

**Office of Science**  
**Notice 01-16**

***Environmental Management Science Program:  
Basic Science Research Related to High Level Radioactive  
Waste***

**Department of Energy  
Office of Science and  
Office of Environmental Management**

**Office of Science Financial Assistance Program Notice 01-16: Environmental Management Science Program: Basic Science Research Related to High Level Radioactive Waste**

**AGENCY:** U.S. Department of Energy (DOE)

**ACTION:** Notice inviting grant applications

**SUMMARY:** The Offices of Science (SC) and Environmental Management (EM), U.S. Department of Energy (DOE), hereby announce their interest in receiving grant applications for performance of innovative, fundamental research to support specific activities for high level radioactive waste; which include, but are not limited to, characterization and safety, retrieval of tank waste and tank closure, pretreatment, and waste immobilization and disposal.

**DATES:** The deadline for receipt of formal applications is 4:30 p.m. E.S.T., March 8, 2001, in order to be accepted for merit review and to permit timely consideration for award in Fiscal Year 2001.

**ADDRESSES:** Formal applications referencing Program Notice 01-16 should be sent to: U.S. Department of Energy, Office of Science, Grants and Contracts Division, SC-64, 19901 Germantown Road, Germantown, MD 20874-1290, ATTN: Program Notice 01-16. This address must be used when submitting applications by U.S. Postal Service Express, commercial mail delivery service, or when hand carried by the applicant.

**FOR FURTHER INFORMATION CONTACT:** Dr. Roland F. Hirsch, SC-73, Mail Stop F-237, Medical Sciences Division, Office of Biological and Environmental Research, Office of Science, U.S. Department of Energy, 19901 Germantown Road,

Germantown, MD 20874-1290, telephone: (301) 903-9009, fax: (301) 903-0567, E-mail: roland.hirsch@science.doe.gov, or Mr. Mark Gilbertson, Office of Basic and Applied Research, Office of Science and Technology, Office of Environmental Management, 1000 Independence Avenue, SW, Washington, D.C. 20585, telephone: (202) 586-7150, E-mail: Mark.Gilbertson@em.doe.gov. The full text of Program Notice 01-16 is available via the World Wide Web using the following web site address: <http://www.sc.doe.gov/production/grants/grants.html>.

**SUPPLEMENTARY INFORMATION:** The Office of Environmental Management, in partnership with the Office of Science, sponsors the Environmental Management Science Program (EMSP) to fulfill DOE's continuing commitment to the clean-up of DOE's environmental legacy. The program was initiated in Fiscal Year 1996. Ideas for basic scientific research are solicited which promote the broad national interest of a better understanding of the fundamental characteristics of highly radioactive chemical wastes and their effects on the environment.

The DOE Environmental Management program currently has ongoing applied research and engineering efforts under its Technology Development Program. These efforts must be supplemented with basic research to address long-term technical issues crucial to the EM mission. Basic research can also provide EM with near-term fundamental data that may be critical to the advancement of technologies that are under development but not yet at full scale nor implemented. Proposed basic research under this Notice should contribute to environmental management activities that would decrease risk for the public and workers, provide opportunities for major cost reductions, reduce time required to achieve EM's mission goals, and, in general, should address problems that are considered intractable without new knowledge. This program is designed to inspire "breakthroughs" in areas critical to the EM mission through basic research and will be managed in partnership with SC. The Office of Science's well-established procedures, as set forth in the Office of Science Merit Review System, available on the World Wide Web at: <http://www.science.doe.gov/production/grants/merit.html> will be used for merit review of applications submitted in response to this Notice. Subsequent to the formal scientific merit review, applications that are judged to be scientifically meritorious, will be evaluated by DOE for relevance to the objectives of the Environmental Management Science Program and for relevance to the technical focus of this solicitation (see "Relevance to Mission" section below). Additional information can be obtained at <http://emsp.em.doe.gov>. Additional Notices for the Environmental Management Science Program may be issued during Fiscal Year 2001 covering other areas within the scope of the EM program.

## **Purpose**

The purpose of the EMSP is to foster basic research that will contribute to successful completion of DOE's mission to clean-up the environmental contamination across the DOE complex.

The objectives of the Environmental Management Science Program are to:

1. Provide scientific knowledge that will revolutionize technologies and clean-up approaches to significantly reduce future costs, schedules, and risks;
2. "Bridge the gap" between broad fundamental research that has wide-ranging applicability such as that performed in DOE's Office of Science and needs-driven applied technology development that is conducted in EM's Office of Science and Technology; and
3. Focus the Nation's science infrastructure on critical DOE environmental management problems.

### **Representative Research Areas**

Basic research is solicited in areas of science with the potential for addressing problems in the clean-up of high level radioactive waste. Relevant scientific disciplines include, but are not limited to, chemistry (including actinide chemistry, analytical chemistry and instrumentation, interfacial chemistry, and separation science), computer and mathematical sciences, engineering science (chemical and process engineering), materials science (degradation mechanisms, modeling, corrosion, non-destructive evaluation, sensing of waste hosts, canisters), and physics (fluid flow, aqueous-ionic solid interfacial properties underlying rheological processes).

### **Project Renewals**

Lead Principal Investigators of record for Projects funded under Office of Science Notice 98-08, Environmental Management Science Program: Research Related to High Level Radioactive Waste, are eligible to submit renewal applications under this solicitation.

### **Program Funding**

It is anticipated that up to a total of \$4,000,000 of Fiscal Year 2001, Federal funds will be available for new Environmental Management Science Program awards resulting from this Announcement. Multiple-year funding of awards is anticipated, contingent upon the availability of appropriated funds. Award sizes are expected to be on the order of \$100,000-\$300,000 per year for total project costs for a typical three-year award. Collaborative projects involving several research groups or more than one institution may receive larger awards if merited. The program will be competitive and

offered to investigators in universities or other institutions of higher education, other non-profit or for-profit organizations, non-Federal agencies or entities, or unaffiliated individuals. DOE reserves the right to fund in whole or part any or none of the applications received in response to this Notice. A parallel announcement with a similar potential total amount of funds will be issued to DOE Federally Funded Research and Development Centers (FFRDCs) and may be accessed on the World Wide Web at [http://www.science.doe.gov/production/grants/LAB01\\_16.html](http://www.science.doe.gov/production/grants/LAB01_16.html). All projects will be evaluated using the same criteria, regardless of the submitting institution.

## **Collaboration and Training**

Applicants to the EMSP are strongly encouraged to collaborate with researchers in other institutions, such as universities, industry, non-profit organizations, federal laboratories and Federally Funded Research and Development Centers (FFRDCs), including the DOE National Laboratories, where appropriate, and to incorporate cost sharing and/or consortia wherever feasible. Refer to <http://www.sc.doe.gov/production/grants/Colab.html> for details.

Applicants are also encouraged to provide training opportunities, including student involvement, in applications submitted to the program.

## **Applications**

Applicants are expected to use the following format in addition to following instructions in the Office of Science Financial Assistance Program Application Guide. Applications must be written in English, with all budgets in U.S. dollars.

- SC Face Page (DOE F 4650.2 (10-91))
- Application classification sheet (a plain sheet of paper with one selection from the list of scientific fields listed in the Application Categories Section)
- Table of Contents
- Project Abstract (no more than one page)
- Budgets for each year and a summary budget page for the entire project period (using DOE F 4620.1)
- Budget Explanation. Applicants are requested to include in the travel budget for each year funds to attend the annual National Environmental Management Science Program Workshop, and also for one or more extended (one week or more) visits to a clean-up site by either the Principal Investigator or a senior staff member or collaborator
- Budgets and Budget explanation for each collaborative subproject, if any

- Project Narrative (recommended length is no more than 20 pages; multi-investigator collaborative projects may use more pages if necessary up to a total of 40 pages)
- Goals
- Significance of Project to the EM Mission
- Background
- Research Plan
- Preliminary Studies (if applicable)
- Research Design and Methodologies
- Literature Cited
- Collaborative Arrangements (if applicable)
- Biographical Sketches (limit 2 pages per senior investigator)
- Description of Facilities and Resources
- Current and Pending Support for each senior investigator

### **Application Categories**

In order to properly classify each application for evaluation and review, the application must indicate the proposer's preferred scientific research field, selected from the following list.

#### **Field of Scientific Research:**

1. Actinide Chemistry
2. Analytical Chemistry and Instrumentation
3. Separations Chemistry
4. Engineering Sciences
5. Geochemistry
6. Geophysics
7. Hydrogeology
8. Interfacial Chemistry
9. Materials Science
10. Other

### **Application Evaluation and Selection**

#### **Scientific Merit**

The program will support the most scientifically meritorious and relevant work, regardless of the institution. Formal applications will be subjected to scientific merit review (peer review) and will be evaluated against the following evaluation criteria listed in descending order of importance as codified at 10 CFR 605.10(d):

1. Scientific and/or Technical Merit of the Project
2. Appropriateness of the Proposed Method or Approach
3. Competency of Applicant's Personnel and Adequacy of Proposed Resources
4. Reasonableness and Appropriateness of the Proposed Budget.

The evaluation will include program policy factors such as the relevance of the proposed research to the terms of the announcement and the Department's programmatic needs. DOE shall also consider, as part of the evaluation, program policy factors such as an appropriate balance among the program areas, including research already in progress. External peer reviewers are selected with regard to both their scientific expertise and the absence of conflict-of-interest issues. Non-federal reviewers may be used, and submission of an application constitutes agreement that this is acceptable to the investigator(s) and the submitting institution.

### **Relevance to Mission**

Subsequent to the formal scientific merit review, applications which are judged to be scientifically meritorious will be evaluated by DOE for relevance to the objectives of the Environmental Management Science Program and for relevance to the technical focus of the solicitation (see section below).

"Researchers are encouraged to demonstrate a linkage between their research projects and significant clean up related problems at DOE sites. Researchers could establish this linkage in a variety of ways - for example, by elucidating the scientific problems to be addressed by the proposed research and explaining how the solution of these problems could improve remediation capabilities." (National Research Council, Board on Radioactive Waste Management, December 1998)

DOE shall also consider, as part of the evaluation, program policy factors such as an appropriate balance among the program areas, including research already in progress. Research funded in the Environmental Management Science Program in Fiscal Year 1996 through Fiscal Year 2001, can be viewed at <http://www.doe.gov/em52/science-grants.html>.

### **Application Guide and Forms**

Information about the development, submission of applications, eligibility, limitations, evaluation, the selection process, and other policies and procedures may be found in 10 CFR Part 605, and in the Application Guide for the Office of Science Financial Assistance Program. Electronic access to the Guide and required forms is available via the World Wide Web at:

<http://www.sc.doe.gov/production/grants/grants.html>. DOE is under no obligation to

pay for any costs associated with the preparation or submission of applications if an award is not made.

### **Technical Focus of the Solicitation**

This research announcement has been developed for Fiscal Year 2001, along with a development process for a long-term program within Environmental Management, with the objective of providing continuity in scientific knowledge that will revolutionize technologies and clean-up approaches for solving DOE's most complex environmental problems. A general description of the high level waste problem can be found in the Background section of this Notice. Detailed descriptions of the specific technical (science) needs and areas of emphasis associated with this problem area are available on the Tanks Focus Area web site at <http://www.pnl.gov/tfa>.

### **Long Term Research Agenda for High Level Radioactive Waste**

The National Academy of Science's National Research Council was requested to assist the DOE in developing a long-range science plan for the management of radioactive high-level waste at DOE sites. The Committee empanelled to study that issue determined that some High Level Waste related problems will require further research and development to minimize risk and program cost and to improve the effectiveness of clean-up. Their recommendations in four topic areas are the focus of this solicitation and are described below. More detailed descriptions of the specific technical (science) needs in these four topic areas are available on the Tanks Focus Area web site at: <http://www.pnl.gov/tfa>.

#### **1. Long-term issues related to tank closure:**

An example of research activities to address this issue is innovative methods for in situ characterization of the High Level Waste remaining in the tanks after retrieval to facilitate tank closure.

#### **2. High-efficiency, high-throughput separation methods that would reduce high-level waste program costs over the next few decades including:**

- a. High-efficiency separation, and
- b. Minimization of the volume of secondary waste.

Applications on separation sciences addressing these two areas are encouraged. The projects should address all types of separations: solids from liquids from gases, High Level Waste from low level waste, and radionuclides from organic compounds.

An example of a project addressing separation issues could be research on processes that remove multiple radionuclides in a single step.

**3. Robust, high loading, immobilization methods and materials that could provide enhancements or alternatives to current immobilization strategies including:**

- a. Alternatives to borosilicate glasses using slurry-fed electric (Joule) melter as an immobilization matrix, and
- b. Alternatives melter techniques.

As an example, a research project might study alternative immobilization matrixes, tailored to either High Level Waste or low level waste, such as cement or crystalline ceramics. Applications to conduct research on alternative melter techniques that would increase the processes available to address different waste streams leading to more efficient immobilization results are encouraged.

**4. Innovative methods to achieve real-time, and, when practical, in situ characterization data for High Level Waste and process streams that would be useful for all phases of the waste management program with emphasis on:**

- a. Characterization of the waste after retrieval, for instance in process streams and melter feeds.

Applications aimed at developing techniques to achieve shorter turn-around times for the analytical results, which in turn would allow better control of High Level Waste processing are encouraged. An example of such a project is research on fiber-optical interrogation to characterize process streams.

Attendant to paragraph 1. above, there was another area highlighted by the National Research Council regarding long-term issues related to characterization of surrounding areas including radionuclide and metal contamination problems in the near-field around the tanks, and engineered surface or subsurface barriers. These topics will be a matter of a future solicitation for research regarding subsurface contamination.

**Specific High Level Waste Science Needs**

Detailed information on the specific high level waste technical (science) needs within the general topic areas of this solicitation are available from the Tanks Focus Area Home Page at: <http://www.pnl.gov/tfa>. Relevance to mission reviews will consider responsiveness to the four topic areas of this solicitation and these corresponding specific technical needs. Additional general science research needs and information is also available at: [http://emsp.em.doe.gov/focus\\_area.htm](http://emsp.em.doe.gov/focus_area.htm).

The aforementioned areas of emphasis do not preclude, and DOE strongly encourages, any innovative or creative ideas contributing to solving EM High Level Waste challenges mentioned throughout this Notice.

For further information regarding the Tanks Focus Area please contact: Mr. Theodore P. Pietrok, Tanks Focus Area, U.S. Department of Energy, P.O. Box 550, Mail Stop K8-50, Richland, WA 99352, telephone: (509)372-4546, Fax: (509)372-4037, E-mail: Theodore\_P\_Pietrok@rl.gov.

## **Background**

Environmental Management (EM) is responsible for the development, testing, evaluation, and deployment of remediation technologies to characterize, retrieve, treat, concentrate, and dispose of radioactive waste stored in the underground storage tanks at DOE facilities and ultimately stabilize and close the tanks. The goal is to provide safe and cost-effective solutions that are acceptable to both the public and regulators.

Radioactive high level waste is stored at four sites across the DOE complex:

1. Hanford Site near Richland, Washington
2. Savannah River Site (SRS) near Aiken, South Carolina
3. Idaho National Engineering and Environmental Laboratory (INEEL) near Idaho Falls, Idaho
4. West Valley Demonstration Project (WVDP) in West Valley, New York

At these sites, 282 underground storage tanks have been used to process and store radioactive and chemical mixed waste generated from weapon materials production and manufacturing. Collectively, these tanks hold approximately 90 million gallons of high-level and low-level radioactive liquid waste in sludge, saltcake, and as supernate and vapor.

Tanks vary in design from carbon or stainless steel to concrete, and concrete with carbon steel liners. Two types of storage tanks are most prevalent: the single-shell and double-shell concrete tanks with carbon steel liners. Capacities vary from 5,000 gallons (19m<sup>3</sup>) to 1,300,000 gallons (4920m<sup>3</sup>). Most tanks are covered with a layer of soil ranging from approximately 3 to 10 feet thick.

Most of the waste is alkaline and contains a diverse mixture of chemical constituents including nitrate and nitrite salts (approximately half of the total waste), hydrated metal oxides, phosphate precipitates, and ferrocyanides. The 784 MCi of radionuclides are distributed primarily among the transuranic (TRU) elements and

fission products, specifically strontium-90, cesium-137, and their decay products yttrium-90 and barium-137. In-tank atmospheric conditions vary in severity from near ambient to temperatures over 93° C. Radiation fields in the tank void space can be as high as 10,000 rad/h.

Hanford has 177 tanks that contain approximately 53 million gallons of hazardous and radioactive waste. There are 149 single-shell tanks that have exceeded their original design life. Sixty-seven of these tanks have known or suspected leaks. Due to several changes in the production processes since the early 1940s, some of the tanks contain incompatible waste components, generating hydrogen gas and excess heat that further compromise tank integrity.

Radioactive waste at SRS consists of 33 million gallons of salt, salt solution, and sludge stored in 51 double-shell underground storage tanks, two of which have been closed (emptied of all waste and filled with grout). Twenty-three tanks are being retired, because they do not have full secondary containment. Nine tanks have leaked detectable quantities of waste from the primary tank to secondary containment.

Unlike the other DOE sites, radioactive waste at INEEL was stored in acidic conditions in stainless steel tanks rather than alkaline conditions. The 11 stainless steel tanks at INEEL store approximately 1.2 million gallons of acidic radioactive liquids. Additionally, approximately 4000 m<sup>3</sup> of calcined waste solids are stored in seven stainless steel bin sets enclosed in massive underground concrete vaults.

At the West Valley Demonstration Project nearly all of the original 600,000 gallon of HLW has been retrieved and vitrified. This site is now in the process of cleaning the storage tanks and preparing for closure.

The general process for waste tank remediation involves a number of critical steps including:

- Safe waste storage
- Waste characterization
- Retrieval of tank waste
- Pretreatment and separation of tank waste
- Waste immobilization
- Tank closure, and
- Immobilized waste disposal

Tank remediation problems within these critical process steps are described below. Several process steps are combined for the purpose of describing related technical issues

## **Characterization and Safety**

DOE, contractors, and stakeholders have committed to a safe and efficient remediation of HLW, mixed waste, and hazardous waste stored in underground tanks across the DOE complex.

Currently, there are only limited fully developed or deployed in situ techniques to characterize tank waste. In situ characterization can eliminate the time delay between sample removal and sample analysis and aid in guiding the sampling process while decreasing the cost (approximately \$1 million is spent for one tank core extrusion) of waste analysis. Most importantly, remote analysis eliminates sample handling and safety concerns due to worker exposure. However, analysis of extruded tank samples allows a more complete chemical and physical characterization of the waste when needed. Knowledge of the chemical and radioactive composition and physical parameters of the waste is essential to safe and effective tank remediation.

There are three primary drivers for the development of new chemical analysis methods to support tank waste remediation: 1) provide analyses for which there are currently no reliable existing methods, 2) replace current methods that require too much time and/or are too costly, and 3) provide methods that evolve into on-line process analysis tools for use in waste processing facilities.

Characterization of the elemental and isotopic chemical constituents in DOE tank waste is an important function in support of DOE tank waste operation and remediation functions. Proper waste characterization enables: safe operation of the tank farms; resolution of tank safety questions; and development of processes and equipment for retrieval, pretreatment, and immobilization of tank waste. All of these operations are dependent on the chemical analysis of tank waste.

Current techniques of tank waste analysis involve the removal of core samples from tanks, followed by costly and time consuming wet analytical laboratory testing. Savings in both cost and time could be realized in techniques that involve in situ probes for direct analysis of tank materials.

Leakage from the single shell tanks at Hanford is among the safety concerns. As indicated earlier many of the 149 single shell tanks are known or suspected to leak. This presents a grave problem for retrieval of waste from these tanks since the baseline method for retrieval is to sluice thousands of gallons of water into the tank to dissolve and suspend the waste. HLW waste leakage into the environment can threaten the ground water. There is a need to develop instrumentation to determine the location of a leak, measure the amounts of contamination that may have leaked, and assess the environmental impact.

Another safety concern is the long-term performance of waste forms. Performance assessments of radionuclide containment rely primarily on the geologic barriers (e.g., long travel times in hydrologic systems or sorption on mineral surfaces). The physical and chemical durability of the waste form, however, can contribute greatly to the successful isolation of radionuclides; thus the effects of radiation on physical properties and chemical durability of waste forms are of great importance. The changes in chemical and physical properties occur over relatively long periods of storage, up to a million years, and at temperatures that range from 100 to 300 degrees Celsius, depending on waste loading, age of the waste, depth of burial, and the repository-specific geothermal agent. Thus, a major challenge is to effectively simulate high-dose radiation effects that will occur over relatively low-dose rates over long periods of time at elevated temperatures. Similarly, there is a paramount need for improved understanding and modeling of the degradation mechanisms and behavior of primary radioactive waste hosts and/or their containment canisters, corrosion mechanisms and prevention in aqueous and/or alkali halide containing environments, and remote sensing and non-destructive evaluation.

Examples of specific science research challenges include but are not limited to: basic measurement science and sensor development required for remote detection of low concentrations of hydrogen inside tanks and in containers; basic analytical studies needed to develop new methods for chemical and physical characterization of solid and liquids in slurries and for development of advanced processing methodologies; basic instrument development needed to perform in situ radiological measurements and collect spatially resolved species and concentration data; basic materials and engineering science needed to develop radiation hardened instrumentation.

### **Retrieval of Tank Waste and Tank Closure**

Underground tanks throughout the DOE complex have stored a diverse accumulation of wastes during the past fifty years of weapons and fuel production. If these tanks were isolated in a manner that would preclude the escape of radiation into the environment for thousands of years, there would be no reason to disturb them. However, a number of the storage tanks are approaching the end of their design life, and 90 tanks have either leaked or are suspected of having leaked waste into the soil and sediments near the tanks.

Recently, dewatering processes have removed much of the free liquid from the alkaline waste tanks. The tanks now contain wastes ranging in consistency from remaining supernate and soft sludge to concrete-like saltcake. Tanks also contain miscellaneous foreign objects such as Portland cement, measuring tapes, samarium balls, and in-tank hardware such as cooling coils and piping. Unlimited sluicing, adding large quantities of water to suspend solids, is the baseline method for sludge

removal from tanks. This process is not capable of retrieving all of the material from tanks. Besides dealing with aging tanks and difficult wastes, retrieval also faces the problem of the tank design itself. Retrieval tools must be able to enter the tanks, which are under an average of 10 feet of soil, through small openings called risers in the tops of the tanks.

Retrieval of tank waste and tank closure requires tooling and process alternative enhancements to mixing and mobilizing bulk waste as well as dislodging and conveying heels. Heel removal is linked to tank closure. The working tools and removal devices being developed include suction devices, rubblizing devices, water and air jets, waste conditioning devices, grit blasting devices, transport and conveyance devices, cutting and extraction tools, monitoring devices, and various mechanical devices for recovery or repair of waste dislodging and conveyance tools.

The areas directly below the access risers are often disturbed or contain a significant amount of discarded debris. Therefore, evaluation of tank waste characteristics by measurements taken at these locations may not be representative of the properties of the waste in other areas of the tanks.

To monitor current conditions and plan for tank remediation, more information on the tank conditions and their contents is required. Current methods used at DOE tank sites are limited to positioning sensors, instruments, and devices to locations directly below access penetrations or attached to a robotic arm for off-riser positioning. These systems can only deploy one type of sensor, requiring multiple systems to perform more than one function in the tank.

Currently, decisions regarding necessary retrieval technologies, retrieval efficiencies, retrieval durations, and costs are highly uncertain. Although tank closure has been completed on only two HLW tanks (at Savannah River), the tank contents proved amenable to waste retrieval using current technology. DOE has just begun to address the issue of how clean a tank must become before it is closed. Continued demonstration that tank closure criteria can be developed and implemented will provide substantial benefit to DOE.

A related problem that retrieval process development is examining the current lack of a retrieval decision support tool for the end users. As development activities move forward toward collection of retrieval performance and cost data, it has become very evident that the various sites across the complex need to have a decision tool to assist end users with respect to waste retrieval and tank closure. Tank closure is intimately tied to retrieval, and the sensitivity of closure criteria to waste retrieval is expected to be very large.

All the existing processes and technologies that could be used as a baseline for tank remediation have not yet been identified. Identifying these processes is one of EM's major issues in addressing the tank problems. The overall purpose of retrieval enhancements is to continue to lead the efforts in the basic understanding and development of retrieval processes in which waste is mobilized sufficiently to be transferred out of tanks in a cost-effective and safe manner. From that basic understanding, data are provided to end users to assist them in the retrieval decision-making process. The overall purpose of retrieval enhancements is to identify processes that can be used to reduce cost, improve efficiency, and reduce programmatic risk.

Basic engineering and separation science studies are needed to support tank remediation of liquids, which contain high concentrations of solids.

### **Pretreatment and Separation Processes for Tank Waste**

About 90 million gallons of HLW are stored in tanks at four primary sites within the DOE complex. It is neither cost-effective nor practical to treat and dispose of all of the tank waste to meet the requirements of the HLW repository program and the Nuclear Waste Policy Act. The pretreatment area seeks to address multiple needs across the DOE complex. The primary objectives are to reduce the volume of HLW, reduce hazards associated with treating LLW, and minimize the generation of secondary waste.

The current baseline technology systems for waste pretreatment at DOE's tank waste sites are expensive, and technology gaps exist. Large volumes of HLW will be generated, while there is limited space in the planned Nuclear Waste Repository for HLW from DOE. Even if adequate space were made available, treatment and disposal of HLW is still very expensive, estimated to be about \$1 million for each canister of vitrified HLW. Only a small fraction of the tank waste, by weight, is made up of HLW radionuclides. The bulk of the waste is chemical constituents intermingled with, and sometimes chemically bonded to, the radionuclides. The chemicals and radionuclides can be separated into HLW and LLW fractions for less costly treatment and disposal.

Most of the tank waste was generated as a result of nuclear fuel processing for weapons production. In that process, irradiated fuel and its cladding were first dissolved, uranium and plutonium were recovered as products, and the highly radioactive fission product wastes were concentrated and sent to the tanks for long-term storage.

Fuel processing at SRS did not change substantially from the beginning of operations in about 1955 to the present. While these wastes are fairly uniform, they still require pretreatment to separate the LLW from HLW prior to immobilization. Liquid waste at INEEL is stored under acidic pH conditions in stainless steel tanks. The original liquid high level waste has been calcined at high temperature to a dry powder. At Hanford, several processes were used over the years (beginning in 1944), each with a different chemical process. This resulted in different waste volumes and compositions. Wastes at Hanford and SRS are stored as highly alkaline material so as not to corrode the carbon steel tanks. The process of converting the waste from acid to alkaline resulted in the formation of different physical forms within the waste.

The primary forms of tank waste include sludge, saltcake, and liquid. The bulk of the radioactivity is known to be in the sludge which makes it the largest source of HLW. Saltcake is characteristic of the liquid waste with most of the water removed. Saltcake is found primarily in older single-shell tanks at Hanford.

Saltcake and liquid waste contain mostly sodium nitrate and sodium hydroxide salts. They also contain soluble radionuclides such as cesium. Strontium, technetium, and transuranics are also present in varying concentrations. The radionuclides must be removed; leaving a large portion of waste to be treated and disposed of as LLW and a very small portion that is combined with HLW from sludge for subsequent treatment and disposition.

Over the years, tank waste has been blended and evaporated to conserve space. Although sludge contains most of the radionuclides, the amount of HLW glass produced (vitrification is the preferred treatment of HLW) could be very high without pretreatment of the sludge. Pretreatment of the sludge by washing with alkaline solution can remove certain nonradioactive constituents and reduce the volume of HLW. Pretreatment can also remove constituents that could degrade the stability of HLW glass. The pretreatment area seeks to address multiple needs across the DOE complex. The primary objectives are to reduce the volume of HLW, reduce hazards associated with treating LLW, and minimize the generation of secondary waste.

The concentration of certain chemical constituents such as phosphorus, sulfur, and chromium in sludge can greatly increase the volume of HLW glass produced upon vitrification of the sludge. These components have limited solubility in the molten glass at very low concentrations. Some sludge has high concentrations of aluminum compounds, which can also be a controlling factor in determining the volume of HLW glass produced. Aluminum above a threshold concentration in the glass must be balanced with proportional amounts of other glass-forming constituents such as silica. There are estimated to be 25 different types of sludge at Hanford distributed among more than 100 tanks. Samples from 49 tanks would represent approximately 93

percent of the sludge in Hanford tanks. Testing of enhanced sludge washing, the combination of caustic leaching and water washing of sludge, on all of these samples is needed to determine whether enhanced sludge washing will result in an acceptable volume of HLW glass destined for the repository and will allow processing in existing carbon steel tanks at Hanford and SRS.

The efficiency of enhanced sludge washing is not completely understood. Inadequate removal of key sludge components could result in production of an unacceptably large volume of HLW glass. Improvements are needed to increase the separation of key sludge constituents from the HLW.

Enhanced sludge washing is planned to be performed batch-wise in large double-shell tanks of nominal one million gallon capacity. This will generate substantial volumes of waste solutions that require treatment and disposal as LLW. Settling times for suspended solids may be excessive and the possibility of colloid or gel formation could prohibit large-scale processing. Alternatives are needed that will reduce the amount of chemical addition required and prevent the possibility of colloid formation. Sludge at SRS and Hanford will be washed to remove soluble components prior to vitrification. Removing suspended solids from the wash solutions is inherently inefficient due to long intervals required for the solids to settle out.

Approximately 1.2 million gallons of acidic liquid waste are stored in single-shell, stainless steel, underground storage tanks at INEEL. In 1992, a Notice of Noncompliance was filed by the State of Idaho stating that the tanks did not meet secondary containment requirements of the Resource Conservation and Recovery Act. Subsequently, an agreement was reached between DOE, the Environmental Protection Agency, and the Idaho Department of Health and Welfare that commits DOE to remove the liquid waste from all underground tanks by the year 2015. Recent discussions with the state of Idaho have accelerated this date to 2012.

The baseline treatment for INEEL liquid and calcine waste was recently reviewed as part of the site's Environmental Impact Statement process. The site is now developing a revised roadmap to pursue direct vitrification of the liquid waste and determine the best path to treat the calcine.

The transuranic extraction process for removal of actinides, or transuranics, from acidic wastes has been tested on actual Idaho waste in continuous countercurrent process equipment. The strontium extraction process shows promise for co-extraction of strontium and technetium and also has been demonstrated on Idaho waste in continuous countercurrent operation.

DOE's underground storage tanks at Hanford, SRS, and INEEL contain liquid wastes with high concentrations of radioactive cesium. Cesium is the primary radioactive constituent found in alkaline supernatant wastes. Since the primary chemical components of alkaline supernatants are sodium nitrate and sodium hydroxide, the majority of the waste could be disposed of as LLW if the radioactivity could be reduced below Nuclear Regulatory Commission limits. Processes have been demonstrated that removed cesium from alkaline supernatants and concentrate it for eventual treatment and disposal as HLW.

At Hanford, cesium must be removed to a very low level (3 Ci/m<sup>3</sup>) to allow supernatant waste to be treated as LLW and disposed of in a near-surface disposal facility. The revised Hanford Federal Facility Agreement and Consent Order, or Tri-Party Agreement (between DOE, Environmental Protection Agency and the Washington State Department of Ecology) also recommends treatment of LLW in a contact-maintained or minimally shielded vitrification facility to speed remediation and reduce costs. Cesium removal performance data are needed to estimate dose rates for this process and provide input to the design of an LLW pretreatment facility for Hanford supernatants.

At SRS, cesium removal from saltcake waste was planned to be accomplished through use of an in-tank precipitation process. Due to safety and technical challenges, that process was abandoned. Three alternatives including alkaline solvent extraction, cesium ion exchange using crystalline silicotitanate and small tank tetraphenylborate precipitation are currently being evaluated for use in treating the SRS saltcake waste. Cesium removal may also be needed to separate cesium from Defense Waste Processing Facility recycle, or offgas condensate, to greatly reduce the amount of cesium that is routed back to the waste storage tanks.

Technetium (Tc)-99 has a long half-life (210,000 years) and is very mobile in the environment when in the form of the pertechnetate ion. Removal of Tc from alkaline supernatants and sludge washing liquids is expected to be required at Hanford to permit treatment and disposal of these wastes as LLW. The disposal requirements are being determined by the long-term performance assessment of the LLW waste form in the disposal site environment. It is also expected that Tc removal will be required for at least some wastes to meet Nuclear Regulatory Commission LLW criteria for radioactive content. To meet these expected requirements, there is a need to develop technology that will separate this extremely long-lived radionuclide from the LLW stream and concentrate it for feed to HLW vitrification.

A number of liquid streams encountered in tank waste pretreatment contain fine particulate suspended solids. These streams may include tank waste supernatant, waste retrieval sluicing water, and sludge wash solutions. Other process streams with

potential for suspended solids include evaporator products and ion exchange feed and product streams. Suspended solids will foul process equipment such as ion exchangers. Radioactive solids will carry over into liquid streams destined for LLW treatment, increasing waste volume for disposal and increasing the need for shielding of process equipment. Streams with solid/liquid separation needs exist at all of the DOE tank waste sites.

Some examples of specific science research challenges include but are not limited to: fundamental analytical chemical studies needed for improvement of separation processes; materials science of waste forms germane to their performance; elucidation of technetium chemistry; basic engineering and separation science studies required to support pretreatment activities and the development of solid/liquid separations; fundamental separations chemistry of precipitating agent and ion exchange media needed to support the development of improved methods for decontamination of HLW; fundamental physical chemistry studies of sodium nitrate/nitrite needed for HLW processing; basic materials science studies concerned with the dissolution of mixed oxide materials characteristic of calcine waste needed to design improved pretreatment processes; basic chemistry of sodium when mixed with rare earth oxides needed for the development of alternative HLW forms.

## **Waste Immobilization and Disposal**

Waste immobilization processes convert radioactive waste into solid waste forms that will last in natural environments for thousands of years. DOE tank wastes requiring immobilization include LLW such as the pretreated liquid tank waste and HLW such as the tank sludge. There are also a number of secondary wastes requiring immobilization that result from tank waste remediation operations, such as resins from cesium and technetium removal operations.

The baseline technologies to immobilize radioactive wastes from underground storage tanks at DOE sites include converting LLW to either grout or glass and converting HLW to borosilicate glass. Grout is a cement-based waste form that is produced in a mixer tank and then poured into canisters or pumped into vaults. Glass waste forms are created in a ceramic-lined metal furnace called a melter. Tank waste and dry materials used to form glass are mixed and heated in the melter to temperatures ranging from 1,800 F to 2,200 F. The molten mixture is then poured into log-shaped canisters for storage and disposal. The working assumption is that the LLW will be disposed of on site, or at the Waste Isolation Pilot Plant if transuranic elements are present. The HLW will be shipped for off-site disposal in a licensed HLW repository, such as the one proposed at Yucca Mountain, Nevada.

Methods are needed to immobilize the LLW fraction resulting from the separation of radionuclides from the liquid and high-level calcine wastes at INEEL. LLW is to be mixed with grout, poured into steel drums, and transferred to an interim storage facility, but alternatives are being considered. Tests must be conducted with surrogate and actual wastes to support selection of a final waste form. SRS has selected saltstone grout (pumped to above ground concrete vaults and solidified) as the final waste form for LLW.

DOE sites at Hanford, SRS, and INEEL will remove cesium from the hazardous radioactive liquid waste in the underground storage tanks. If cesium is removed, it costs less to treat the rest of the waste. However, cesium removal from tank waste, while cost-effective, creates a significant volume of solid waste that must be turned into a final waste form for ultimate disposal. The plan is to separate cesium from the liquid waste using ion exchange or other separations media, treat the cesium-loaded separations media to prepare it for vitrification, and convert the cesium product into a glass waste form suitable for final disposal. Personnel exposures during processing and the amount of hazardous species in the offgases must be kept within safe limits at all times.

The effectiveness of advanced oxidation technology for treating organic cesium-loaded separations media prior to vitrification is not proven. After a suitable melter feed is obtained, vitrification of the cesium-loaded media must be demonstrated. Technology development is needed because: 1) Compounds are in the separation media that must be destroyed or they will cause flammability problems in the melter and decrease the durability and waste loading of the final waste form; 2) High beta/gamma dose rates are associated with handling cesium-containing waste; and 3) Cesium volatilizes in the melter and becomes a highly radioactive offgas problem.

Confidence and assurance that long-term immobilization will be successful in borosilicate glass warrants research and improved understanding of the structural and thermodynamic properties of glass (including the structure and energetics of stable and metastable phases), systematic irradiation studies that will simulate long term self-irradiation doses and spectra, (including archived glasses containing Pu or Cm, and over the widest range of dose, dose rate and temperature) and predictive theory and modeling based on computer simulations (including *ab initio*, Monte Carlo, and other methods).

Some examples of specific science research challenges include but are not limited to: fundamental chemical studies needed to determine species concentrations above molten glass solutions containing heavy metals, cesium, strontium, lanthanides, actinides, with and without a cold cap composed of unmelted material; materials science studies of molten materials that simulate conditions anticipated during

vitrification and storage in vitrified form of HLW needed to develop improved processes and formulations; fundamental physical chemistry studies of sodium nitrate/nitrite mixtures needed for HLW stabilization.

## **References for Background Information**

Note: World Wide Web locations of these documents are provided where possible. For those without access to the World Wide Web, hard copies of these references may be obtained by writing Mark A. Gilbertson at the address listed in the FOR FURTHER INFORMATION CONTACT section of this Notice.

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