Environmental Management
Separations Technology Challenges

Fifty years of nuclear weapons production and government-sponsored nuclear energy research and development have left the U.S. with millions of gallons of highly radioactive waste, thousands of tons of used nuclear fuel and special nuclear material, and enormous quantities of contaminated soil, water, and facilities. The overall challenge and largest cleanup program in the world has been underway for 20 years and currently involves over a million acres in 13 states. Within the last two and a half years, the ARRA program has reduced the footprint by 464 square miles, 50 % of the total amount to be cleaned up in the program. The remaining clean-up inventory contains 90 million gallons of radioactive waste, safely stored in 230 tanks, 1.7 trillion gallons of contaminated groundwater, and over 3,000 excess contaminated nuclear facilities with significant quantities of curies as hold-up in process equipment and miles of pipelines. In addition, billions of cubic meters of contaminated soil and debris exist at the sites. Estimated life cycle costs of the EM clean-up approach $350 billion and could take an additional fifty years to complete. At the apex of these clean-up efforts lies a need for a fundamental understanding of the separations chemistry of the contaminants of concern. The challenge at the fundamental chemistry level runs the gamut of nearly infinite dilute solutions to molten inorganic salts. The engineering and scale-up challenges are just as enormous. Significant breakthroughs in separation chemistry and engineering can effect significant improvements to reducing the technical risks involved in the EM clean-up and significantly reduce life cycle costs and schedules.

Examples of *separations* research areas with potential for significant impact are highlighted in the following pages:

- Technetium chemistry, removal, and immobilization
- Mercury chemistry, removal, and immobilization
- Hexavalent Chromium detoxification and removal
- Radioactive iodine chemistry, removal, and immobilization
- Removal of Non-Radioactive Species from High Level Waste
- Removal of key Radionuclides for Tank Closure
- Integrated subsurface remedial strategies for site closure
- Contaminants of Concern during Demolition and Disposal

<u>Technetium chemistry, removal, and immobilization</u>

Challenge: Technetium is a long-lived radionuclide that exists as an anion under most environmental conditions, and contributes significantly to long term risk at sites such as Hanford and Savannah River. The complex chemical behavior of technetium in tank waste and subsurface environments, limited incorporation in mid- to high temperature immobilization processes (i.e., vitrification, steam reformation, etc.), and high mobility in subsurface environments makes technetium one of the most difficult contaminants to address in the DOE complex.

- Technetium, a long-lived radionuclide, is primarily present in alkaline tank waste at the Hanford and Savannah River sites, but is also present in the subsurface in some contaminated plumes. A substantial portion of the technetium in tank wastes will partition to the immobilized low activity waste form.

- "EM should emphasize development of the scientific understanding of the partitioning of ^{99}Tc and other key radionuclides relevant to processing and retention in waste forms." (EM TEG recommendation)
- Rhenium has been used as a surrogate, but has limitations.
- Tc in the process systems/pipelines of the Gaseous Diffusion Plant (GDP) at East Tennessee Technology Park (ETTP in Oak Ridge) has resulted in significant time delays and additional expenses. Similar issues may be present at the GDPs at Portsmouth and Paducah.
- There is limited understanding of the chemical adsorption or desorption of Tc on metal waste streams
- There are limited direct measurements of the chemical speciation of Tc in tank waste or subsurface sediments.
- Technetium is a key contaminant in meeting regulatory requirements for near surface land disposal performance due to the large inventory of Tc to be disposed in low-activity or secondary waste streams.
- There is limited understanding of the behavior, form, and mobility of Tc in sedimentary environments associated with past-practice co-disposed waste streams, and the impacts on environmental remediation.
- An acceptable baseline technology for remediating Tc in subsurface environments does not exist

Opportunities: Improved management and disposition of the technetium in the tank waste at both Savannah River and Hanford, and the GDPs at ETTP and possibly Portsmouth and Paducah, would help resolve its long-term impact. An improved understanding of technetium behavior in the groundwater and soil is needed to better predict long-term fate and transport phenomena. Specifically, an improved scientific understanding of the chemistry of Tc retention in sedimentary phases associated with past-practice, co-disposed waste streams as a function of chemical factors including redox conditions, solid phase formation and incorporation, complexation and speciation is needed. Improved remediation technologies for groundwater are also needed to provide long-term solutions. Fundamental studies that enable understanding of the chemistry occurring across a range of conditions, along with comparisons of non-radioactive surrogates (e.g. Re), would expand the ability to perform large scale experiments and further improve behavior predictions. Potential technologies that could be applied include inorganic sequestering agents, additives, or techniques and improved selective absorbents. These materials could conceptually be deployed in a variety of in-situ and ex-situ configurations, such as active barriers, grout additives, subsurface fixatives, and waste stream treatment or pump-and-treat facilities. Development of improved ion exchange media or precipitation agents could enable substantially simplified removal processes. Studies of subsurface speciation, chemistry, and mobility could be beneficial, as well as computer modeling or tools that improve understanding and predictions of contaminant migration.

<u>Mercury chemistry, removal and immobilization</u>

Challenge: Historic uses of mercury at the Oak Ridge Reservation have resulted in extensive environmental contamination. Remedial actions have reduced mercury input to a local creek by more than 90%, but stream water and fish remain impacted, primarily as a result of dynamic mercury methylation/demethylation processes and other complex ecolological and biogeochemical interactions. Additionally, deactivation and decommissioning (D&D) activities

at Oak Ridge are expected to result in physical disturbances that may release additional mercury to soil, groundwater, and surface water. While mercury contamination is an impending issue at the Oak Ridge Reservation, mercury contamination is or will be problematic throughout the complex.

Opportunities: Development of in-situ remediation and characterization technologies and a systems approach to assessing contaminant fate and transport is a key strategy for attaining regulatory compliance during D&D and long-term stewardship of sites contaminated with mercury. For D&D of facilities, development of a technology to characterize and segregate mercury-contaminated debris (e.g., wood, cinder block, bricks, concrete) requiring treatment to meet applicable regulatory requirements for worker protection and waste disposal is needed. Additionally, approaches developed to address mercury may be adaptable for use with other metals, radionuclides, and organic contaminants, particularly in co-contaminated matrices. Cost-effective technical solutions are needed for waterborne mercury remediation, soil treatment, source zone identification, mercury characterization, and conceptual and numerical modeling of contaminant fate and transport. Waterborne mercury can be addressed through the development and demonstration of innovative methods that utilize specialized resins, unique nanomaterials, or chemical addition to transform, absorb, and/or remove mercury. Both in-situ and ex-situ soil treatment methods are needed for removing mercury or stabilizing it within environmental matrices. The development of effective treatment methods for mercury depends upon a sound understanding of mercury speciation, reactivity and association with minerals and materials, as well as technical approaches for separating mercury from a variety of matrices.

Hexavalent Chromium detoxification and removal

Challenge: Chromium is a metal used in a wide variety of industrial processes. Hexavalent chromium is mobile, mutagenic, carcinogenic, and acutely toxic. It was released to groundwater and soil at DOE sites as a consequence of leakage or disposal practices. At the Hanford site, for example, hexavalent chromium was used in reactor cooling water to prevent corrosion. Large volumes of this water were discharged to retention basins for ultimate discharge to the Columbia River through outfalls. Hexavalent chromium-bearing liquid wastes from other reactor operations were also discharged to the ground via cribs, trenches, french drains, or leaks. As a result, groundwater and soil in the Hanford 100 Area and the Central Plateau are contaminated. Oak Ridge and other DOE sites also possess groundwater and soil contaminated with chromium above regulatory limits.

Opportunities: Although it is feasible to remove high levels of hexavalent chromium from groundwater using pump and treat methods, removal efficiency and cost-effectiveness decline as concentrations decrease. Alternate in-situ and ex-situ separations processes that have been studied and tested at various scales for chromium treatment include in-situ redox manipulation, calcium polysulfide treatment, and electrocoagulation. These approaches have demonstrated varying degrees of success but have also experienced operational complications from heterogeneities in subsurface geochemistry, hydrogeology, or groundwater composition. Refinements to chromium separation processes are needed to reduce dependence upon current pump and treat approaches that will pose a long-term expense for treating high-volume, low-concentration waste streams.

Radioactive iodine chemistry, removal, and immobilization

Challenge: Iodine-129 is a long-lived radionuclide that exists as an anion under most environmental conditions which contributes significantly to long-term risk at sites such as Hanford and Savannah River. The complex chemical behavior of iodine in subsurface environments, limited long-term retention in immobilization processes, and high mobility in subsurface environments makes iodine one of the most difficult contaminants to address in the DOE complex.

- Iodine-129 has a long half life ($1.6x10^7$ years) and is present in the wastes and groundwater at both the Hanford Site and Savannah River Site. Iodine-129 at the Savannah River Site constitutes a very small portion of the total radiological releases, approximately 0.00002%, but contributes 13% of the offsite population dose, illustrating how the properties of this radionuclide magnify its risk.
- There is limited understanding of the behavior, form, and mobility of iodine in sedimentary environments associated with past co-disposal of waste streams, and the impacts on environmental remediation.
- An acceptable baseline technology for remediating iodine in subsurface environments does not exist.

Opportunities: Improved iodine chemical speciation, inventory measurements, and behavior in the final waste forms at both Savannah River and Hanford would help resolve its long-term impact. An improved understanding of iodine chemical behavior in groundwater and soil is needed to better predict long-term fate and transport phenomena. Specifically, increased scientific understanding of the chemistry of iodine retention in sedimentary phases associated with past-practice, co-disposed waste streams as a function of chemical factors including redox conditions, solid phase formation and incorporation, complexation and speciation is needed. Coupling the results of studies of subsurface speciation and chemistry with computer modeling would allow improved utility of the results and enable broader understanding of the macroscopic behavior. Improved remediation technologies for groundwater are also needed to provide long-term solutions. Potential technologies that could be applied include inorganic sequestering agents, additives, or selective absorbents. Development of selective ion exchange media or precipitation agents could enable subsequent development of new removal processes. These materials could conceptually be deployed in a variety of in-situ and ex-situ configurations, such as active barriers, grout additives, subsurface fixatives, and waste stream treatment or pump-and-treat facilities. Development of waste forms or additives to current waste forms with long-term retention properties would be beneficial to improve the sites' performance assessments.

Removal of Non-Radioactive species from High Level Waste

Challenge: Non-radioactive constituents in tank sludge waste limit the amount of waste that can be incorporated into the final glass waste form at both Hanford and Savannah River. The primary limiting constituents are aluminum, sodium, chromium, and sulfur. Improved removal of these constituents from the sludge and partitioning them into the aqueous waste would reduce the volume of High Level Waste glass produced. Furthermore, although aluminum is removed by caustic addition, the amount of caustic needed to maintain its solubility in downstream processes causes an enormous increase in the waste processing duration and low activity waste form volume. A related challenge is phosphate at the Hanford Waste Treatment Plant. The primary risk associated with phosphate is the formation of solids during treatment of the aqueous phase that would cause process plugs, or upsets, or constrained operating conditions.

Opportunities: Achieve a more effective separation of constituents, by (a) removing species that limit waste loading in high-level glass, (b) removing constituents that may limit or bound the operating conditions of other processes (e.g., phosphate), and (c) develop additives to stabilize aluminum solubility or develop improved prediction tools and control of aluminum solubility. Development of a process to remove species, such as phosphate, would be integrated with an approach for disposition of the phosphate-laden stream without further treatment. Aluminum solubility is a very significant cost and schedule driver, especially at Hanford. Establishing reliable methods to maintain and predict aluminum solubility to ensure it does not plug the cesium ion exchange process at Hanford, or the solvent extraction system at Savannah River, would reduce the amount of sodium hydroxide added.

Removal of Key Radionuclides for Tank Closure

Challenge: Rapidly removing waste from underground storage tanks is critical to limit environmental releases and to efficiently operate the waste treatment plants. However, emptying underground tanks containing radioactive waste, while ensuring protection of the environment, is challenging. The majority of the waste is removed with mechanical methods (pumps, sprayers, crawlers, etc.) and may be followed with chemical cleaning with oxalic acid or caustic. Small amounts of waste heels are increasingly difficult to retrieve with mechanical methods, due to their rheological properties and/or the presence of obstructions in the tanks. Chemical tank cleaning methods are time-consuming, generate large volumes of secondary waste, and do not increase solubilization of important radionuclides to ease their removal. Tank closure is currently achieved by filling the emptied and cleaned tanks with grout. Determination of the readiness of the emptied tank for closure is not straightforward from technical and regulatory perspectives.

Opportunities: Significant cost and schedule savings can be achieved through a combination of new technologies and methods to efficiently empty tanks to the maximum extent practical. Improving chemical cleaning methods that target key radionuclides and eliminate generating secondary waste could provide substantial benefits. Removing long-lived alpha-emitting actinides is expected to have a direct impact on short-term retrieval efforts and long-term closure. Conversely, developing sequestration materials and methods to inhibit migration of key radionuclides from residues in closed tanks could also result in significant cost and schedule savings and minimize subsequent downstream impacts of secondary wastes.

Integrated Subsurface Remedial Strategies for Site Closure

Challenge: Many of the subsurface contamination problems at legacy nuclear weapons sites currently have no practical remedy. Historic operations at these sites resulted in disposal of wastes to the ground, enabling contaminants to disperse in soil and groundwater. While excavation and controlled disposal may be used to address shallow contaminated soils, remediation of deeper environments is complicated by the presence of co-mingled contaminants that may be present at low concentrations and dispersed widely within heterogeneous matrices. Left untreated, contaminants will migrate to groundwater or surface water, presenting a long-term risk to environmental resources, human health, and the environment. The current treatment approach for groundwater is pumping and treating, but many active pump and treat systems are

inefficient in extracting contaminants from the subsurface, and do not achieve cleanup goals within reasonable timeframes and costs.

Opportunities: Strategies are needed to transition active physical removal of contaminants to more effective and efficient monitored attenuation remedies. Both natural and enhanced attenuation can be thought of as in-situ separation processes. Separation of contaminants is achieved by diminishing their migration, either through naturally-occurring physical, biological, or geochemical reactions or via the addition of amendments designed to retard mobility. Advances in attenuation-based approaches require research and development in several areas. First, improved tools for economical, preferably noninvasive subsurface characterization are required to establish contaminant composition, extent, and surroundings such that separations processes can be successfully developed and applied. Second, improved chemical amendments and appropriate delivery methods are necessary to facilitate uniform contaminant immobilization, reaction, and/or sequestration. Third, a greater understanding of contaminant flux is needed to define achievable remedial action objectives for sites with persistent contamination. Fourth, demonstrated technologies for monitoring and predicting remediation performance in subsurface environments are required.

Contaminants of Concern during Demolition and Disposal

Challenge: DOE currently has thousands of excess buildings waiting decommissioning, such as nuclear reactors, chemical separations, and spent-fuel processing facilities that are contaminated with radionuclides and hazardous chemicals. Decommissioning involves demolishing the facility, segregating materials, and disposing of large volumes of highly contaminated materials and equipment in (controlled and approved) landfills. Current decommissioning methods are costly, with significant potential risk for personnel. New in-situ approaches such as entombment are being investigated to facilitate decommissioning. However, the long-term behavior of entombed structures needs to be monitored and understood. Therefore, a scientific basis is needed not only in the development of these new approaches but also in the fate of decommissioned facilities. These developments could significantly reduce costs and risks to human health and the environment, while closing these massive and complex facilities.

Opportunities: Scientific understanding of the interactions among contaminants and construction materials is fundamental to developing more effective D&D strategies and technologies. Research is needed to gain a better understanding of the fate and behavior of radionuclides and hazardous materials in construction materials. Research areas of interest include how contaminants bind to different building materials, how they penetrate into these materials, migration into pores, fissures, and welds, and time-dependent aging effects. For facilities that undergo in-situ decommissioning, developing key scientific data related to degradation of the materials of construction is needed. There will be certain levels of chemical and radiological contaminants remaining that are entombed in a grouted structure. The objective is to develop an understanding of the degradation mechanisms and the resulting products of degradation. Studies are needed to understand these materials and how they are speciated and complexed with environmental media. This will support a more complete understanding of the fate and transport characteristics of these materials, including effectiveness of natural and enhanced in-situ attenuation in the subsurface. These data will provide the technical underpinning for key decisions regarding D&D end states for high risk facilities. Additionally, improved protocols for decontaminating equipment can be developed by performing research to

further understand interactions between construction materials and radioactive contaminants. This knowledge can then be applied to expanding the capabilities of existing decontamination agents and developing new decontamination agents that can ‘extract’ contaminants from pores and cracks in the materials or treat the materials in-situ. Additional options may be to develop bio- and nanomaterials for decontamination. The new agents and materials would then be integrated with equipment and techniques for remote application and removal of decontamination agents. Long-term monitoring technologies and modeling of decommissioned structures is paramount in the development of risk-based approaches that could reduce cost and schedule.