RADIONUCLIDE SEPARATION AND PROCESSING FOR RECYCLE OR DISPOSAL

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ABSTRACT

The U.S. Department of Energy (DOE) Office of Technology Development (OTD) is sponsoring research and development on advanced radiochemical separations, at a modest level, with the long-term goals of reducing the volume of deep geologic repository-disposed waste and the toxicity of low-level waste disposed as cement grout in a near-surface vault. This will help reduce overall environmental risks and the cost of waste management.

INTRODUCTION

Removal of certain radionuclides, hazardous metals and chemicals, and other constituents from radioactive defense wastes has received considerable attention from DOE because of the potential reduction in environmental risks and waste management costs. Over the past several years, research and development of advanced separations technologies for a number of waste categories have been supported by OTD. Demonstration of these technologies with actual waste streams, as well as further developments and refinements, are still needed.

The primary goals of this program are to minimize the environmental impact and risk of waste treatment and disposal and to minimize life cycle costs. This will be accomplished by:

- Reducing the volume of waste that must be disposed in a geologic repository,
- Reducing the toxicity of low-level waste (LLW) that is disposed as cement grout in a near-surface vault, and
- Minimizing the volume of LLW grout.

The secondary goals of this program are to identify high-value waste constituents for potential recycle and to develop technologies for transfer to commercial use.

The first priorities of this program are the high-level wastes (HLW) in the underground storage tanks at Hanford and the calcined HLW in bins at Idaho, because they constitute the bulk of DOE wastes destined for disposal in a geologic repository. The HLW at the Savannah River Site and at West Valley will not be affected by this program because their vitrification and disposal projects are already underway.

Radionuclides and other constituents under consideration for separations include the transuranic (TRU) elements (neptunium, plutonium, americium and curium), the long-lived soluble fission products (technetium-99 and iodine-129), the high-heat producing fission products (strontium-90 and cesium-137), the long-lived soluble activation product carbon-14, the elements that degrade borosilicate glass waste forms (aluminum, phosphorous and chromium), the strategic metals (rhodium, palladium and ruthenium), and RCRA elements and compounds.

Application of separation technologies to different waste streams is complex because they contain multiple constituents. The type of separation process required, the efficiency required, and its economic justification will depend on site-specific and waste-specific details, including waste composition, local regulatory decisions and criteria, and negotiated agreements with the host state and regional EPA. As a result, while particular separations technologies like TRUEX and SREX may have generic applicability to separating TRU elements and strontium, specific details will dictate whether they will work or be cost effective for a particular waste stream.

HANFORD HIGH-LEVEL WASTE

The acidic liquid HLW from reprocessing defense reactor fuels for plutonium, which began in 1944, were made alkaline (pH 14) by adding caustic soda and were stored in underground concrete storage tanks lined with carbon steel. Over the years, 149 of these single-shell tanks (SST) were built and eventually they began to leak. Today, 66 of these SSTs are known to be or suspected of leaking (1), posing a threat to contaminate the ground-water. The maximum migration of these SST wastes into the ground is estimated to be 75m.(1) When the SSTs began to leak, new underground double-shell tanks (DST) were built, and there are now 28 DSTs, none of which have leaked. However, at least two of these DSTs are generating hydrogen gas, which is considered to be the priority safety issue at Hanford because of the possibility of fire or explosion.

The 149 SSTs contain a total (2) 165,500 m^3 of waste, all of which is currently treated as HLW, approximately 250,000 Mg. Each tank contains salt cake, liquid supernate, and sludge at the bottom of the tank. The tanks are not well characterized and have a large variation in constituents, complicating plans for separations and processing. The cost of taking and analyzing a core sample from a SST is about $500,000. Approximately 16% of the SST waste volume is supernate, 56% is salt cake and 28% is sludge. By mass, the supernate is 58% sodium compounds, 40% water and 2% other compounds; the salt cake is 90% sodium compounds and 10% water; and the sludge is 55% sodium compounds, 34% water, 11% other compounds and 5.2 ppm TRU elements (132,000 Ci).

The 28 DSTs contain 79,300m^3 of HLW, approximately 100,000 Mg. Four of the DSTs contain slurry that was generated by transferring the supernate from SSTs in order to reduce leakage and then concentrating it by evaporation. The other DSTs store slurry from more recent reprocessing wastes, from complexant concentrate waste, neutralized cladding removal waste, and Plutonium Finishing Plant waste. By mass, the slurry is 37% sodium compounds, 56% water, 7% other compounds, and 1.3 ppm TRU elements (96,000 Ci). It is clear that both SST and DST waste is very dilute, containing a very small *volume of* radionuclides. The schedule for cleaning up the Hanford HLW is subject to the Triparty Agreement signed by DOE, EPA and the State of Washington.

IDAHO HIGH-LEVEL WASTE

The HLW stored at Idaho resulted primarily from reprocessing Naval reactor fuels. Acidic liquid waste is stored in underground stainless steel tanks that are housed inside concrete vaults. The waste is then converted into a calcine powder and stored retrievably in stainless steel bins inside reinforced concrete vaults. There are 3,500 m^3 of HLW stored as calcine, containing 90% of the radioactivity, and 8,500 m^3 of liquid HLW containing 10% of the radioactivity. The Idaho waste is uniform, well characterized, problem free. The calcine waste form is expected to be satisfactory for storage for 500 years. Nevertheless Idaho Land Disposal Restrictions require submission of a plan for waste minimization and disposal by May 1992. Failure to comply would prevent further waste generation and would shut down the Idaho Chemical Processing Plant (ICPP).

ECONOMIC BENEFITS OF ADVANCED SEPARATIONS

The preferred waste form for permanent disposal of HLW is vitrified borosilicate glass inside a stainless steel canister. Approximately 25 to 30 volume percent of the vitrified glass is HLW and the balance is glass frit, unless the HLW contains aluminum, phosphorous or chromium. The cost of making a glass canister is about $500,000. (3)

Recent estimates for the Hanford SST and DST HLW disposal indicate that sludge wash of the waste, primarily to rid the waste of sodium and other soluble compounds, without further separations and processing, would require 40,000 (4) canisters. If advanced separations are implemented to partition TRU elements, cesium, strontium, and technetium, the required canisters for disposal of the remaining 2,000 m^3 of HLW (less than 10 m^3 are radionuclides) would be about 12,000. That is a savings of $14 billion in vitrification costs and may alleviate the need for a second repository. More sophisticated separations processes could probably reduce the required number of HLW canisters to about 100 or 200.

The sludge wash and advanced separations will generate 940,000 m^3 of aqueous LLW, which will be disposed of as 1,600,000 m^3 of cement grout in 300 near-surface concrete vaults. The cost of LLW disposal is projected to be $5,800 per *$m^3$ of liquid* or $3,400 per m^3 of grout.(5) The cost of vitrification and disposal of a m^3 of HLW, which requires six canisters, at a cost of $860,000 per canister, including the $360,000 repository charge, is $5,160,000; or 890 times the cost of disposal of a m^3 of LLW.

Since the Idaho HLW is in calcine form, processing the waste with aqueous solvent extraction would require dissolving the calcine in nitric acid, which would generate a large volume of aqueous LLW. As an alternative, Idaho is exploring a glass-ceramic *waste form and the* possibility of pyrochemical processing.

NATIONAL ACADEMY OF SCIENCES STUDY

OTD is sponsoring a three-year independent study of separations technology and transmutation systems (STATS) by the National Academy of Sciences. Prof. Norman Rasmussen is chairman of the STATS Panel. The panel will assess the feasibility, readiness and economic justification of separations and transmutations, as well as institutional issues. They will issue interim reports and a final report by late summer 1994.

FY 1991 ACCOMPLISHMENTS

- Completed first bench-scale TRUEX tests of plutonium and americium in nitric acid solution at Argonne National Laboratories. Decontamination factor of 10^7 was achieved with a single pass.
- Organized a workshop of 35 radiochemical separations specialists to assess separations needs, the development status of separations processes, funding priorities, and program strategies.
- Upgraded the Generic TRUEX Model.
- Designed a super-high-throughput centrifugal contactor.
- Developed flow sheets for technetium-ruthenium and iodine-xenon aqueous-based post-transmutation separations and initiated experiments to measure separations factor values.
- Defined elements of a systems model to be used in evaluation of TRUEX for high-level waste in a single-shell tank at Hanford.
- Issued feasibility report on best vitrification technology for ICPP HLW.
- Issued "Status Report: The Glass-Ceramic Processing Flow Sheet for ICPP HLW."
- Chose non-radioactive, non-hazardous simulant for testing ICPP calcine HLW (calcium carbonate).

FY 1992 OBJECTIVES

- Complete Program Strategy Document, continue assessment of needs and potential/existing technologies. Develop EM-30/50 coordinated effort to identify waste streams and their needs along with appropriate technology developments, beginning with the Idaho calcine waste.
- Continue development of a total mass-balance model for a waste-treatment system and start development of process flow diagrams for promising technologies for Hanford and Idaho.
- Measure performance of a few selected sequestering agents for removal of Sr, Cs, and TRUs on actual HLW, and evaluate computer design of selective new sequestering agents.
- Define and test separations components amenable to use in modular processing concept.
- Investigate pyrochemical methods for the Idaho HLW, conduct equipment feasibility studies, and evaluate waste form candidates (glass, glass-ceramic, and metal) to accept the pyrochemical waste streams.
- Develop and validate thermodynamic data base required to predict behavior of sludge during washing, leaching, and dissolution.

- Continue evaluation of Idaho HLW process options; issue report on actinide separations/fission product separations.
- Develop separations chemistry for conversion and destruction of waste in an accelerator system. Demonstrate Tc/Ru separations.
- Combine TRUEX/SREX extraction into one process to extract U, TRUs, Tc, and Sr.
- Evaluate several other promising concepts for the separation of technetium.
- Initiate cooperative R&D to develop methods of separating cesium and noble metals from high-level waste.

IMPLEMENTATION OF A SEPARATIONS STRATEGY

The following key steps will be followed to focus the developmental efforts conducted:

- Identify the specific categories of waste streams where separations processes can play a major role. Process requirements, such as safety and regulatory issues, and time frame of opportunity, will be considered.
- Evaluate and, as appropriate, develop alternative systems level waste management strategies for the waste categories and assess the specific role/performance of separations technologies within the overall framework and compare this with existing technology to identify gaps.
- Identify commonalities in the separations technology gaps that cross cut the various waste categories.
- Establish priorities based on system-level considerations of cost savings, technological benefit, and probability of success.

This program will also assess the technology and cost effectiveness of radionuclide transmutation. The combination of chemical separations and transmutations has the attractive potential for bringing closure to the problem of long-lived radionuclide disposal.

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