECHNOLOGY NEEDS

The residue remaining from C/D processing contains TRU elements (primarily plutonium and americium), and will thus constitute feed for vitrification to HLW glass. Incentive exists to reduce the quantity of HLW glass by removing non-radioactive bulk components from the residues. This task addresses that need by applying metallurgical and ceramic processing expertise and technology.

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### ACCOMPLISHMENTS

In laboratory experiments using a simulated C/D residue, four methods of C/D residue quantity reduction were tested. Of the four technologies tested, hydrogen reduction followed by carbonyl volatilization satisfied the stated objectives of removing iron, nickel, and bismuth from the residue with minimal secondary waste streams. In turn, a treated residue directly amenable to vitrification was produced. The carbonylation treatment has been demonstrated with C/D residues derived from genuine Hanford tank waste. The tests produced a separated, nonradioactive, iron-rich deposit and a treated residue reduced in weight by 20 to 30 percent.

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### BENEFITS

C/D is an alternative to the Tri-Party Agreement (TPA) reference pretreatment processing technology, water, and alkaline washing. Laboratory tests with genuine waste conducted in FY93 and FY94 showed that more of the bulk waste is solubilized by C/D than by simple water washing. Benefits from the destruction of organic complexing agents, nitrate, and nitrite also are realized by C/D processing of genuine waste. The reference flowsheet water/alkaline wash approach does not address these waste pretreatment goals, thus necessitating separate organic destruction and NO<sub>x</sub> abatement process steps.

Chief among the components dissolved and removed from the insoluble high-level fraction are aluminum, chromium, and phosphate. Because of the difficulty of incorporating aluminum, chromium, and phosphate in vitrified (glass) waste forms, removal of these components is significant in minimizing the volume of HLW glass. For example, dissolution of aluminum from a sludge containing large concentrations of aluminum increased from 5 percent (water washing) to 99 percent (C/D). Similarly, chromium dissolution from a sludge rich in

chromium improved from 3 percent (water washing) to 99.9 percent (C/D) while phosphate dissolution improved from 20 percent (water washing) to 99 percent (C/D) in a phosphate-rich sludge.

Calcination/dissolution also addresses processing problems that currently require additional process steps in the reference flowsheet. First, C/D destroys organic complexing agents responsible for solubilizing  $^{90}\text{Sr}$  (a fission product) and  $^{241}\text{Am}$  (a transuranic isotope) in waste liquors. Once the organics are destroyed, the  $^{90}\text{Sr}$  and  $^{241}\text{Am}$  become insoluble in the product alkaline C/D solution and exhibit high-level solids. In the reference process, the organics cause these radionuclides to report to the nominal "low-level" stream rather than segregating to the insoluble high-level fraction. The reference flowsheet will thus require a separate organic destruction step (or a currently unknown  $^{90}\text{Sr}/^{241}\text{Am}$  extraction process) to address this problem.

In the reference flowsheet, the nitrate and nitrite, most of which is soluble, will be consigned to the low-level glass plant. Thermal decomposition of the nitrate and nitrite in the glass melter can cause foaming in the glass. Oxides of nitrogen ( $\text{NO}_x$ ) produced during the thermal decomposition also must be scrubbed before discharge to the atmosphere. Therefore, either a separate nitrate/nitrite destruction process unit must be installed ahead of the melter, or glass foaming must be tolerated and a large capacity  $\text{NO}_x$  removal capability installed for the melter. In contrast, C/D readily converts nitrate and nitrite present in the Hanford waste to hydroxide and benign off-gases. Therefore, the C/D process eliminates the problems of  $\text{NO}_x$  off-gas at the low-level glass plant.

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## EM FOCUS AREA

High-Level Waste Tank Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

Collaborators on this project include PNL, Westinghouse Science and Technology Center, and the U.S. Bureau of Mines. In addition, it is anticipated that there will be opportunities to consult with Russian counterparts to benefit from their knowledge of actinide chemistry. In return they will become better acquainted with the methods being pursued in tank waste remediation. The data and recommendations developed through this activity will first be transferred to the Tank Waste Remediation System, and then to related projects.

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TTP Number: RL432004

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### 3.3 PYROCHEMICAL TREATMENT AND IMMOBILIZATION OF IDAHO CHEMICAL PROCESSING PLANT HIGH-LEVEL WASTE CALCINE

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#### TASK DESCRIPTION

This task seeks to establish the feasibility of a pyrochemical treatment for Idaho Chemical Processing Plant (ICPP) HLW calcine. The pyrochemical treatment consists of high-temperature processing for the removal of inert materials, electrolytic separation of the actinides, and fission products in a molten metal/molten salt environment.

The work is divided into two phases. In the first phase, the R&D needs associated with demonstrating the feasibility of the pyrochemical treatment will be established. Research and engineering programs to address these needs will be outlined. In the second phase, the technical feasibility of the process will be demonstrated. Scientific and engineering data will be provided for an integrated, small-scale demonstration. Subsequently, an integrated process demonstration will be proposed. A Demonstration, Testing, and Evaluation Test Plan will also be developed.

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#### TECHNOLOGY NEEDS

About 3500 m<sup>3</sup> of radioactive HLW calcine is currently stored at the ICPP. DOE Order 5820.2A directs that all new and readily retrievable HLW be processed and disposed of in a geologic repository according to the requirements of the Nuclear Waste Policy Act (NWPA) as amended. ICPP HLW is a mixed waste. The disposal technology must be developed to support near-term relief on the Land Disposal Restriction (LDR) deadline, as well as meeting long-term LDR compliance for storage. The State of Idaho Non-Consent Order of April 1992 requires operation of a calciner. Storage of the resulting calcine will fall directly under 40 CFR Part 268, which requires further treatment using technologies to be developed.

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#### ACCOMPLISHMENTS

A revised process flowsheet was established based on results of preliminary testing. Extensive thermodynamic calculations on calcine volatiles and chloride volatility processes were conducted. Extensive testing of the calcine volatiles process (to volatilize cesium, cadmium, technetium, and mercury) was completed on nonradioactive pilot-plant calcine and on actual radioactive calcine. Greater than 99 percent of the cesium, 50 percent of the cadmium, 94 percent of the mercury, and 99 percent of the technetium were volatilized from the calcine in 5 hours at 1000°C. This process would be favorable if removing the cesium and technetium in a front-end process would result in facility shielding savings in the remaining treatment portion of the facility.

The chloride volatility process was demonstrated on nonradioactive and radioactive alumina calcine, which represents about 20 percent of the total volume of ICPP calcine. Aluminum and boron oxides were reacted with CCl<sub>4</sub> to produce metal chlorides, which have relatively low volatilization temperatures. More than 86 percent of the mass of the alumina calcine was removed as aluminum chloride, resulting in a significant volume reduction.

Tests with radioactive calcine indicated that no detectable radionuclide contamination was present in the condensed aluminum chloride volatiles. The chloride volatility process did not appear to be feasible with the zirconium-based calcines due to the presence of CaF<sub>2</sub>, which reacts with zirconium and aluminum to form nonvolatile metal fluorides. Removal of the fluoride from the calcine would be required to make this process feasible for zirconium-based calcines. To date, up to 60 percent of the fluoride has been successfully removed in tests conducted at LLNL.

The final process under investigation is the metal reduction process, which has not yet been successfully demonstrated. Some separation of metals from the calcine/salt matrix has occurred, although not to the extent necessary to render the remaining salt a low-level waste.

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## BENEFITS

More than 80 percent by weight of the ICPP HLW calcine material is nonradioactive and nonhazardous. If the nonradioactive material is separated from the radioactive and hazardous components, cost savings to DOE in disposal charges to a geologic repository would be significant. The principal incentive for partitioning actinides from the fission products and the remaining bulk waste is the cost of disposing of the long-lived radioisotopes. By reducing the volume of this waste, potentially billions of dollars can be saved in disposal costs. Furthermore, concentrating the actinide and fission products as metal alloys opens numerous new opportunities for immobilizing, packaging, and storing and/or disposing of the waste.

DOE can realize a potential profound cost savings in reduced numbers of HLW canisters sent to a repository by using a pyrochemical treatment process for ICPP calcine. Glass-ceramic and glass waste forms can immobilize HLW generated by pyrochemical treatment. The waste form would depend on feasibility, processability, and durability. In either case, the anticipated HLW volume reduction is more than twice that of the current most favorable alternative.

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## EM FOCUS AREA

High Level Waste Tank Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

This is a joint project involving INEL and subcontract work by LLNL. Results of this joint effort could be applied to contaminated materials across the DOE Complex if their composition is compatible with a molten salt process.

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TTP Number: ID421201

## BIBLIOGRAPHY OF KEY PUBLICATIONS

None at this time.

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## SLUDGE WASHING AND DISSOLUTION OF MELTON VALLEY STORAGE TANK WASTE

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### TASK DESCRIPTION

The focus of this task is on experimental and modeling research developed to support the comprehensive sludge/supernatant processing flowsheet work conducted for the High-Level Waste Tank Remediation Focus Area. The primary emphasis is dissolution of the tank waste sludge before pretreatment at Hanford.

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 MVST at ORNL are used for experiments on sludge washing and dissolution. The aim of the washing is to minimize the amount of sludge containing TRU through dissolution of the inert components. TRU dissolution at this stage is to be avoided. The sludge residues are then subjected to a series of leachings to try to remove TRUs, leaving a non-TRU residue.

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### TECHNOLOGY NEEDS

The DOE site tank waste disposal strategy should include mixing the sludge with an acid or base before further treatment. The chemical interactions within the sludge must be understood for planning subsequent treatment strategies, such as vitrification, TRUEX, or any of the other high-level waste separation technologies.

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### 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. This information is useful for both MVST and Hanford tank wastes. Frequent discussions between staff from ORNL and PNL help ensure that results of these studies are applicable to sludge treatment at both sites. Two letter

reports on thermodynamic modeling and initial sludge tests have been issued.

Acid treatment of MVST sludge has revealed important aspects of sludge chemistry and treatment strategies: 1) It is difficult to remove cesium from the sludge. Cesium removal required dissolution of sludge solids. 2) Cobalt can be separated from europium by dissolving the cobalt species at pH 6.6 and leaving the europium in the solid. Separation of other species is evaluated by continuing analysis of leachates. 3) A gel formed in acidic leachates that were left undisturbed for several weeks.

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### BENEFITS

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

The technologies tested in this project would potentially benefit all DOE sites that manage alkaline nitrate waste liquids/sludges. An outstanding example of this benefit is the Hanford tank wastes. If vitrified without separation, approximately 200,000 canisters of waste would be generated at a cost of approximately \$150 billion. Separations technology can reduce the number of canisters by about a factor of 10, with most of the waste volume as low-level waste that is more easily and inexpensively managed via onsite disposal. This could result in direct savings of tens of billions of dollars and reduce the amount of waste sent to a repository. Regulatory requirements are also met by using this separations technology.

## EM FOCUS AREA

High-Level Waste Tank Remediation

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### COLLABORATION/TECHNOLOGY TRANSFER

This project is directly related to efforts currently being pursued by the High-Level Waste Tank Remediation Focus Area. All results obtained in studies of MVST sludge will be used in a comparative evaluation of Hanford tank sludge. PNL will be collaborating with ORNL's efforts on this project. The technologies tested in this project would potentially benefit all DOE sites that must manage alkaline nitrate waste liquids/sludges.

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TTP Number: OR132012

### BIBLIOGRAPHY OF KEY PUBLICATIONS

None at this time.

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## 3.5 ALUMINUM REMOVAL FROM WASHED SLUDGE

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### TASK DESCRIPTION

The purpose of this project is to reduce the volume of storage tank sludge for treatment by removing aluminum and other nonradioactive components. Successful dissolution and separation of aluminum and other components from solid tank waste could substantially reduce the amount of waste requiring valuable repository space.

Because of the difficulties in obtaining and working with actual radioactive waste sludge, a Hanford sludge simulant was prepared for use in most of these studies. Samples of dried synthetic sludge were washed with NaOH solutions ranging in concentration from 0.1 M to 6.0 M. Samples were analyzed for the following elements: aluminum, chromium, zinc, bismuth, cerium, strontium, zirconium, and iron.

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### TECHNOLOGY NEEDS

Storage tank sludge generally contains mixtures of hydrated metal oxides, hydroxide, 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, along with several other waste constituents, is amphoteric. Consequently, in addition to forming insoluble hydroxides and oxides, these substances also have the potential of forming soluble chemical species under highly caustic conditions. If these substances could be preferentially solubilized, then the volume of the remaining radioactive waste to be treated and/or stored would be significantly reduced.

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### ACCOMPLISHMENTS

Of the sludge elements analyzed, aluminum, chromium, and zinc showed the highest solubility in NaOH solutions. About 30 percent of the chro-

mium was removed from the sludge by a single water wash, and the solubility did not increase significantly in NaOH solutions. The solubility of aluminum was slight in distilled water, and increased as the NaOH concentration was increased from 0.1 to 6.0 M. The amount of zinc that was removed increased significantly in the 3.0 M and 6.0 M NaOH solutions. The removal of iron and bismuth approached 2 percent, but the rest of the elements studied showed less than 1 percent removal.

Sequential washing of the sludge surrogate with 3.0 M NaOH removed 84 percent of the aluminum, 39 percent of the chromium, and 65 percent of the zinc. A mixing time of four hours was sufficient to remove the aluminum. The maximum amount of zinc was also removed after four hours. Dissolution of all of the elements increased when the temperature was raised to 80°C.

Preparation and testing of additional sludge surrogates is continuing. These tests will measure the dissolution behavior of additional components such as uranium and thorium. The time, temperature, and NaOH concentration will be optimized for the dissolution of selected components. These studies will be extended to test the dissolution behavior of actual sludge samples.

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### BENEFITS

The technology developed in this project would be of potential benefit to the Hanford and INEL sites in particular, because of the high aluminum content in their waste storage tanks. Separating the aluminum would result in a smaller amount of solid tank waste in downstream processing, and a substantial reduction in the amount of waste requiring valuable repository space.

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## EM FOCUS AREA

High-Level Waste Tank Remediation

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### COLLABORATION/TECHNOLOGY TRANSFER

This project is conducted at ORNL, on surrogate waste and waste from the MVSTs. The surrogate recipes for aluminum extraction are carried out using surrogate recipes agreed to by ORNL and Hanford. As a result this work will be used for evaluation of both Oak Ridge and Hanford Tank Waste.

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## 3.6 COLLOID FORMATION IN SLUDGE WASHING

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### TASK DESCRIPTION

This task assesses the potential for the formation and stabilization of the bulk sludge materials as colloids during the washing of sludges at Hanford site or MVST. 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 TRU waste.

Minor components in the tank wastes such as silicic acid and organics will receive special evaluation 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 dissolution of inert components such as aluminum hydroxide. Experimental tests are currently conducted with cold surrogate waste. Hot-cell tests with actual waste sludge from MVST and from currently generated TRU wastes at the Radiochemical Engineering and Development Center are planned for FY95.

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### TECHNOLOGY NEEDS

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 the tank sludges. Colloids, if formed, could contaminate supernates with TRU elements because colloids are often neither filterable nor easily coagulated.

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### ACCOMPLISHMENTS

Cold laboratory investigations were conducted at ORNL and Georgia Tech on the hydrous alumina colloidal particles preparation by precipitation tech-

niques. 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, 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 were produced after precipitates were washed with five equal portions of demineralized water. The colloids remained dispersed in the liquid phase for several days. Electrolyte concentrations at which the colloids formed were determined by chemical analysis. Initial scouting studies indicated the rare earth element neodymium will serve as an actinide stand-in for cold studies. Neodymium is readily detected by spectrophotometric means.

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### BENEFITS

Benefits of this technology include gathering data that will permit design of a successful process for washing tank waste sludges. Formation of colloids during washing could be avoided. Consequently, add-on systems to coagulate and collect them as solids could be eliminated.

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### PROPOSED FUTURE ACTIVITIES

Future studies will emphasize hot tests with actual MVST and spiked surrogate wastes based on sludge washing parameters established in previous cold tests with surrogates. Tests on alumina decladding wastes, and acid dissolution residues from operations at the Radiological Development and Engineering Center will be conducted. 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 of operational windows and/or pretreatment options, which will eliminate colloidal losses of actinides. Several cold studies continue to support these hot tests to more firmly define the chemical and physical mechanisms involved in colloidal formation and its avoidance. Most of the hot cell cold work will be conducted at Georgia Tech by subcontract.

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## EM FOCUS AREA

High-Level Waste Tank Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

ORNL will be collaborating with Georgia Tech on this project. Most of the hot cell cold work will be conducted at Georgia Tech. This work has potential applications to the tank operations at SRS, ORNL, INEL, or Fernald, in addition to the Tank Waste Remediation System at Hanford.

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TTP Number: OR132012

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## 3.7 SELECTIVE LEACHING OF TANK SLUDGE BY THE ACT\*DE\*CON™ PROCESS

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### TASK DESCRIPTION

The objective of this project is to assess 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 and plutonium-contaminated Mound soil. Pilot stage testing at INEL Pit-9 has also been conducted.

A three-phased approach is used in this project: laboratory-scale testing with spiked-waste simulants, laboratory-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 materials meet low-level radioactive waste criteria, they can be disposed of as LLW. If the sludges contain levels of TRU waste greater than 10 nCi/g, they can be treated in a contactor with the ACT\*DE\*CON™ process. The mechanical action in the process can further break the sludge and dissolve the TRU waste. Anion exchange could be used to recover the uranium, technetium, iodine, and TRU. Cesium and strontium will be recovered by cation exchange. Alternately, the ACT\*DE\*CON™ solution stream could be evaporated and sent directly to vitrification.

### TECHNOLOGY NEEDS

The actinides are a constituent of major importance in Hanford tank sludge. Vitrification of the washed sludge with no pretreatment could be prohibitively expensive, so a method that can remove the contaminants of greatest concern from the sludge represents a significant economic benefit. There is currently a dearth of technologies dealing with the treatment of sludges and solids that might also be amenable to in-tank application.

The ACT\*DE\*CON™ process seems to have a low probability for success in treating Hanford SST waste, but if successful, may provide significant HLW reduction benefits. This 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) this process could likely be performed in-tank, and if thus implemented, would avoid many costs associated with a facility.

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### ACCOMPLISHMENTS

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

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### BENEFITS

Identifying the chemical species in tank sludges is important. The chemical properties of a species describe the reactions of that substance with other substances; for example, whether the species will dissolve in acid/base. In turn, the benefits of developing sludge dissolution/leaching technology are:

- Reduction of risk: The development of pretreatment technology to produce waste fractions that are compatible with final waste forms reduce the long-term risk of contamination to

workers, the general public, and the environment; and

- Reduction of cost: Development of pretreatment technologies that can effectively fractionate and subsequently reduce waste volumes may substantially reduce waste packaging and final disposal costs;

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

- The need to add large quantities of acid (nitric, hydrofluoric, oxalic, etc.) to the wastes to dissolve the TRUs for acid-side processing (AP) would be eliminated. Thus, alkaline-side processing could result in smaller generated volumes of LLW in the pretreatment of tank wastes.
- The required processing facility might be smaller than that required for AP, 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.
- The method would provide an alternative to AP in the event that AP proves to be unreliable in the pretreatment of tank wastes.

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## EM FOCUS AREA

High-Level Waste Tank Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

The ACT\*DE\*CON project is being performed in collaboration with Bradtec and Chemical Waste Management. It is expected that the technology developed in the project will be transferred to EM-30 and will be integrated into the overall Tank Waste Remediation Strategy.

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TTP Number: RL332018

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**SELECTIVE  
SORBENTS/LIGANDS**

**Section 4.0**



Increasingly, advances in separations technology occur through the design of new, relatively exotic molecules, or "ligands," that exhibit exceptional selectivity for target ions or molecules in solution. A familiar example is the "crown ether" family of ligands that provide a ring structure that can be sized to fit only a target species in solution such that other, more abundant species are rejected due to steric, charge, and other chemical factors. Such ligands provide the thermodynamic basis for impressive advances in chemical separations, and yet are useful only if the ligand (e.g., a crown ether ring) can be separated from the waste stream by attachment to some separable substrate.

Both the ligand and substrate must endure whatever chemical and radiation environments may be encountered in a separation process. The substrate must be integrated into a total separation process; for example, a packed bed system, membrane system, or system involving solid-liquid separation of the substrate from the waste being treated.

The ESP Program is designing, developing, and testing new ligands and joining ligands to new substrates. Molecular modeling of the affinity of ligands for target species in aqueous solutions, developing extremely selective ligands based on naturally occurring compounds, attaching ligands to particles that are held in membranes, and attaching ligands to soluble polymers that can be separated by ultrafiltration are being investigated. ESP supported the following tasks in this category during FY94:

- High-Capacity, Selective Solid Sequestrants for Innovative Chemical Separations: Membrane-Supported, Bound-Particle Approach;
- Derivatives of Natural Complexing Agents for the Removal of Plutonium from Waste Streams;
- Removal and Recovery of Toxic Metal Ions from Aqueous Waste Streams by Utilization of Polymer Pendant Ligands;
- Sequestering Agents for the Removal of Transuranics from Radioactive Waste; and
- Russian Separations Technologies.

## 4.1 HIGH-CAPACITY, SELECTIVE SOLID SEQUESTRANTS FOR INNOVATIVE CHEMICAL SEPARATIONS: MEMBRANE-SUPPORTED, BOUND-PARTICLE APPROACH

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### TASK DESCRIPTION

This task is to develop high-capacity, selective solid extractants for cesium, strontium, chromium, silver, technetium, and noble metals from nuclear wastes. To achieve this goal, PNL is collaborating with industrial partners. The task 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 Corporation working in cooperation with IBC Advanced Technologies, Provo, UT. 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, chemical, and radiolytic stability of materials with demonstrated potential for application in radiochemical separations are being determined.

Empore™ extraction membrane technology, developed by 3M, provides a state-of-the-art method for emeshing 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. Highly selective molecular recognition agents are attached to the surface of particles held in the Empore™ membrane. These membranes are placed in cartridges or filters, allowing the solution to pass through, thus permitting the selective solid extractant to remove the metal ion. Under severe radiation fields PTFE becomes brittle, although other materials of web construction have successfully complemented this original concept.

The membranes are able to achieve equal or better performance than ion exchange columns with a very high surface area, consisting of small (10-micron) active particles. No adhesive or binders are needed, 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 <sup>60</sup>Co source. In addition, other membranes have been made with a range of support particles selected to meet DOE's needs.

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### TECHNOLOGY NEEDS

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 across the DOE Complex, specific applications at Hanford have been targeted.

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### ACCOMPLISHMENTS

The first opportunity to test the 3M/IBC system with actual radioactive waste was successfully completed at INEL using acid radioactive waste containing both <sup>137</sup>Cs and <sup>90</sup>Sr. Synthetic "mimic" wastes were used to test the system both at the 3M laboratory and INEL prior to 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 continue to be improved upon.

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## BENEFITS

The benefits gained by developing this technology are cost reduction in separating and disposing of nuclear wastes. A further benefit is the availability of this technology for selective sequestering of cesium, strontium, and technetium.

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

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.

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## EM FOCUS AREA

High-Level Waste Tank Remediation; Facility Transitioning, Decommissioning, and Final Disposition

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## COLLABORATION/TECHNOLOGY TRANSFER

A solicitation of interest and capabilities was issued in FY92 through the Commerce Business Daily (CBD). The purpose was to identify candidate advanced separation materials and processes to be investigated and candidate industry/university teams to collaborate with PNL in the proposed studies. A request for Proposals (RFP) was issued to qualified respondents from the CBD notice. 3M has issued a subcontract with IBC Industries, Provo, UT for the production of selective ligands. This technology, developed by 3M, IBC, and PNL has been tested at INEL, and future testing is planned at a number of other sites across the DOE Complex.

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TTP Number: RL321204

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## 4.2 DERIVATIVES OF NATURAL COMPLEXING AGENTS FOR THE REMOVAL OF PLUTONIUM FROM WASTE STREAMS

### TASK DESCRIPTION

The objective of this task is to develop a separation system that uses a highly selective complexing agent derived from a natural material to remove plutonium (and perhaps other TRUs) from high ionic strength waste waters, which may vary in pH depending on the exact flowsheet.

In nature, bacteria and other microorganisms produce siderophores, low-molecular-weight multidentate iron chelators, to scavenge ferric ion from their environments. Siderophores usually use the three chelating groups shown in Figure 4.2. 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 ligands expected to show high selectivity for strong Lewis acidic metals and then evaluate the extent of this selectivity through thermodynamic measurements;
- Determine the speciation of the metal-ligand complexes over a range of pH values, temperatures, and ionic strengths likely to be encountered in waste streams;
- Synthesize and evaluate solid/liquid and liquid/liquid extractants using simulated waste streams; and
- Test the engineered materials on actual waste and determine the economic feasibility of using such materials in an actual process.

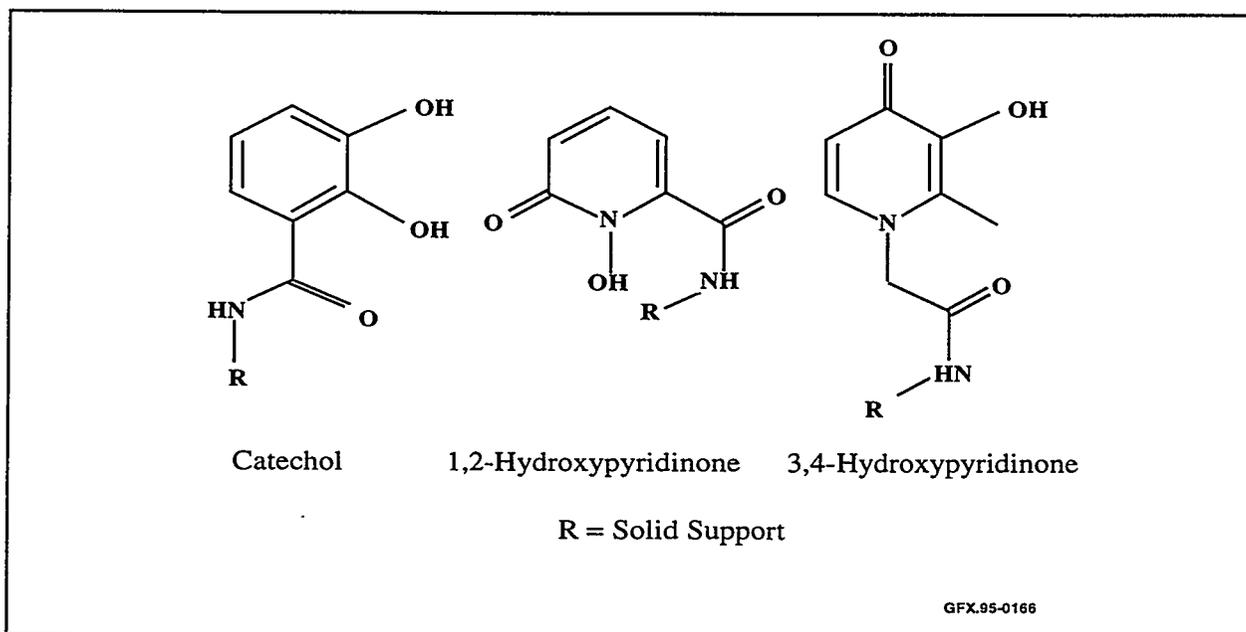


Figure 4.2. Solid/Liquid Extractants.

## TECHNOLOGY NEEDS

Efficient chemical processes for the selective removal of actinide elements are needed for the treatment and minimization of wastes such as those found at Hanford and other DOE sites. Before this objective can be accomplished, new metal complexing agents capable of withstanding harsh chemical and radiation environments must first be developed and then modified for use in practical extraction systems.

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## ACCOMPLISHMENTS

The siderophore binding units catechol and 1,2-hydroxypyridinone, along with the analog unit 3,4-hydroxypyridinone, have been modified for use as solid/liquid extractants. These materials display rapid kinetics and high loading capacities. The selectivity of these solid/liquid extractants is currently being determined. The formation constants of these bidentate binding groups have been determined with Th(IV) and with Fe(III) as a possible competitor. The formation constants indicate that the chelating groups should be highly selective for Pu(IV) and Th(IV) over most other metal ions.

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## BENEFITS

Development of highly selective and efficient ligands capable of complexing plutonium or other actinide elements over a wide range of solution composition have the potential for drastically reducing the volume of certain waste streams. Thus, the cost of treatment or disposal will be reduced. 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.

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## EM FOCUS AREA

Mixed Waste Characterization, Treatment and Disposal; Landfill Stabilization; Facility Transitioning, Decommissioning, and Final Disposition

## COLLABORATION/TECHNOLOGY TRANSFER

Collaborators with the Lawrence Livermore National Laboratory on this task include Glenn T. Seaborg Institute for Transactinium Science and the University of California at Berkeley.

Should these types of ligands prove to be an efficient reagent for the selective removal of actinide elements, chemical companies within the private sector will be apprised of the potential markets both in the U.S. and abroad for such a reagent.

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TTP Number: SF232003

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## 4.3 REMOVAL AND RECOVERY OF TOXIC METAL IONS FROM AQUEOUS WASTE STREAMS BY UTILIZATION OF POLYMER PENDANT LIGANDS

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### TASK DESCRIPTION

The purpose of this project is to investigate polymer pendant ligand technology for the removal and recovery of economical and toxic metal ions from DOE waste streams. Polymer pendant ligands are organic ligands, bound to cross-linked, modified divinylbenzene-polystyrene beads, that are capable of selectively complexing metal ions. The metal ion removal step usually occurs through a complexation or ion exchange phenomena. Thus, recovery of the metal ions and reuse of the beads is readily accomplished.

The research objectives, which were achieved this fiscal year, include (1) synthesis of selective polymer pendant ligands for removal and recovery of the metal ions, and (2) determination of rates of both removal and recovery of these metal ions. Part of the objectives include gaining industrial partners for implementation of the polymer pendant ligand technology.

The studies have initially focused on the waste waters of the Berkeley Pit in Butte, MT, with emphasis on the following metal ions:  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Pb}^{2+}$ . Because  $\text{Fe}^{3+}$  was dominant in the Berkeley Pit waste water (approximate pH equals 2.5), special attention was placed on devising  $\text{Fe}^{3+}$  selective polymer pendant ligands to more easily remove and recover the other economically important metal ions, such as  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Al}^{3+}$ .

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### TECHNOLOGY NEEDS

The removal and recovery of metal ions from aqueous waste streams will demand a considerable amount of attention for technology development. In addition to developing a range of technologies for specific metal ion removal and recovery applications, the advantage in having a generic-based technology

is that it can accommodate a range of applications on the treatment of metal ion and waste streams. The cost effectiveness of the polymer pendant ligand technology would make an excellent alternative to precipitation techniques.

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### ACCOMPLISHMENTS

The first priority for this task was to develop selective polymer pendant ligands for iron ( $\text{Fe}^{3+}$ ) removal and recovery. The experimental studies at Lawrence Berkeley Laboratory (LBL) have started on this aspect. The polymer pendant catechol derivatives, sulfonated catechol, sulfonated 2-6-LICAMS, and sulfonated 3,3-LICAMS, are ideal biomimetic candidates for an  $\text{Fe}^{3+}$  selective polymer pendant ligand. They are structurally similar to bacteria that selectively sequester  $\text{Fe}^{3+}$  in biological systems. See Figure 4.3.

Therefore, the above-designated polymer pendant ligands were synthesized, and the iron selectivity was evaluated. From pH values of 0.5 to 2.5, the following order was found for removal of  $\text{Fe}^{3+}$  from aqueous solution: 3,3-LICAMS >>>> CATS >> 2-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  $\text{Fe}^{3+}$  from the beads and reuse of the beads were accomplished with a 2N  $\text{H}_2\text{SO}_4$  solution. These important  $\text{Fe}^{3+}$  results have allowed for removal and recovery of the divalent metal ions such as  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  with the 2-6 LICAMS polymer pendant ligands. Finally, the above-designated polymer pendant ligands benefited other DOE remediation problems. For example, the polymer pendant ligands selectively removed several radionuclides and other metal ions such as  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  from aqueous solutions.

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## BENEFITS

The polymer pendant ligand technique is more cost effective than any in-depth precipitation or bioremediation treatment to remove toxic metals at waste sites such as Berkeley Pit, Hanford, Los Alamos, and Rocky Flats. The technique minimizes the total metal content at the sites. The functionalized polymer technique can be used before the toxic metal waste is placed in the environment, thus minimizing health risks and further remediation problems. The estimated savings of this technique to remediate the Berkeley Pit would be substantial because the metal ions can be recovered from the divinylbenzene-polystyrene beads.

## EM FOCUS AREA

Contaminant Plume Containment and Remediation; Mixed-Waste Characterization, Treatment and Disposal; Facility Transitioning, Decommissioning and Final Disposition

## COLLABORATION/TECHNOLOGY TRANSFER

Initial contact with an industrial partner for application, engineering and pilot plant and manufacture of LBL polymer pendant ligands was made in FY94. Talks have been initiated with Purus, Inc. of San Jose, CA. A formal subcontract is anticipated with Purus in FY95.

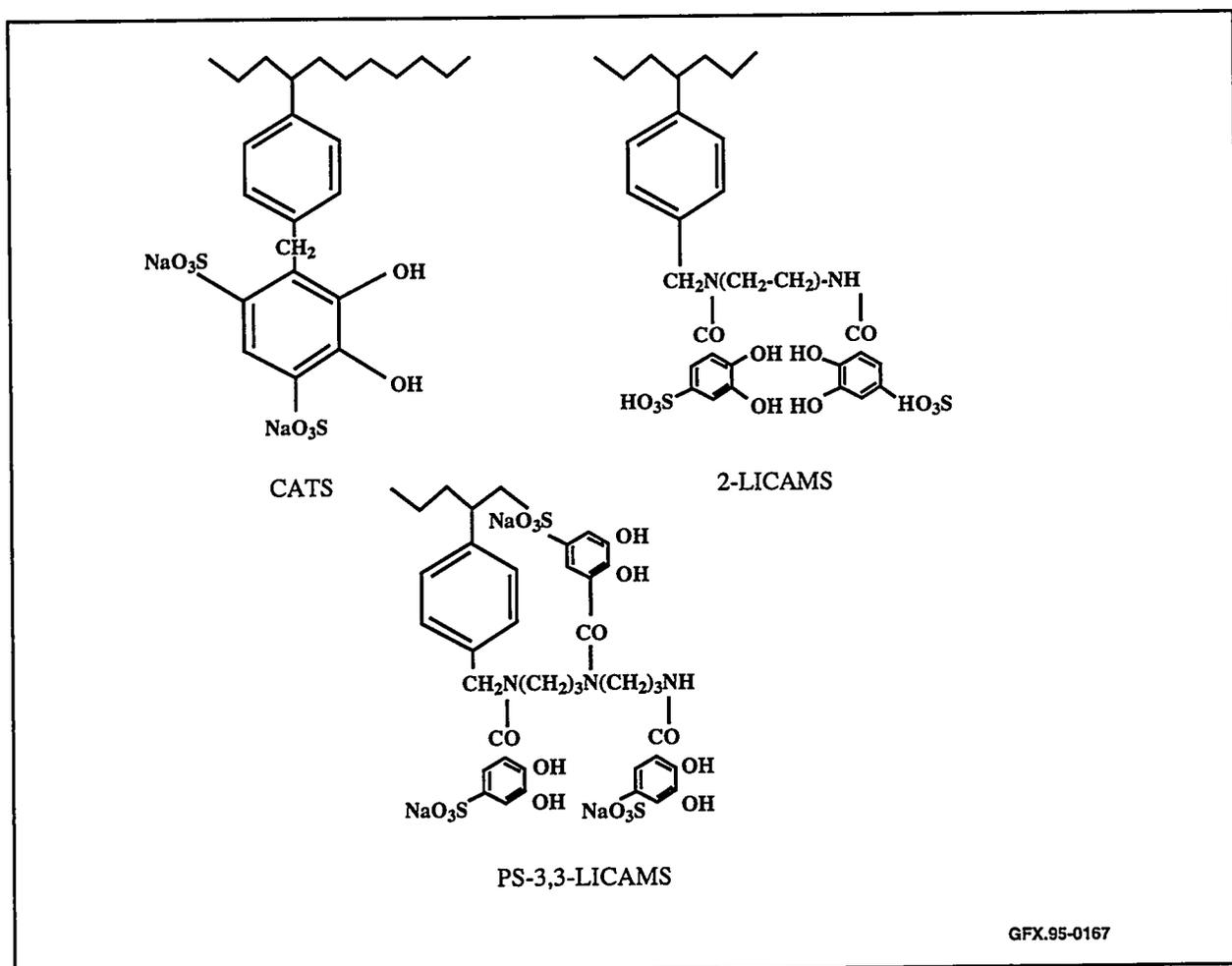


Figure 4.3. Biomimetic Candidates for Selective Polymer Pendant Ligands.

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## 4.4 SEQUESTERING AGENTS FOR THE REMOVAL OF TRANSURANICS FROM RADIOACTIVE WASTE

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### TASK DESCRIPTION

This task will develop a series of metal ion-specific extraction systems for removing actinides and other hazardous metal ions from waste water streams. The emphasis is on polymer-supported systems, but liquid-liquid extraction systems are also under investigation as part of the subtasks. The task will initially focus on metal contaminants (especially plutonium and americium) in waste streams at the Plutonium Facility and the Waste Treatment Facility at LANL and at RFP. In addition, applications at other DOE facilities are also possible.

The goal of this task is to reduce the concentration of a targeted metal ion to extremely low levels. This reduction requires that the extraction system has both a high binding strength and a high selectivity for the target ion in the presence of competing metal ions. The task involves small-scale testing of extraction systems for the required selectivity and binding constants, followed by an engineering assessment at a larger scale to allow comparison to competing separation technologies. Extraction systems under investigation include polyhydroxamic acids, bis(acylpyrazolones), malonamides, polyphosphonic acids, and derivatives of dithiophosphinic acid.

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### TECHNOLOGY NEEDS

There is an urgent need for alternative technologies for treatment of radioactive waste water to meet regulatory limits, decrease disposal costs, and minimize waste. More stringent discharge regulations are anticipated from DOE, the U.S. Environmental Protection Agency (EPA), and the states that will require considerably lower metal ion concentrations in the effluent water from facilities such as the Los Alamos Waste Treatment Facility.

In particular, this technology would address the need to replace precipitation methods that generate large volumes of radioactive sludge at LANL

and RFP, and reduce TRU wastes that will be generated from processing the plutonium-contaminated residues that exist at DOE facilities. This technology is also applicable to radionuclide-specific treatment of multiple aqueous waste streams at Hanford, generated by the cleanup of the storage tank wastes, and various environmental contamination sites.

An important subset of the waste waters 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. The separate waste streams can be treated by other technologies that are better established from a regulatory viewpoint.

#### Subtask 1: Development of Water-Soluble Chelating Polymers for Actinide Complexation

Description. The application of water-soluble chelating polymers/ultrafiltration to the treatment of waste waters contaminated with low levels of RCRA and radioactive metal ions is a relatively new separations technology being developed at LANL. Metal ion separation, as shown in the figure, involves the retention of metal ions bound to the chelating water-soluble polymer. 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 may be directly disposed of. The metal ions can also be recovered by pH adjustment and the polymer recycled for further metal ion recovery.

The advantages of this separation technology for dilute metal ion solutions is in the rapid kinetics due to the homogeneity of the process. In addition, by careful selection of the water-soluble chelating polymer, selective metal ion complexation can be obtained. Recently, this separation technology was successfully demonstrated on a pilot scale for the

recovery of nickel and zinc from 150 gallons of plating bath rinse waters at Boeing Aerospace in Seattle.

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 pyrazolone polymers have been tested for metal ion retention at pHs of 1-6 and ionic strengths between 0.1N and 4.0N sodium nitrate with solutions of tracer americium and plutonium. The results of the studies indicated that both polymers have high retention (>99.9 percent) when working in the optimum pH range. Both polymers showed higher retention as the nitrate concentrations were increased. The phosphonic acid polymer has proved to be the best polymer for the complexation of americium and plutonium with distribution values of one to two orders of magnitude higher than the acylpyrazolones. The preparation of the hydroxamic acid polymers is being optimized and have not been evaluated for actinide retention.

Polymers for americium and plutonium retention in the presence of other metal ions to determine the selectivity of the polymers in a competitive environment need further evaluation. The hydroxamic acid polymer will undergo the same systematic evaluation. There are also plans to investigate the ability of these polymers to retain other actinide metal ions such as Th and U. The long-term goal is to set up an ultrafiltration unit at the plutonium facility by the end of FY95 for an on-line demonstration/evaluation of this technology for the recovery of americium and plutonium, which are currently released to the waste treatment facility.

#### Subtask 2: Malonamides for Extraction of Transuranic Elements

Description. The objective of this subtask is to evaluate several malonamide extraction systems for actinide partitioning. This subtask includes developing improved preparation and purification techniques, overcoming current third-phase formation problems, and improving stability and extraction coefficients. The compounds  $[R_1R_2NC$

$(O)CHR_3C(O)NR_1R_2]$  chosen are based on the extensive work of Musikas, Madic, and coworkers in France to optimize the substituents on both the carbonyl amide nitrogens ( $R_1, R_2$ ) and the methylene carbon ( $R_3$ ). They found that an unsymmetrical combination of alkyl groups (e.g., methyl and butyl) on the amide nitrogens and a 14-carbon alkyl chain on the methylene carbon were a good compromise. This ligand still has a third-phase formation problem in hydrocarbon solvents at moderate nitric acid concentrations (>3.5 to 4.5 M nitric acid).

Accomplishments. One significant problem inhibiting the use of malonamide extractants in practical applications was the tendency to form third phases when alkane diluents were used at nitric acid concentrations of approximately 4N or higher. Improved solvent systems to reduce the formation of third phases were developed. The acid working range using solvent modifiers composed of specially prepared monoamides ( $R_1R_2NC(O)R_3$ ) were extended. The monoamide functions similarly to tributylphosphate was used as a phase modifier to prevent third-phase formation with bifunctional organophosphorous extractants such as CMPO. One potential advantage of the monoamide-malonamide systems was that they are nonphosphate based and could be oxidized by thermal or chemical means to leave less radioactive residue for disposal.

Four monoamide compounds were tested as phase modifiers of the organic solution to try to extend the working range of these extraction systems. One of the monoamides was commercially available. The other three monoamides were prepared at LANL to test a range of functionality predicted to stabilize these solutions. Two of the prepared monoamides worked well for inhibiting third phase formation and extended the working range of the organic phase up to 10N nitric acid. The commercial monoamide did not perform well and was dropped from the survey. Initial measurements of the distribution ratios of several metal ions showed that the new malonamide-monoamide systems were at least as good as the original malonamide extraction system. There was some indication of enhanced extraction in the new systems. Currently, more complete extraction studies are in progress.

### Subtask 3: Development of Soft Donor Extractants for Trivalent Actinide/Lanthanide Separations

Description. The objective of this subtask is to evaluate extraction systems that have demonstrated good bench-scale separations of the trivalent actinides from the lanthanides for application at a process scale. A variety of chemical systems have been developed to separate trivalent actinides from lanthanides based on the slightly stronger complexation of the trivalent actinides with ligands that contain soft donor atoms, for example, nitrogen and sulfur in comparison to oxygen. The greater stability of the actinide complexes in these systems has often been attributed to a slightly greater covalent bonding component for the actinide ions relative to the lanthanide ions.

Several synergistic extraction systems that use ligands with a combination of oxygen and sulfur donor atoms to achieve a good group separation of the trivalent actinides and lanthanides are being investigated. These systems could be applied to advanced partitioning schemes for nuclear waste. For example, the removal of relatively small amounts of americium from certain Hanford tank wastes that contain large amounts of stable lanthanum could greatly reduce the amount of material requiring disposal as high-level or TRU-level waste.

Accomplishments. Three different dithiophosphinic acid ( $R_2PS_2H$ )/synergist systems were tested for their ability to separate trivalent actinides from trivalent lanthanides. Remarkable separation factors were achieved. For example, the combination of dicyclohexyldithiophosphinic acid and tributylphosphate showed separation factors up to 800 for americium over europium in a single extraction stage. In addition, some of the dithiophosphinic acid systems tested showed good stability to oxidation and hydrolysis over two to three weeks. Further characterization of the extraction properties and chemical and radiation stability of these systems are in progress.

Application in a liquid-liquid extraction process will likely require extractants soluble in alkane solvents. Previous studies indicated a series of acylthiopyrazolone and thioacylpyrazolone compounds that show high separation factors for ex-

tracting the trivalent actinides over the lanthanides. Derivatives of these compounds are being prepared, including aliphatic substituents, that will enhance solubility in alkane solvents.

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## **BENEFITS**

This technology can provide a cost-effective replacement for sludge-intensive precipitation treatments and yield effluents that meet increasingly stringent discharge requirements. At LANL, improved extraction technology is used to reduce the TRU content of waste streams from the Plutonium Facility at potential savings of millions of dollars in capital and operating costs for renovations to the Waste Treatment Facility. The polymer filtration technology systems can also assist the effort at Rocky Flats to address Interagency Agreement requirements to develop and evaluate radionuclide treatment technologies, including treatment of environmental surface waters. Applications for these systems at Hanford and other DOE facilities are also likely.

Potential application exists for the water-soluble polymers for decontamination and decommissioning. The polymer solution can be used to wash surfaces and remove contaminating metal ions. The metal ions could then be concentrated and recovered through the ultrafiltration operation and the polymer reused for further cleaning. Water-soluble polymers very similar to those prepared for this project have already shown promise for removing lead from soils at Superfund sites. This work is proceeding to the demonstration phase.

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## **EM FOCUS AREA**

Facility Transitioning, Decommissioning, and Final Disposition; Landfill Stabilization; Contaminant Plume Containment and Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

Participants in this project include scientists from RFP, University of Arizona, the University of New Mexico, Tennessee Technical University, and the University of Tennessee. In addition to reduction of TRU content of waste streams at LANL, application of the improved extraction technology and polymer filtration technology systems at DOE facilities, including Hanford and RFP, is likely. The collaborative effort is seeking to identify the most cost-effective technology for treating RFP waste streams. Potential application also exists for the water-soluble polymers for decontamination and decommissioning.

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 recycling metals from electroplating operations. A successful demonstration was conducted at Boeing Aerospace in Seattle, WA.

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TTP Number: AL121217

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**OTHER  
SEPARATIONS AREAS**

Section 5.0



## 5.0

## OTHER SEPARATIONS AREAS

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Several topics on chemical processes important to ESP are difficult to classify in the scheme of traditional separations and are grouped in this document as "Other Separation Areas." One such area is the electrochemical destruction of nitrate, nitrite, and organic species in HLW tank supernatant. Electrochemical processing could be used to generate and recycle caustic waste, to eliminate organic complexing agents that impede separation of cations, and to electrochemically precipitate species such as pertechnetate, chromate, or noble metals.

The ESP Program also supports work on the separation of tritiated water from water using a selective polymer membrane. This process is being developed to substantially reduce the concentration of tritium in the waste where it is not necessary to provide a concentrated tritium stream from the separation.

Research on crystallization is also being conducted. Fractional crystallization of sodium nitrate/phosphate salts from HLW tank supernatant produces a bulk waste stream with little radioactivity. This provides an opportunity to dispose of a significant fraction of tank waste as below regulatory concern pending favorable discussions with regulatory authorities.

The ESP Program supported the following tasks in this category during FY94:

- Development and Evaluation of Electrochemical Methods of Destroying Nitrates and Nitrites in HLW and LLW;
- Separation of Tritiated Water from Water Using Composite Membranes;
- Significant Volume Reduction of Tank Waste by Selective Crystallization;
- Aqueous Phase Catalytic Exchange for Detritation of Water; and
- Technology Evaluation and Process Definition: Unit Process Level and Global Level.

## 5.1 DEVELOPMENT AND EVALUATION OF ELECTROCHEMICAL METHODS OF DESTROYING NITRATES AND NITRITES IN HIGH-LEVEL WASTE AND LOW-LEVEL WASTE

### TASK DESCRIPTION

The aim of this task is to develop and evaluate the various electrochemical methods for 1) destroying nitrates, nitrites and organic compounds in HLW and LLW, and 2) removing radionuclides and hazardous metals from alkaline waste solutions. See Figure 5.1. 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 are effectively separated from the waste. Metal ions can be reduced, producing solid phases or deposits on the electrodes that can be removed.

In addition to electrochemical reduction, the corresponding electrochemical oxidation reactions oxidize organics to carbon dioxide and water. This work will include examination of divided parallel-plate, packed bed, and fluidized bed electrochemical cells. Identification of electrocatalysts for these destruction reactions will be considered.

The task consists of five major subtasks: (1) determination of optimum reactor conditions for the destruction and removal of hazardous waste components, (2) development of engineering process models, (3) laboratory-scale tests with radioactive materials, (4) pilot-scale tests, and (5) analysis and evaluation of the testing data.

### TECHNOLOGY NEEDS

Performance assessments of LLW forms indicate that nitrate and nitrite are among the major contributors to potential environmental release and personnel exposure risk. The presence of organic material in alkaline wastes is also a safety concern during interim storage.

Electrochemical treatment is one possible technology for the destruction of nitrates, nitrites, and organics. This treatment removes radionuclides and hazardous metals from waste solutions. The advan-

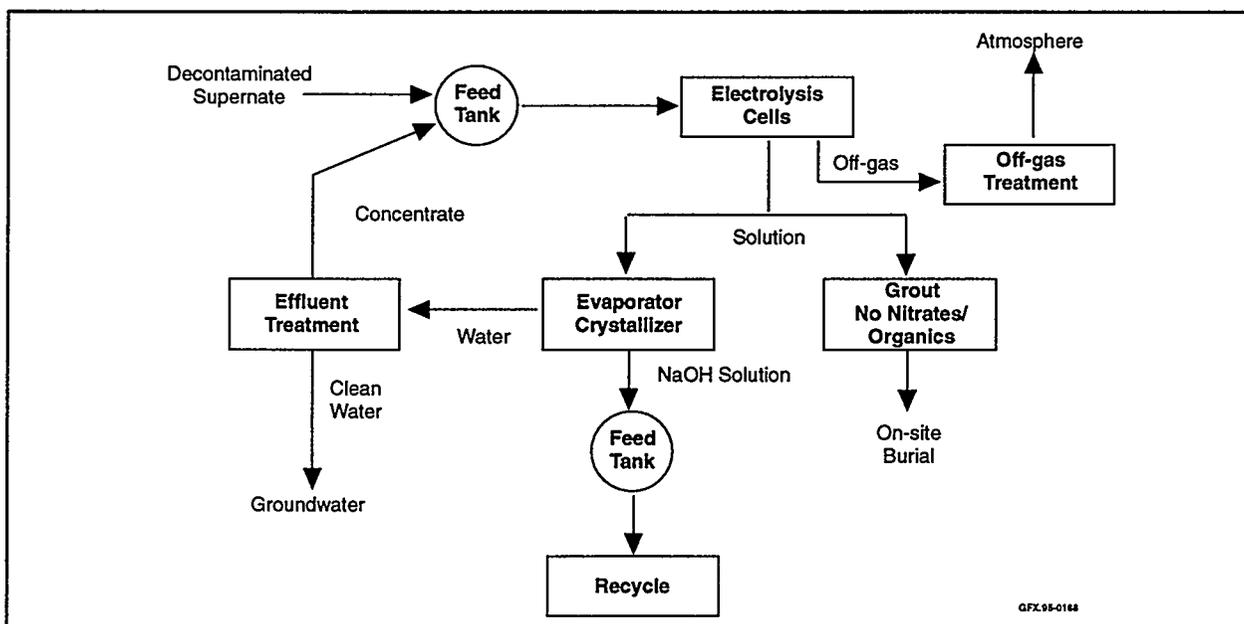


Figure 5.1. Removal of Nitrates/Organics from High-Level Waste by Electrolysis.

tage of this method is that in the case of nitrate and nitrite reduction, one equivalent of nitrate destroyed results in one equivalent of hydroxide being produced; thus there is no addition of any material to the waste stream. Furthermore, by recovery and recycle of the sodium hydroxide produced considerable reduction (possibly up to 75 percent) in the volume of waste requiring disposal could be achieved. Similarly for organics, the destruction produces innocuous materials without the addition of any material to the system.

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## ACCOMPLISHMENTS

Radioactive testing was initiated at the Savannah River Technology Center 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 in Hanford Site HLW have been initiated in an engineering-scale flow reactor at PNL. Evaluation of fluidized-bed and packed-bed electrochemical reactors has been 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 is in progress at the University of South Carolina.

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## BENEFITS

The benefits of successfully implementing this technology include 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 LLW forms available for permanent disposal. Removal of radionuclides increase operating flexibility. Recovery and recycling of 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 LLW.

## EM FOCUS AREA

Mixed Waste Characterization, Treatment and Disposal; High-Level Waste Tank Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

Collaborators with SRTC include PNL, the University of South Carolina, and Texas A & M University. At PNL, parametric studies for the oxidation of organic compounds in Hanford Site HLW have been initiated in an engineering-scale flow reactor. The University of South Carolina has contributed engineering models for the parallel-plate reactor and an evaporator for the destruction of nitrate and nitrite, and has begun evaluation of porous-metal cathodes, gas-diffusion anodes, and kinetic studies. Texas A & M University collaborators have begun evaluation of fluidized-bed and packed-bed electrochemical reactors for the destruction of nitrite and nitrate and the removal of hazardous metals.

The electrochemical destruction of nitrite, nitrate, and organic compounds has applicability across the DOE Complex at those sites storing wastes containing these species. The technology also has potential application to the treatment of alkaline nitrate and nitrite wastes generated at NASA facilities. The technology may also have application to concentrated alkaline waste streams produced in private industry such as the battery manufacturing and waste treatment facilities.

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## 5.2 SEPARATION OF TRITIATED WATER FROM WATER USING COMPOSITE MEMBRANES

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### TASK DESCRIPTION

This task involves composite membranes to remove tritium from contaminated water at DOE sites. Aromatic polyphosphazenes were chosen as the polymeric material for the membranes being investigated because of their excellent radiological, thermal, and chemical stability.

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### TECHNOLOGY NEEDS

Remediation of tritium-contaminated ground water is currently achieved by natural decay using the 12.3 year half-life of tritium and long times for migration of water through geologic formations. Regulatory agencies are growing concerned with this approach. Processes for removing tritiated water (e.g., combined electrolysis-catalytic exchange) are available. However, these processes require extensive capital or energy expenditures. Experience with membrane systems in industry indicates that they are inherently energy efficient. Furthermore, reverse-osmosis technology has been well developed for desalination and other industrial/municipal applications. Separation of tritiated water from contaminated water using composite membranes is a technology that must be further investigated.

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### ACCOMPLISHMENTS

Poly(diphenoxy)phosphazene (PN<sub>x</sub>) and several carboxylated derivatives were solvent cast on non-woven polyester backing to form composite membranes. These composite membranes were tested with Hanford well water containing 10 pCi/mL HTO. Small test cells were used. The PN<sub>x</sub> single-pass separated HTO up to 36 percent throughout the temperature range of 2°C to 25°C. The 10 percent carboxylated PN<sub>x</sub>-membrane showed HTO separation (depletion) up to 74 percent at 4°C to 12°C. Mass balance experiments accounted for the tritium. Further confirmation that the separation is

not a transient effect was shown with the separation of deuterated water.

The reverse-osmosis concept was used to prepare a preliminary design and cost estimate for a membrane system to remove tritium from contaminated water in the Hanford Site K-East Basin. The assumptions for the preliminary design and costs included a tapered design (cascade), 40 percent depletion of tritium per pass and a final permeate of less than 20 pCi/mL. Fractional crystallization can remove clean NaNO<sub>3</sub> from the waste, thereby reducing the volume of LLW glass by as much as 70 percent.

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### BENEFITS

Waters containing unacceptable tritium concentrations above environmental release limits or drinking water standards are released at DOE sites, including Hanford, SRS, and possibly Mound. One example is the 242 evaporator at Hanford, which has discharged up to 150 gallons per minute of water containing tritium at approximately 2.2 mCi/L. Currently, water from some test wells at Hanford contain tritium concentrations approaching 6x10<sup>7</sup> pCi/L. The Tri-Party Agreement requires that tritiated water in fuel storage basins be treated or relocated. There are no currently acceptable removal options for tritium remediation other than migration with time through geologic formations. The proposed 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 found in nuclear power plants in Canada and at 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

ppm range due to neutron emission/capture (uranium fission).

The polyphosphazene membrane system may be able to separate HTO from water in the mCi range, which could be extremely helpful to the Tritium Aqueous Waste Recovery System (TAWRS) developed by Mound Technologies and SRS, as well as other catalytic systems. The membrane system (bypass side) would concentrate HTO (in the 100-500 Ci/L range) in streams too dilute for the catalytic system while reducing the amount of HTO in the reject stream. This should provide an added amount of tritium for separation that would otherwise become part of a waste stream. In each case, the membrane technology should be applicable for remediation/cleanup of the contaminated streams.

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## EM FOCUS AREA

Facility Transitioning, Decommissioning, and Final Disposition

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## COLLABORATION/TECHNOLOGY TRANSFER

This work represents a collaborative effort among potential users of the technology, including PNL, INEL, WHC, and SRS. A number of membrane manufacturers, including Eastman Kodak, DuPont, Dow Chemical USA, Monsanto, Amicon, Millipore, and the Pall Corporation, have already shown interest in the membrane system being developed.

The technology has application to several DOE facilities. Waters containing unacceptable tritium concentrations are released at DOE sites, including Hanford, SRS, and possibly Mound. Tritium is found in nuclear power plants in Canada and at SRS. The membrane system may be able to separate HTO from water in the mCi range which could be helpful in several catalytic systems.

A contract with the University of Arizona went into effect on May 1, 1994 to build a bench-scale continuous crystallizer using simulated Hanford waste.

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TTP Number: RL342027

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## 5.3 SIGNIFICANT VOLUME REDUCTION OF TANK WASTE BY SELECTIVE CRYSTALLIZATION

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### TASK DESCRIPTION

The objective of this task is to develop and demonstrate a scaleable process to reclaim sodium nitrate ( $\text{NaNO}_3$ ) from Hanford waste tanks as a clean nonradioactive salt. On a dry weight basis, two-thirds of all the nuclear waste stored in Hanford's underground storage tanks is sodium nitrate. Fractional crystallization can remove clean  $\text{NaNO}_3$  from the waste, thus reducing the volume of LLW glass by as much as 70 percent.

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### ACCOMPLISHMENTS

Initial flowsheet conditions were developed using simulated wastes. The process feasibility was demonstrated when essentially nonradioactive  $\text{NaNO}_3$  (28 pCi/g) was recovered from a 101-SY tank composite sample. A  $^{137}\text{Cs}$  decontamination factor of 14 million was achieved.

Laboratory experiments with simulated waste were conducted to explore the effects of crystallization parameters on the  $\text{NaNO}_3$  crystals. Data were obtained to allow prediction of decontamination factors as a function of solid/liquid separation parameters. Experiments with actual waste from Tank 101-SY were done to determine the extent of contaminant occlusions in  $\text{NaNO}_3$  crystals. The occlusion rate determines the theoretical maximum decontamination factor for a single-stage crystallization. This rate defines the size of an operating plant. In preparation for defining surrogate waste compositions, SSTs were categorized according to the weight percent  $\text{NaNO}_3$  in each tank. An internal memo report was issued.

A contract with the University of Arizona went into effect on May 1, 1994 to build a bench-scale continuous crystallizer using simulated Hanford waste. The principal investigator is Alan Randolph, an internationally known crystallization expert with expertise in Hanford waste chemistry. He was in-

strumental in the selection of the design of Hanford's 242-A and 242-S evaporator/crystallizers that have been used since the mid-1970s to reduce the volume of tank waste.

A detailed process flowsheet and computer model were created using the ASPENPlus steady state process simulator. This is the same program used by the Tank Waste Remediation System (TWRS) program for waste pretreatment and disposal projections. Therefore, evaluations can be made of the effect of the clean salt process on the LLW volume and composition resulting from the TWRS baseline flowsheet. Calculations, using the same assumptions as the TWRS baseline, indicated that the number of low-level glass vaults would be reduced from 44 to 16 if the clean salt process were incorporated into the baseline flowsheet.

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### BENEFITS

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

- Waste Reduction - up to 90 percent reduction in the volume of LLW glass could be achieved by recovering the sodium nitrate and aluminum nitrate;
- Waste Minimization - current baseline tank waste treatment schemes call for the use of more than 30 million pounds of process chemicals in one year. By regenerating the process chemicals instead of purchasing them, additional waste will not be generated;
- Removal of Nitrate - this process will significantly reduce the amount of nitrate in the waste stream;
- Improved Ion Exchange Performance - the decreased sodium concentration will enhance ion exchange performance because the con-

aminant to sodium ratio will be an order of magnitude higher. This higher magnitude will increase the selectibility of the radionuclides, increasing the decontamination factors; and

- Recycle - secondary wastes will decrease significantly because recycle will be used throughout the process. Clean water will be recycled back to the tank waste treatment process as well as the regenerated chemicals.

Removal of  $\text{NaNO}_3$  and other salts from the LLW stream, especially those salts that are problematic with respect to glass formulation (fluoride, phosphate, sulfate), can lead to much higher waste loading in the vitrification process. Recent flowsheet modeling using AspenPlus predicts that full-scale implementation of the process could reduce the volume of LLW glass by as much as 90 percent.

Combination of the fractional crystallization process with salt-splitting technology, such as the ESP-funded electrochemical destruction process being developed at Westinghouse Savannah River Company, has the potential to convert tank waste into useable products for waste pretreatment. For example,  $\text{NaNO}_3$  can be converted electrochemically into  $\text{HNO}_3$  and  $\text{NaOH}$ , the latter of which is needed for the Tank Waste Remediation System (TWRS) baseline waste pretreatment (enhanced sludge washing).

Flowsheets are designed to install the fractional crystallization process either before or after the cesium ion exchange (CSIX) process in the TWRS baseline flowsheet. A third option being considered and modeled is complete elimination of the CSIX plant and the LLW stream.

The fractional crystallization process is applicable to all types of aqueous low level waste feed. Optimal feeds are those that are high in nitrate and low in aluminum, such as the salt cake wastes. Double shell slurry wastes typically contain large amounts of aluminate and other salts that lead to higher nitric acid consumption. Application of the process at

other DOE sites is possible, wherever bulk separation of  $\text{NaNO}_3$  is required.

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## EM FOCUS AREA

High-Level Waste Tank Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

The main goal of this task is the integration of the process into the EM-30 tank waste treatment scheme. Application of the fractional crystallization process at other DOE sites is possible, wherever bulk separation of  $\text{NaNO}_3$  is required. Combination of the fractional crystallization process with salt-splitting technology, such as the electrochemical destruction process being developed at WSRC, has the potential to convert tank waste into useable products for waste pretreatment. In addition to WHC, the project involves the efforts of University of Arizona.

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## 5.4 AQUEOUS PHASE CATALYTIC EXCHANGE FOR DETRITIATION OF WATER

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### TASK DESCRIPTION

The purpose of this task is to evaluate a U.S.-manufactured catalyst suitable for hydrogen isotope exchange between hydrogen and water. The catalyst is manufactured by Hamilton Standard, a subsidiary of United Technologies. It will be compared with a Canadian catalyst that is unavailable for use in the United States.

In this task, Hamilton Standard catalysts are cold tested for deuterium exchange in water with tritium in gaseous hydrogen. The exchange efficiencies and the mass transfer coefficients will be compared with the Canadian catalyst. If necessary, the catalysts will be modified to improve the efficiencies. Promising catalysts will be hot tested using tritiated water.

A computer model will be developed to simulate conceptual designs, based on existing data from a Canadian catalyst. A dual column-dual temperature concept developed at the University of South Carolina will be evaluated. Efficiency measurements and isotope detection systems are also under development.

A small-scale system will be built for the cold test and can demonstrate the dual column-dual temperature concept. The separation systems can be designed for applications such as detritiation of heavy water reactor moderator (1 ppm tritium range), detritiation of high level contaminated water (1 ppb range), and detritiation of effluent water (1 ppt range).

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### ACCOMPLISHMENTS

Technical Task (TT) and QA plans have been written and reviewed by SRTC management. The recommendation was made that these plans may not be required this time because the cold test is being

performed at the University of South Carolina. Catalysts are purchased through procurement, and hot testing will be performed at SRTC later in the year. TT and QA Plans for the hot tests will be implemented at that time.

Canadian government and Chalk River Personnel were contacted on the possibility of nondefense applications of their catalysts. The Canadian government now allows their catalyst for environmental restoration and waste management. However, development continues on a Hamilton Standard catalyst for detritiation of defense-related project. Chalk River also has offered their expertise and experience for detritiation process design.

The exchange data on Canadian catalysts was re-analyzed to test the kinetic model. A better interpretation was developed based on this new model, which includes the separation stage concept that was not in the earlier model.

A computer program was developed to simulate the dual-column-bithermal system. Based on the results of the computer simulation, a pilot-scale test was proposed to the management of the Effluent Treatment Facility at SRS.

A contract was issued with the University of South Carolina to set up the cold test for hydrogen deuterium exchange for U.S.-manufactured catalysts for side-by-side comparison with the Canadian catalyst. The cold test system (H-D exchange test) was designed. The required parts and equipment were ordered.

Hamilton Standard agreed to supply several existing catalysts for preliminary screening tests for hydrogen isotope exchange. To release their catalyst materials, nondisclosure agreements were signed by Hamilton Standard, USC, and SRTC. A subcontract to Hamilton Standard through USC was initiated to build a test system for catalyst performance.

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## BENEFITS

Aqueous phase catalysis for hydrogen isotope exchange is preferable to the competing technology of vapor phase isotope exchange because the aqueous phase process does not require vaporization of the contaminated steam. The process is less energy intensive and requires less capital investment in the process plant.

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## FUTURE ACTIVITIES

Future activities include counter current separation using tritiated water and a wet-proofed catalyst to verify previous data from cold tests. The data will be for the design of a pilot-scale test. A complete flow sheet will be provided for an application at SRS. Pilot-scale, dual-temperature, dual-column system and tests using protium-deuterium separation will be conducted to determine scale-up parameters. Exchange kinetics and separation factor of an improved wet-proof catalyst will be measured. The data will be used to optimize the catalyst.

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## EM FOCUS AREA

Facility Transitioning, Decommissioning, and Final Disposition

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## COLLABORATION/TECHNOLOGY TRANSFER

The project involves the efforts of Savannah River Technology Center, the University of South Carolina, and Hamilton Standard, the manufacturer of the specialized catalyst. In addition, Chalk River has offered their expertise and experience for detritiation process design.

Beyond the tasks described here, the detritiation systems being developed here can be modified for various applications, such as detritiation of heavy water reactor moderator, high-level contaminated water, and effluent water.

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TTP Number: SR142002

## BIBLIOGRAPHY OF KEY PUBLICATIONS

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Baumgarten, P. K., and D. W. Howard, Moderator Detritiation at the Savannah River Plant, *Fusion Technology*, 8, 1985.

King, C. M., M. V. Van Brunt, R. B. King, and A. R. Garber, *Concepts for Detritiation of Waste Liquids*, WSRC-MS-91-027, Westinghouse Savannah River Company, SRS, Aiken SC, 1991.

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## 5.5 TECHNOLOGY EVALUATION AND PROCESS DEFINITION: UNIT PROCESS LEVEL AND GLOBAL LEVEL

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### TASK DESCRIPTION

The purpose of this task is to evaluate and compare radionuclide separations/processing technologies being developed or considered by the ESP. The results from this system integration and analysis effort will be used by the ESP to guide its research and development in separations technology.

Waste treatment must produce disposal fractions that are less troublesome than the original material. Researchers seeking effective treatment methods may lack the expertise to fully understand the implications of their approach in terms of tertiary waste streams or the extent to which a unique new process will affect upstream or downstream processes. This task will develop and demonstrate mass balance methods that clarify the effect of including individual processes in an integrated waste treatment system, such as the Hanford cleanup system. The methods measure treatment effectiveness and allow researchers to understand waste stream interrelationships to determine how a particular treatment technology can best be used in a cleanup system.

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### TECHNOLOGY NEEDS

Thermal treatment, dissolution, separation, and chemical destruction technologies are fundamental to the treatment of a wide variety of DOE wastes. These technologies are needed to separate, concentrate, destroy, or package the hazardous constituents for appropriate disposal, leaving the waste in a safe, more easily disposable form. The economics and environmental performance of waste treatment depend on the efficiency, selectivity, and completeness of the separation, concentration, and destruction processes. Current technologies are often cumbersome. They are usually capable of accomplishing only a small percentage of what could ultimately be achieved with the introduction of advanced technologies.

The incentive to develop and apply advanced and emerging separation technologies to extract and concentrate the hazardous components is thus obvious. However, processing generates its own set of secondary and tertiary waste streams. Similarly, the cost and environmental implications of final facility decommissioning are important factors. It is therefore not always clear whether a newly proposed technology or unit process will reduce or exacerbate the waste problem. Analysis of this issue is complicated by the fact that several unit processes will likely be combined to treat a waste stream and, in addition to the obvious interconnections such as recycle, there are often interactions where changing one process changes the waste generating characteristics of the other processes.

Thus, a clear indication of the benefits of a particular unit process/modification can be obtained by conducting a mass balance analysis of the waste treatment system for a particular waste stream, taking into account all wastes. The analysis can be extended to incorporate a wide range of issues such as cost, worker exposure, environmental impact, safety, manpower, and facility liabilities.

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### ACCOMPLISHMENTS

The FY94 task work consisted of systems studies of Hanford tank waste pretreatment alternatives from a site-wide perspective to evaluate the benefit and cost of integrating ESP technologies into site waste remediation systems. Numerous flowsheets have been proposed for processing the Hanford tank wastes. On one extreme are minimal treatment flowsheets containing a few separations that moderately concentrate radionuclides into a HLW glass product. To the other extreme are complex flowsheets with dozens of separation processes intended to minimize the HLW volume and radiotoxicity of the LLW glass or grout product.

An advanced separations process strategy called the Clean Option was evaluated as a Hanford tank waste pretreatment alternative. The Clean Option represents an aggressive and complex pretreatment flowsheet. It was compared with two other flowsheet alternatives of decreasing complexity to quantify the tradeoff of greater capital equipment/operating costs for aggressive separations with the reduced waste disposal costs and decreased environmental/health risks.

The Clean Option evaluation performance measure results showed that advanced separations could sharply reduce the HLW volume (greater than 1000 canisters of 0.625 m<sup>3</sup> volume) and associated disposal costs and achieve a LLW Class A disposal product. However, these results require higher separation costs and could result in greater occupational health risk due to increases in worker exposure to radioactivity from more extensive separation operations. Clean Option could potentially reduce HLW volume to the point vitrification could be incorporated directly into the separations plant as an acid process, eliminating the need for a separate vitrification facility.

Furthermore, use of compact processing units to perform operations that would otherwise be done in a central facility (e.g., alkaline ion exchange processing of supernate and salt cake to remove cesium, strontium, and technetium) could potentially reduce the total cost by nearly 25 percent. Also, tertiary non-process waste (i.e., wastes that did not result directly from splitting or partitioning of the main process streams) was substantially increased with the more extensive processing operations. The contribution of tertiary waste processing and disposal to total cost could potentially be as much as 30 percent for a complex flowsheet such as the Clean Option.

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## BENEFITS

This task evaluates developing technologies in terms of their effect as part of an integrated tank waste remediation system at a site. Using an auditable, well-recognized process analysis methodology that

compares proposed and existing technologies for a specific application yields performance measures that describe the benefit of completing development of the technology. This analysis provides an objective way to select promising technologies for further ESP investment. It also provides feedback to the process developers identifying modifications needed to improve the effectiveness and compatibility of their proposed technologies.

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## CURRENT AND FUTURE ACTIVITIES

Current task work continues flowsheet evaluation and integration. It is focused on continuing the systems studies to show the effect of sludge parameters on TWRS HLW and LLW glass volumes and on generation of secondary waste. The current Hanford technical baseline process strategy, involving an in-tank enhanced sludge wash using caustic leaching with subsequent cesium ion exchange, will be used as the reference for future process evaluation work. The work will continue to focus on TWRS at the Hanford Site and evaluate the role of ESP technologies relative to TPA milestones, specifically, the 1998 TPA decision milestone regarding the extent of processing that will be required for the Hanford tank sludge. Participation in pertinent EM-30 working groups was begun to determine how the systems work can best assist the groups in meeting their objectives. Collaboration with EM-30 task work associated with developing tank waste blending strategies for HLW glass volume minimization will be done to share model and blending strategy information.

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## EM FOCUS AREA

High-Level Waste Tank Remediation

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## COLLABORATION/TECHNOLOGY TRANSFER

The results from this systems integration and analysis can be used facility-wide and across boundaries to indicate the benefits of a proposed unit process/modification. PNL and WHC are involved in technology transfer at the unit process level and global level, respectively.

A portion of the criteria for success of this task is the export of the approach to the broad DOE waste management community or sites. This technology transfer has to do with both the method being used and the software models being developed, and will be applied to other uses on those sites.

Collaboration with EM-30, in particular EM-30 working groups concerned with the waste treatment process has been an integral part of the project development. This participation in the specific working groups is being used to determine how the systems can best meet the groups' objectives.

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TTP Number: RL411205, RL332008

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Knutson, B. J., G. Jansen, B. D. Zimmerman, S. E. Seeman, L. Lauerhass, and M. Hoza, *Extensive Separations (CLEAN) Processing Strategy Compared to TRUEX Strategy and Sludge Wash Ion Exchange*, WHC-EP-0791, Westinghouse Hanford Company, Richland, Washington, 1994.

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**DOE  
BUSINESS OPPORTUNITIES**

**Section 6.0**



## WORKING WITH THE DOE OFFICE OF ENVIRONMENTAL MANAGEMENT

DOE provides a range of programs and services to assist universities, industry, and other private-sector organizations and individuals interested in developing or applying environmental technologies. Working with DOE Operations Offices, as well as management and operating contractors, EM employs a number of mechanisms to identify, integrate, develop, and adapt promising emerging technologies. These mechanisms include contracting and collaborative arrangements, procurement provisions, licensing of technologies, consulting arrangements, reimbursable work for industry, and special consideration for small business. EM facilitates the development of subcontracts, R&D contracts, and cooperative agreements to work collaboratively with the private sector.

### COOPERATIVE RESEARCH AND DEVELOPMENT AGREEMENTS (CRADAs)

CRADAs are mechanisms for collaborative R&D. They are agreements between a DOE R&D laboratory and any non-federal source to conduct cooperative R&D that is consistent with the laboratory's mission. The partner may provide funds, facilities, people, or other resources. DOE provides the CRADA partner with access to facilities and expertise; however, external participants receive no federal funds. Rights to inventions and other intellectual property are negotiated between the laboratory and the participant. Certain generated data may be protected for up to five years. Several companies may combine their resources to address a common technical problem. Funds can be leveraged to implement a consortium for overall program effectiveness.

### PROCUREMENT MECHANISMS

DOE-EM procurement mechanisms are for technology development in the form of unsolicited proposals and formal solicitations, although the latter are preferable. The principal contractual mechanisms used by EM for industrial and academic response include Research Opportunity Announcements (ROAs) and Program R&D Announcements (PRDAs).

EM utilizes the ROA to seek advanced research and technologies for a broad scope of cleanup needs. The ROA supports applied research ranging from concept feasibility to full-scale testing. In addition, the ROA is open continuously for a full year following the date of issue and includes a partial procurement set-aside for small businesses. Typically, ROAs are published annually in the Federal Register, announced in the Commerce Business Daily, and provide multiple awards.

PRDAs are program announcements which solicit a broad mix of advanced development and demonstration proposals. A PRDA requests proposals for a wide-range of technical solutions to specific EM problem areas. Multiple awards, which may have distinct approaches or concepts, are generally made. Numerous PRDAs may be issued each year.

EM awards grants and cooperative agreements if 51 percent or more of the overall value of the effort is related to a public interest goal. Such goals include possible non-DOE or other federal agency participation and advancement of present/future U.S. capabilities in domestic and international environmental cleanup markets. They may also include technology transfer, advancement of scientific knowledge, or education and training of individuals as well as business entities.

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For more information about PRDAs and ROAs, contact:

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## LICENSING OF TECHNOLOGIES

DOE contractor-operated laboratories can license DOE/EM-developed technology and software. In situations where DOE retains the ownership of a new technology, the Office of General Counsel will serve as the licensing agent. Licensing activities are conducted according to existing DOE intellectual property provisions.

## TECHNICAL PERSONNEL EXCHANGE ASSIGNMENTS

Personnel exchanges provide opportunities for scientists from private industry and DOE laboratories to work together at various sites on environmental restoration and waste management problems. Private industry must contribute substantial cost-sharing for these personnel exchanges. To encourage such collaboration, the rights to any resulting patents go to the private sector company. These personnel exchanges, which can last from three to six months, result in the transfer of technical skills and knowledge.

## CONSULTING ARRANGEMENTS

Laboratory scientists and engineers are available to consult in their areas of technical expertise. Most contractors which operate laboratories have consulting provisions. Laboratory employees who wish to consult can sign non-disclosure agreements, and are encouraged to do so.

## REIMBURSABLE WORK FOR INDUSTRY

DOE laboratories are available to perform work for private industry and other federal agencies, as long as the work pertains to the mission of a respective laboratory and does not compete with the private sector. The special technical capabilities at DOE laboratories are incentives for the private sector to use DOE's facilities and contractor expertise. An advanced class patent waiver gives ownership of any inventions resulting from the research to the participating private sector company.

## INTERACTIONS WITH SMALL BUSINESSES

EM seeks the participation of small businesses in its RDDT&E programs (1) through collaborative efforts with the National Laboratories, or (2) directly via solicitations issued by the DOE Small Business Innovation Research (SBIR) Program Office and the Small Business Technology Transfer (T2) Pilot Program (STTR). EM also has established a partial procurement set-aside for small firms (500 employees or less) for applied research projects through its ROA.

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**For further information about SBIR and STTR programs, please contact:**

U.S. Department of Energy  
Small Business Innovation Research Program Hotline  
ER-16 GTN  
Washington, D.C. 20585  
(301) 903-5707

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## **EM CENTER FOR ENVIRONMENTAL MANAGEMENT INFORMATION**

The EM Center for Environmental Management Information is designed to provide ready access to prospective research and business opportunities in waste management, environmental restoration, and decontamination and decommissioning activities. The Center can identify links between industry technologies and program needs. It connects potential partners to an extensive complex-wide network of DOE headquarters and operations office contacts. To reach the EM Center for Environmental Management Information, call 1-800-736-3282.

## **OFFICES OF RESEARCH AND TECHNOLOGY APPLICATIONS**

The Offices of Research and Technology Applications (ORTA) serve as technology transfer agents for the federal laboratories. They coordinate technology transfer activities among laboratories, industry, and universities. ORTA offices license patents and foster communication between researchers and technology customers.

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**ACRONYM  
LISTING**

**Section 7.0**



ABS	aqueous biphasic separation
Am	americum
ANL	Argonne National Laboratory
AP	acid-side processing
°C	degree Celsius
CAC	continuous annular chromatograph
C/D	calcination/dissolution
CIEX	continuous ion exchanger
Cm	curium
CMPO	octyl (phenyl) -N,N-diisobutylcarbamoyl-methylphosphine
Co	cobalt
CRADA	Cooperative Research and Development Agreement
Cs	Cesium
CSIX	Cesium Ion Exchange
CST	crystalline silicotitanate
D&D	decontamination and decommissioning
DOE	U.S. Department of Energy
EM	Office of Environmental Management
EPA	Environmental Protection Agency
ESP	Efficient Separations and Processing
g	gram
HLW	High-Level Waste
I	iodine
ICPP	Idaho Chemical Processing Plant
ID	Integrated Demonstrations
INEL	Idaho National Engineering Laboratory
IP	Integrated Program

$K_d$	distribution coefficient
$K_{sp}$	solubility product
L	liter
LLW	low-level waste
LANL	Los Alamos National Laboratory
LDR	Land Disposal Restriction
M	molar
MACS	magnetically-assisted chemical separation
mCi	millicurie
mL	milliliter
MVST	Melton Valley Storage Tanks
Na	sodium
NaOH	sodium hydroxide
$NaNO_3$	sodium nitrate
nCi	nanocurie
Ni	nickel
$NO_x$	oxides of nitrogen
NWPA	Nuclear Waste Policy Act
ORNL	Oak Ridge National Laboratories
OTD	Office of Technology Development
PBI	polybenzimidazole
PEG	polyethylene glycol
PNL	Pacific Northwest Laboratory
$PN_x$	poly(diphenoxy) phosphazene
ppb	parts per billion
PPG	polypropylene glycol
ppm	parts per million
PTFE	polytetrafluoroethylene
Pu	plutonium

PUREX	plutonium-uranium extraction
QA	Quality Assurance
RCRA	Resource Conservation and Recovery Act
R&D	Research and Development
RDDT&E	Research, Development, Demonstration, Testing, and Evaluation
RFP	Rocky Flats Plant
Se	selenium
SNL	Sandia National Laboratories
Sr	Strontium
SREX	Strontium Extraction Process
SRS	Savannah River Site
SST	single-shell tanks
TALSPEAK	Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Complexes
TAWRS	Tritium Aqueous Waste Recovery System
TBP	tributylphosphate
Tc	technetium
Th	thorium
TPA	Tri-Party Agreements
TT	Technical Task
TTPs	Technical Task Plans (TTPs)
TRU	transuranic
TRUEX	Transuranic Element Extraction Process
TWRS	Tank Waste Remediation System
UST	underground storage tank
WIPP	Waste Isolation Pilot Plant
WSR	Westinghouse Savannah River



**APPENDIX**

**Section 8.0**



## APPENDIX

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### TECHNICAL TASK PLANS

Technical Task Plans (TTPs) identify and summarize funded work managed by OTD at headquarters, the field and the national laboratories. All tasks require a TTP number, which contains eight characters assigned by DOE Headquarters. The format consists of two alpha characters followed by six numerical characters. Characters 1 and 2 designate the DOE Operations Office/Funding Allotment Code. Character 3 denotes the laboratory/contractor/university designator. Character 4 denotes the fiscal year in which the task is first funded. The below characters reflect TTPs from FY94-95.

Characters 1, 2 & 3

AL0 Albuquerque Operations Office  
AL1 Los Alamos National Laboratory (LANL)  
AL2 Sandia National Laboratory, Albuquerque (SNLA)/Martin Marietta  
AL3 Sandia National Laboratory, Livermore (SNLL)  
AL4 Kansas City Plant (KCP)/Allied-Signal Aerospace  
AL9 RUST GEOTECH  
CH0 Chicago Operations Office  
CH1 Ames Laboratory  
CH2 Argonne National Laboratory (ANL)/University of Chicago  
CH3 Brookhaven National Laboratory (BNL)/Associated Universities, Inc.  
CH5 National Renewable Energy Laboratory  
FN0 Fernald Environmental Management Project (FEMP)  
FN1 Fluor Daniel Environmental Restoration Management Company  
HQ0 OTD Headquarters  
ID0 Idaho Operations Office  
ID1 Idaho National Engineering Laboratory (INEL)/EG&G  
ID4 Westinghouse Idaho Nuclear Company  
ID6 Babcock & Wilcox, Inc  
ID7 Lockheed Idaho Technology Company  
ME0 Morgantown Energy Technology Center (METC)  
NV0 Nevada Operations Office

OH0 Ohio Operations Office  
OH1 Fernald Environmental Management Project (FEMP)  
OH2 EG&G Mound Applied Technologies  
OR0 Oak Ridge Operations Office  
OR1 Martin Marietta Energy Systems (MMES)  
OR3 Oak Ridge Institute for Science and Education  
PE0 Pittsburgh Energy Technology Center  
PE1 MSE, Inc.  
RF0 Rocky Flats Environmental Technology Office  
RF1 Rocky Flats Plant/EG&G  
RL0 Richland Operations Office  
RL2 Kaiser Engineers Hanford Company (KEH)  
RL3 Pacific Northwest Laboratory (PNL)/Battelle Memorial Institute  
RL4 Westinghouse Hanford Company  
SF0 Oakland Operations Office  
SF1 Lawrence Berkeley Laboratory (LBL)/University of California  
SF2 Lawrence Livermore National Laboratory (LLNL)/University of California  
SF3 Energy Technology Engineering Center (ETEC)  
SR0 Savannah River Operations Office  
SR1 Westinghouse Savannah River Company (WSRC)

Character 4

1	FY 1991
2	FY 1992
3	FY 1993
4	FY 1994
5	FY 1995
6	FY 1996
7	FY 1997
8	FY 1998
9	FY 1999
0	FY 2000