Office of Energy Research
Notice 98-08

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

Department of Energy
Office of Energy Research and
Office of Environmental Management

Energy Research Financial Assistance Program Notice 98-08: Environmental Management Science Program: Research Related to High Level Radioactive Waste

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

ACTION: Notice inviting grant applications

SUMMARY: The Offices of Energy Research (ER) and Environmental Management (EM), U.S. Department of Energy, 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: Potential applicants are strongly encouraged to submit a brief preapplication. All preapplications, referencing Program Notice 98-08, should be received by DOE by 4:30 P.M. E.S.T., January 27, 1998. A response encouraging or discouraging a formal application generally will be communicated to the applicant within three weeks of receipt. The deadline for receipt of formal applications is 4:30 P.M., E.D.T., April 16, 1998, in order to be accepted for merit review and to permit timely consideration for award in Fiscal Year 1998.

ADDRESSES: All preapplications, referencing Program Notice 98-08, should be sent to Dr. Roland F. Hirsch, ER-73, Mail Stop F-240, Office of Biological and Environmental Research, U.S. Department of Energy, 19901 Germantown Road, Germantown, MD 20874-1290. Preapplications will be accepted if submitted by U. S. Postal Service, including Express Mail, commercial mail delivery service, or hand delivery, but will not be accepted by fax, electronic mail, or other means.

After receiving notification from DOE concerning successful preapplications, applicants may prepare and submit formal applications. Applications must be sent to:

U.S. Department of Energy, Office of Energy Research, Grants and Contracts Division, ER-64, 19901 Germantown Road, Germantown, MD 20874-1290, Attn: Program Notice 98-08. The above address for formal applications must also be used when submitting formal applications by U.S. Postal Service Express Mail, any commercial mail delivery service, or when hand carried by the applicant.

FOR FURTHER INFORMATION CONTACT: Dr. Roland F. Hirsch, ER-73, Mail Stop F-240, Office of Biological and Environmental Research, Office of Energy Research, U.S. Department of Energy, 19901 Germantown Road, Germantown, MD 20874-1290, telephone: (301) 903-5349, fax: (301) 903-0567, E-mail: roland.hirsch@oer.doe.gov, or Mr. Mark Gilbertson, Office of Science and Risk Policy, 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. This Notice is also available on the World Wide Web at ***http://www.er.doe.gov/production/grants/fr98_08.html***.

SUPPLEMENTARY INFORMATION: The Office of Environmental Management, in partnership with the Office of Energy Research, sponsors the Environmental Management Science Program (EMSP) to fulfill DOE's continuing commitment to the cleanup of DOE's environmental legacy. The program was initiated in Fiscal Year 1996. We are soliciting ideas for basic scientific research which promotes 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 ER. ER's well-established procedures, as set forth in the Energy Research Merit Review System, as published in the Federal Register, March 11, 1991, Vol. 56, No. 47, pages 10244-10246, will be used for merit review of applications submitted in response to this Notice. This information is also available on the World Wide Web at ***http://www.er.doe.gov/production/grants/merit.html***. 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. Additional information can be obtained at ***http://www.em.doe.gov/science***.

Additional Notices for the Environmental Management Science Program may be issued during Fiscal Year 1998 covering other areas within the scope of the EM program.

Purpose

The need to build a stronger scientific basis for the Environmental Management effort has been established in a number of recent studies and reports. The FY 1998 Conference Report for Appropriations for Energy and Water Development, Report 105-271, dated September 26, 1997, on page 92 states the following:

"The conferees are pleased with the progress to date in implementing the environmental science program ..."

The Environmental Management Advisory Board Science Committee (Resolution on the Environmental Management Science Program, May 2, 1997) made the following observations:

"EMSP results are likely to be of significant value to EM" "Early program benefits include: improved understanding of EM science needs, linkage with technology needs, and expansion of the cadre of scientific personnel working on EM problems" "Science program has the potential to lead to significant improvement in future risk reduction and cost and time savings."

The objectives of the Environmental Management Science Program are to:

- Provide scientific knowledge that will revolutionize technologies and clean-up approaches to significantly reduce future costs, schedules, and risks;
- "Bridge the gap" between broad fundamental research that has wide-ranging applicability such as that performed in DOE's Office of Energy Research and needs-driven applied technology development that is conducted in EM's Office of Science and Technology; and
- 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 cleanup 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).

Program Funding

Up to a total of $4,000,000 of Fiscal Year 1998 Federal funds is expected to be available for new Environmental Management Science Program awards resulting from this Notice. Multiple-year funding of grant awards is anticipated, contingent upon the availability of 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 grant. 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. Under no circumstances will DOE be obligated to fund in whole or part any costs incurred in the preparation of an application, or funding any 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). 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 FFRDCs, including the DOE National Laboratories, where appropriate, and to incorporate cost sharing and/or consortia wherever feasible.

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

Collaborative research applications may be submitted in several ways:

(1) When multiple private sector or academic organizations intend to propose collaborative or joint research projects, the lead organization may submit a single application which includes another organization as a lower-tier participant (subaward)

who will be responsible for a smaller portion of the overall project. If approved for funding, DOE may provide the total project funds to the lead organization who will provide funding to the other participant via a subcontract arrangement. The application should clearly describe the role to be played by each organization, specify the managerial arrangements and explain the advantages of the multi-organizational effort.

(2) Alternatively, multiple private sector or academic organizations who intend to propose collaborative or joint research projects may each prepare a portion of the application, then combine each portion into a single, integrated scientific application. A separate Face Page and Budget Pages must be included for each organization participating in the collaborative project. The joint application must be submitted to DOE as one package. If approved for funding, DOE will award a separate grant to each collaborating organization.

(3) Private sector or academic applicants who wish to form a collaborative project with a DOE FFRDC may not include the DOE FFRDC in their application as a lower-tier participant (subcontract). Rather, each collaborator may prepare a portion of the proposal, then combine each portion into a single, integrated scientific proposal. The private sector or academic organization must include a Face Page and Budget Pages for its portion of the project. The FFRDC must include separate Budget Pages for its portion of the project. The joint proposal must be submitted to DOE as one package. If approved for funding, DOE will award a grant to the private sector or academic organization. The FFRDC will be funded, through existing DOE contracts, from funds specifically designated for new FFRDC projects. DOE FFRDCs will not compete for funding already designated for private sector or academic organizations. Other Federal laboratories who wish to form collaborative projects may also follow guidelines outlined in this section.

Preapplications

A brief preapplication may be submitted. The original and five copies must be received by January 27, 1998, to be considered. The preapplication should identify on the cover sheet the institution, Principal Investigator name, address, telephone, fax and E-mail address, title of the project, and the field of scientific research (using the list in the Application Categories section). The preapplication should consist of up to three pages of narrative describing the research objectives and the plan for accomplishing them, and should also include a paragraph describing the research background of the principal investigator and key collaborators if any.

Preapplications will be evaluated relative to the scope and research needs of the DOE's Environmental Management Science Program by qualified DOE program managers from both ER and EM. Preapplications are strongly encouraged but not required prior to submission of a full application. Please note that notification of a successful preapplication is not an indication that an award will be made in response to the formal application.

Application Format

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

- ER 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
- 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 EMSP
    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 preapplication and application for evaluation and review, the documents must indicate the applicant's preferred scientific research field, (please use only the designation on this list and please select only one field of scientific research) from the following list of Field of Scientific Research:

1. Actinide Chemistry
2. Analytical Chemistry and Instrumentation
3. Interfacial Chemistry
4. Separations Science
5. Computer and Mathematical Sciences
6. Engineering Sciences
7. Materials Science
8. Physics
9. 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.

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. These objectives were established in the Conference Report for the Fiscal Year 1996 Energy and Water Development Appropriations Act, and are published in the Congressional Record--House, October 26, 1995, page H10956.

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 and Fiscal Year 1997 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 Energy Research Financial Assistance Program. Electronic access to the Guide and required forms is made available via the World Wide Web at ***http://www.er.doe.gov/production/grants/grants.html***.

Major Environmental Management Challenges

This research announcement has been developed for Fiscal Year 1998, 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. The following is an overview of the technical challenge facing the Environmental Management Program in the area of High Level Radioactive Waste which is the focus of this announcement. More detailed descriptions of the specific technical needs and areas of emphasis associated with this problem area can be found in the Background section of this Notice.

High-level Radioactive Waste Tanks. The Department is the guardian of over 300 large storage tanks containing over 90 million gallons of highly radioactive wastes, which include organic and inorganic chemical compounds, in solid, colloidal, slurry, and liquid phases. The environment within the tanks is highly radioactive and chemically harsh. A few of the tanks have leaked to the environment while others are corroding.

Specific areas of emphasis in technology needs and research challenges related to high level waste (HLW) tank problems include, but are not limited to:

- Characterization and Safety
- Retrieval of Tank Waste and Tank Closure
- Pretreatment and Separation Processes for Tank Waste
- Waste Immobilization and Disposal

Historically, characterization of tank waste has been very expensive, has failed to obtain representative data for many tanks, and has generated safety concerns from worker exposure to radioactive waste. Within the Characterization and Safety area there is the need to develop systems to identify chemical and physical characteristics of the waste *in situ*, improve data quality and timeliness, and reduce safety concerns.

In the Retrieval of Tank Waste and Tank Closure area, there is the need to develop cost-efficient methods to remove saltcake, sludge, and waste heels and close a high-level waste tank that may contain a flammable gas environment. Some sites have numerous tanks that contain saltcake so that the potential cost savings of less expensive saltcake retrieval methods is very large.

Pretreatment and Separation Processes for Tank Waste will separate tank wastes into low- and high-level fractions, thereby significantly reducing the volumes of high-level waste requiring disposal. These separations include not only chemical separations, but also physical separations.

Low level waste (LLW) immobilization will reduce waste volumes and produce waste forms that are chemically and physically durable. EM is applying two technologies (grout and glass) to the same waste stream to allow an unbiased appraisal of the true costs and risks associated with implementing each technology for full-scale tank waste remediation. Both technologies must be robust enough to handle the range of constituents found in the tank wastes.

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

Background

Environmental Management (EM) is responsible for the development, testing, evaluation, and deployment of remediation technologies within a system architecture 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.

Within the DOE complex, 335 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 over 90 million gallons of high-level and low-level radioactive liquid waste in sludge, saltcake, and as supernate and vapor. Very little has been treated and/or disposed of in final form.

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 (19m3) to 1,300,000 gallons (4920m3). The tanks are covered with a layer of soil ranging from a few feet to tens of feet thick.

Most of the waste is alkaline and contains a diverse portfolio 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. Tank void-space radiation fields can be as high as 10,000 rad/h.

EM is focusing attention on four DOE locations:

- Hanford Site near Richland, Washington
- Idaho National Engineering and Environmental Laboratory near Idaho Falls, Idaho
- Oak Ridge Reservation near Oak Ridge, Tennessee
- Savannah River Site near Aiken, South Carolina

Hanford has 177 tanks that contain approximately 55 million gallons of hazardous and radioactive waste. There are 149 single-shell tanks that have exceeded their life expectancy. 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.

The 11 stainless steel tanks at Idaho store approximately 2 million gallons of acidic radioactive liquids. Additionally, approximately 4000 m3 of calcined waste solids are stored in seven stainless steel bins enclosed in massive underground concrete vaults.

Dilute low-level waste (LLW) supernatants and associated sludge at Oak Ridge are stored in the inactive Gunite and associated tanks, the old hydrofracture tanks, and other tanks. The wastes from underground collection systems are currently being retrieved and consolidated in the stainless steel central treatment/storage tanks, including eight Melton Valley Storage Tanks.

Tank waste at Savannah River consists of 33 million gallons of salt, salt solution, and sludge containing waste stored in 51 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.

Most of the participant sites share four problem areas. These areas are:

- Characterization and Safety
- Retrieval of Tank Waste and Tank Closure
- Pretreatment and Separation Processes for Tank Waste
- Waste Immobilization and Disposal

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.

Moisture is one of the key elements influencing the safety status of some of Hanford's HLW tanks. Ferrocyanides were added to tank wastes to increase the available storage space when production outstripped the ability to provide adequate storage space.

Organics from some of the extraction processes used at Hanford ended up in tanks because of inefficient reagent recovery processes. Moisture provides a thermal buffer for the prevention of ignition and propagation of thermal reactions in waste containing ferrocyanides or organics. Insufficient moisture level raises the possibility of explosion. The conditions for a thermal event are reduced by the presence of water in the wastes. A method is needed to measure and quantify tank waste water concentrations *in situ*.

The need for chemical characterization of the tank wastes is driven by both safety and operational considerations. Safety drivers include the monitoring of organic chemicals and oxidizers to address flammability and energetics, nitrate and nitrite levels to address corrosion concerns, plutonium levels to address criticality prevention considerations, and detection of organic and inorganic species to identify chemical incompatibility hazards associated with ferrocyanides, nitrates, sulfates, carbonates, phosphates, and other oxyanions. Operational concerns include the monitoring of phosphate levels driven by the potential formation of sodium phosphate crystals, thereby increasing the viscosity of the waste by formation of a gelatinous matrix which will reduce the ability of pumps to transfer and retrieve 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.

Single-shell and double-shell waste tank construction is common across the DOE complex. The single-shell tanks present potential environmental hazards because only a single barrier contains the liquids and any breach in the barrier will cause contaminant spillage. A sluicing method being considered to retrieve the waste requires thousands of gallons of water, raising the possibility of HLW leakage into the surrounding environment. In other tanks, water is added to prevent the waste matrix from drying and provides a deterrent from possible ignition due to flammable gases. There is a need to develop instrumentation to determine the location of a leak, the amounts of materials that were exposed, and the quantity of the contaminant material.

Assessments of the long-term performance of waste forms is rare; 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. Thus 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 in Hanford, Savannah River, Oak Ridge, and Idaho have stored a diverse accumulation of wastes during the past fifty years of weapons and fuel production. If these tanks were entrapped in a manner that would preclude the escape into the environment for hundreds 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. At the four sites, 90 tanks have either leaked or are assumed to have 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, is 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.

The hermetic sealing and closure of containment vessels and the long term resistance to corrosion and stress corrosion cracking and failure of such seals and closures warrants attention. Routine or conventional welding and joining procedures, while adequate to form hermetic seals in a non-hostile environment, may result in local composition gradients across weld or join interfaces and heat-affected-zones that create local electrochemical cells that are vulnerable to galvanic degradation and/or corrosion related cracking. Research is needed to establish reliable welding or joining procedures that will not result in either the establishment of local gradients in chemical composition or in grain-boundary depletion of passivating chemical elements at welding or joining closures.

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

DOE has about 90 million gallons of HLW and LLW 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 current baseline technology systems for waste pretreatment at DOE's tank waste sites are expensive. 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 waste, by weight, is made up of radionuclides. The bulk of the waste is chemical constituents intermingled with, and sometimes chemically bonded to, the radionuclides. However, the chemicals and radionuclides can be separated into HLW and LLW fractions for easier treatment and disposal.

Most of the waste stored in tanks was put there 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 tanks for long-term storage.

Fuel processing at Savannah River 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. Waste at Idaho is stored at acidic pH in stainless steel tanks. Much of it has already been calcined at high temperature to a dry powder. Tank wastes at Oak Ridge are small in volume (less than 1 million gallons) and radionuclide inventory (0.16 MCi) compared to other sites (33 million gallons and 534 MCi at Savannah River and 55 million gallons and 198 MCi at Hanford).

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 Savannah River 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 waste in tanks are 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.

Waste in tanks 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. If the alkaline sludge washing is not effective, some sludge may need to be dissolved in acid and treated by extraction techniques to make a suitable feed to HLW vitrification. This option is currently outside the sites baseline.

The pretreatment functional 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 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 Savannah River.

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 batchwise in large double-shell tanks of nominal one million gallon capacity. This will generate substantial volumes of waste solutions which 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 Savannah River, Hanford, and Oak Ridge will be washed to remove soluble components prior to HLW vitrification. Removing suspended solids from the wash solutions is inherently inefficient due to long intervals required for the solids to settle out. The baseline process for sludge washing at Savannah River and Hanford is done batchwise in large, one-million gallon underground storage tanks. This requires large volumes of wash solution, powerful mixing pumps, and long settling times. Retrieval of waste using large volumes of dilution water is planned at Hanford. To consider the benefits of flocculent addition and the possibility of using countercurrent decantation to help optimize sludge washing, the settling characteristics of the solids need to be determined.

Baseline sludge washing processes at both Hanford and Savannah River call for large volumes of caustic (sodium hydroxide) solution. The supernatant from sludge washing then becomes feed to LLW treatment. The added caustic can be recovered after washing and recycled to subsequent sludge washing steps. In addition, the HLW sludge at Hanford and Savannah River contains large quantities of sodium salts that can, in principle, be recovered as sodium hydroxide and also be recycled.

Approximately 1.8 million gallons of acidic liquid waste are stored in single-shell, stainless steel, underground storage tanks at Idaho. In 1992 a Notice of Noncompliance was filed 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 Idaho liquid wastes produced after 2012 is the full treatment option, wherein actinides and fission products will be removed from the liquid waste and HLW calcine. The depleted stream will be processed to Class A LLW standards and the radionuclides will be immobilized in an HLW fraction.

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 contain liquid wastes with high concentrations of radioactive cesium. The various processes for retrieving and redissolution of HLW calcine for pretreatment are not fully demonstrated.

DOE's underground storage tanks at Hanford, Savannah River, Oak Ridge, and Idaho 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/m3) 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 Savannah River, cesium removal by ion exchange may be needed as an alternative to the current in-tank precipitation process. Cesium ion exchange 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; fundamental chemical studies associated with high temperature (500 C) calcination of nitrate solutions using agents others than sugar needed for advanced HLW calcination processing.

Waste Immobilization and Disposal

Waste immobilization technology converts radioactive waste into solid waste forms which will last in natural environments for thousands of years. Wastes requiring immobilization at DOE sites include LLW such as the pretreated liquid waste from waste tanks 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 2,700 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 Idaho. 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. Savannah River has selected saltstone grout (pumped to above ground concrete vaults and solidified) as the final waste form. Savannah River would like to evaluate LLW glass as an alternative to saltstone disposal.

DOE sites at Hanford, Savannah River, Idaho and Oak Ridge 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 volatizes 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.

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