Scientific Opportunities to Reduce Risk in Nuclear Process Science - 9279

P. R. Bredt, A. R. Felmy, P. A. Gauglitz, A. P. Poloski, J. D. Vienna
Pacific Northwest National Laboratory
902 Battelle Boulevard
Richland, WA

B. A. Moyer
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831

D. Hobbs, B. Wilmarth
Savannah River National Laboratory
Savannah River Site
Aiken, SC 29808

M. McIlwain
Idaho National Laboratory
P.O. Box 1625
Idaho Falls, ID 83415

K. Subramanian
URS Washington Division
Washington Savannah River Company
766-H
Aiken SC 29808

S. Krahn, N. Machara
U.S. Department of Energy (DOE-EM-21)
1000 Independence Ave., SW
Washington, DC 20585

ABSTRACT

Cleaning up the nation's nuclear weapons complex remains as one of the most technologically challenging and financially costly problems facing the U.S. Department of Energy (DOE). Safety, cost, and technological challenges have often delayed progress in retrieval, processing, and final disposition of high-level waste, spent nuclear fuel, and challenging materials. Some of the issues result from the difficulty and complexity of the technological issues; others have programmatic bases, such as strategies that may provide undue focus on near-term goals or difficulty in developing and maintaining stakeholder confidence in the proposed solutions. We propose that independent basic fundamental science research addressing the full cleanup life-cycle offers an opportunity to help address these challenges by providing 1) scientific insight into the fundamental mechanisms involved in currently selected processing and disposal options, 2) a rational path to the development of alternative technologies should the primary options fail, 3) confidence that models that predict long-term performance of different disposal options are based upon the best available science, and 4) fundamental science discovery that enables transformational solutions to revolutionize the current baseline processes.

Over the last 3 years, DOE's Office of Environmental Management (EM) has experienced a fundamental shift in philosophy. The mission focus of driving to closure has been replaced by one of enabling the long-term needs of DOE and the nation. Resolving new challenges, such as the disposition of DOE spent nuclear fuel, have been added

to EM's responsibilities. In addition, the schedules for addressing several elements of the cleanup mission have been extended. As a result, EM's mission is no longer focused only on driving the current baselines to closure. Meeting the mission will require fundamental advances over at least a 30-year window if not longer as new challenges are added. The overall intent of this paper is to foster a dialogue on how basic scientific research can assist DOE in executing its cleanup and environmental management mission.

In this document, we propose that such scientific investments should not be focused solely on what may be viewed as current DOE needs, but also upon longer-term investments in specific areas of science that underpin technologies presently in use. In the latter regard, we propose four science theme areas: 1) the structure and dynamics of materials and interfaces, 2) coupled chemical and physical processes, 3) complex solution phase phenomena, and 4) chemical recognition phenomena. The proposed scientific focus for each of these theme areas and the scientific opportunities are identified, along with links to major risks within the initiative areas identified in EM's Engineering and Technology Roadmap. The authors encourage feedback from our colleagues in the nuclear waste and related fields.

INTRODUCTION

This paper is a high-level summary of a publically available report by the authors [1]. That report contains much more detail around each of the scientific challenges the U.S. Department of Energy (DOE) faces in cleaning up the nation's high-level waste (HLW) legacy along with a much more detailed list of references.

The problem of retrieving, processing, and disposing of HLW, spent nuclear fuel, and other excess nuclear materials is nothing new. There exists published work dating to the early 1970s and, in some respects, to the 1940s in which the problems associated with HLW are discussed. It is beyond the scope of this work to review this early literature. However, DOE now has well defined processing plans for the major HLW streams, and has initiated several major construction projects to implement these plans at the Hanford, Savannah River, and Idaho sites. As well, defined waste acceptance criteria have been established for disposal facilities such as the Yucca Mountain Repository and the Waste Isolation Pilot Plant that did not previously exist. These developments have resulted is a renewed focus on resolving known technical challenges that must be overcome to achieve the cleanup objectives as well as recognition that research is needed to address challenges posed by those stream without defined processing plans.

Numerous studies by the National Research Council (NRC) [2–8] and DOE strategic planning efforts [9–12] have defined the importance of the issues and articulated the need for continuing investments in research and technology development focused on supporting DOE site needs. For example, a recent multi-year program plan developed by the DOE Office of Engineering and Technology (OET) identified 122 potential research activities to reduce the technical risk and uncertainty in the department's major HLW cleanup sites [13]. These research activities were developed to address technology needs identified in the OET Roadmap [14] in the areas of Waste Storage, Waste Retrieval, Tank Closure, Pretreatment, and Stabilization. The large number of potential needs, coupled with the broad range of technological challenges spanning fundamental research to technology deployment, makes it difficult to define the precise role that basic science can play in the resolution of these issues; thus, the need for this paper.

There has been a fundamental shift in the DOE Office of Environmental Management's (EM's) mission focus and the opportunities for basic research over the last 3 years. EM was previously focused on addressing a fixed set of cleanup challenges using existing technologies. These activities were viewed as achievable with only incremental research and development (R&D) investments centered on applied modifications to meet unique aspects of the cleanup. The mission focus is now based on reducing the long-term risks and uncertainties in cleanup challenges for DOE and the nation. New challenges have been added to EM's responsibilities, both broadening the mission and increasing the mission duration. As reflected in the OET Roadmap, two new areas have been added to the issues in Waste Processing: Spent Nuclear Fuel and Challenging Materials. Addressing these new elements will require the development of new processes incorporating innovative solutions to many fundamental science challenges. In addition, the schedules for addressing several elements of the previous mission have been extended. For example, the Waste Treatment Plant at Hanford was scheduled to begin operations in 2007 and finish immobilizing HLW

within 20 years. Under the current baseline, the plant will begin operations in 2019 and finish in roughly 2049. This combination of an extended mission as well as additional challenges provides significant opportunities to reduce the risk and uncertainty through basic science research.

With these factors in mind, and based on the groundwork laid by previous reports (mentioned above), we have grouped the basic science needs into four theme areas: 1) the structure and dynamics of materials and interfaces, 2) complex solution phase phenomena, 3) coupled chemical and physical processes, and 4) chemical recognition phenomena. Table I summarizes fundamental science questions within each theme area.

Table I. Scientific Opportunities to Reduce Risk in Nuclear Process Science. Addressing these opportunities will require basic research ranging from fundamental chemical and physical investigations to advanced theoretical and computational modeling to technology development enabling transformational engineering solutions.

Science Theme	Scientific Opportunities/Questions	EM Risks[a]
Structure and Dynamics of Materials and Interfaces	*Can we better characterize the heterogeneous materials in waste tanks and improve our understanding of dissolution/precipitation during retrieval and processing?*	*4,5,8,10,11,16,25,28, 29,30,31,35,48*
	Is it possible to more accurately characterize the chemical changes that occur in slurries and solutions in real-time?	*6,7,8,10,11,15,17,22, 23,26,27,33,34,39*
	Is it possible to develop alternative immobilization and treatment technologies that mitigate the current issues associated with long-term release?	*10,11,18,19,20,21,22, 23,27,41,42,43,44*
	Can we extend our existing kinetic and thermodynamic stability models of minerals and organic complexes over hundreds or even thousands of years?	*18,19,20*
	What is the nature of the solid-water interaction in cementitious materials and associated microenvironments, and how does one predict changes over geologic timescales?	*18,19,20,41,43,44*
	How fast will glass react in the disposal environment? With exceedingly long time scales, how will the various reactions between glass and its surrounding environment progress?	*42,46*
	What are the mechanisms governing corrosion of materials in contact with high-salt aqueous systems, and what are the additional effects of radiation on these materials?	*1,2,3,9,13,24,33,34*
	What are the mechanisms of complex surface chemistry modifications and their impacts on foaming and antifoaming for mixtures of insoluble particle species in concentrated electrolyte solutions?	*5,6,13,17,40*
Complex Solution Phase Phenomena	*Can we predict the thermodynamics of concentrated electrolyte and mixed-solvent-electrolyte systems to very high concentrations?*	*4,5,8,10,11,16,25,27, 28,29,30,31,35,37,38, 48*
	How do changes in ion solvation and chemical speciation in concentrated electrolytes impact water activities and exchange rates and hence the kinetics of precipitate formation or dissolution?	*4,5,8,10,11,16,25,27, 28,30,31,35,38,48*
	How do we predict the evolution of vapor-phase species from tank supernatants resulting from radiolysis and changing tank chemistry?	*3,7,13,24,43,45*
	What is the nature of the glassy state? Molecules in a glass are	*25,42,44,46*

3

Science Theme	Scientific Opportunities/Questions	EM Risks[a]
	arranged much like those in liquids but are more tightly packed. Where and why does liquid end and glass begin?	

Table I (Contd)

Science Theme	Scientific Opportunities/Questions	EM Risks[a]
Coupled Chemical And Physical Processes	*Can we expand our current fundamental models of colloidal behavior to predict variability and dynamics in more complex chemical and physical systems?*	*4,5,6,8,10,11,12,13, 14,28,31,32,33,34,40*
	Can advanced computational fluid dynamics techniques predict rheological structure and the resulting rheological behavior of complex fluids under varying flow conditions?	*8,11,12,13,14,15,26, 31,32,33,47,45,46*
	Can the thixotropic rheological properties be predicted through a combination of rheological structure modeling and computational fluid dynamics under transient conditions?	*11,12,13,14,15,32,33,4 5,46,47*
	Can the yield stress of slurries be predicted through a combination of dynamic rheological structure models and colloidal properties?	*4,5,6,8,10,11,12,13, 14,28,31,32,33,34,40*
	Can advanced computational fluid dynamics techniques assist in predicting the performance of complex processing equipment with thixotropic non-Newtonian fluids?	*11,12,13,14,15,32,33,4 5,46,47*
	What is the nature of bubble slurry interactions that influence the distribution of bubble sizes in multiphase slurries?	*6,13,32,40*
	What is the nature of bubble retention and release on the microscopic level, and what are the effects of slurry composition?	*5,6,13,40*
	Can cold-cap behavior and reactions be predicted with broadly varying chemical compositions through a better fundamental understanding of the interplay between reactions of solid, liquid, and gas phases?	33,41,43,45,46
Chemical Recognition Phenomena	*What are the fundamental interactions that maximize differences in binding affinity and thereby maximize the selectivity of binding phenomena?*	*7,9,18,20,21,22,23, 25,35,36,37,38,39*
	What is the nature of the interactions of the components of matrix environments with target species of interest for separations and sensing?	*4,5,8,9,10,11,15,16, 17,18,19,21,23,28,29,3 7,38,41,43*
	Can the structure of complexes and the thermodynamics of complexation processes involving small donor molecules and ions be predicted in condensed media?	*7,9,18,20,21,22,23, 25,35,36,37,38,39*
	Can molecules and materials be designed to have predictable binding properties for target contaminant species? Can functional attributes be incorporated into the molecular design so that the designed receptors behave predictably in separations or sensing?	*7,9,18,20,21,22,23, 25,35,36,37,38,39*
	How can receptors be designed to function efficiently in different types of separation systems?	*7,9,18,20,21,22,23, 25,35,36,37,38,39*
	How can reporter groups, such as fluorophores and chromophores, be coupled with binding groups and tethered to surfaces to most efficiently signal binding without interfering with the binding process itself?	*7,17,21,22,23,39*
	What is the structural nature of contaminant species on or in complex solid materials, such as building materials, soils, and metals, and what chemistry can be applicable to forced release?	*8,9,10,11,16,18,19, 20,21,22,23*
	What are the chemical speciation and bonding preferences of a contaminant of interest in its matrix, including influences of shape and H-Bonding?	*21,22,23,36,37,39*
(a) EM risks from Table II.		

5

Theme Area 1: Structure and Dynamics of Materials and Interfaces

Scientific challenges associated with HLW retrieval and treatment include an improved understanding of the structure and dynamics of the materials and interfaces. This includes the wastes themselves as well as waste storage and processing equipment and the final waste forms. The waste solids are a combination of minerals and amorphous compounds ranging from crystalline saltcake waste to insoluble sludge. Compounding the composition complexity of the tank wastes is the presence of organic solvents and organic complexants used in some of the chemical separation processes at the facilities along with the radiolytic and chemical degradation of these organic compounds. The behaviors of wastes, including particle agglomeration and coalescence, foaming, and solution/vapor interactions, must be predicted and controlled during storage and processing. Challenges related to tank closure and residual waste include 1) understanding the reactivity of amorphous and crystalline solids, 2) the quantification of the long-term contaminant release from the residual waste, 3) the impact of tank filling materials and the corrosion of steel tank liners on contaminant chemistry, and 4) the fate/transport of contaminants in the environment.

A full definition of the fundamental challenges that are the basis for the use-inspired scientific questions listed in Table I is not possible in the space of this paper, and the reader is referred to the full report [1]. However, the following background on tank corrosion is given as an example of how the fundamental science questions have been developed.

While awaiting retrieval and treatment, the safe storage of HLWs in tanks is maintained through comprehensive structural integrity programs—which include corrosion-control programs, non-destructive evaluations, and fracture-mechanics analyses. The corrosion-control programs were initially designed to protect the tank carbon steel in a long-term storage condition. Under this program, hydroxide and nitrite are the primary corrosion inhibitors. Nitrite is native to the tank waste as a result of the decomposition of nitrate that was added originally as nitric acid from fuel processing operations. Hydroxide in the form of NaOH is currently added to maintain alkalinity. Since any sodium added to the waste increases the eventual volume of waste that must be immobilized, minimizing these additions shortens the mission and reduces costs. The concentration of hydroxide and nitrite needed to inhibit corrosion was determined through empirical models based on coupon tests. Observed corrosion in the tanks indicates that these models significantly overpredicted corrosion rates. Also, these models are not sufficient to predict corrosion at other locations in the tank system, such as the vapor space/liquid-air interface typically occurring under thin film or pseudo-atmospheric conditions that will be discussed later in this document. This presents a fundamental question:

> *Question: What are the mechanisms governing corrosion of materials in contact with high-salt aqueous systems, and what are the additional effects of radiation on these materials?*

Theme Area 2: Coupled Chemical and Physical Processes in Environmental Applications

Rheological behavior in slurries is dependent on a complex combination of chemical and physical parameters. Ionic strength, pH, zeta potential, solids concentration, surface chemistry, particle shape, particle-size distribution, temperature history, shear history, and time all affect the flow behavior of the slurry. These parameters change slowly during storage and dramatically during waste retrieval and processing. In a typical retrieval process, the initial tank farm slurry is retrieved with water jets and sent to the waste processing facility. The retrieved slurry feed will then be processed through several unit operations involving separations of radionuclides and non-radioactive waste components. Changes including pH, dissolved salt content, solids volume fraction, particle size, and solid/liquid chemistry occur during separations and conversion to the final waste form. These physiochemical changes shape the inter-particle colloidal forces. This theme area encompasses fundamental-science challenges associated with the modeling and better understanding of how these forces are affected by changes in these coupled chemical and physical environments.

An example of a computational science challenge in this theme area is driven by the need to predict the rheological behavior of slurries based on known or anticipated particle and solution properties. Colloidal variables govern the interaction potential between particles. The interparticle attractive forces generated by this potential often result in flocculation or coagulation. In flowing systems, the flocs can be broken down, resulting in varying rheological structure under differing flow conditions [15]. The distribution of flocs that result from the shearing forces present in flowing systems results in a system of "flow units" that govern the observed viscosity of the slurry [16]. The size, shape, and distribution of the flow units can be described as the "rheological structure" of the system. Recent advances in computational-fluid-dynamics techniques now allow for the possibility of coupling colloidal force models with the Navier Stokes equations. The aggregate size distribution can be determined by solving the population balance equation (PBE) at every computational node in the domain of interest. The Direct Quadrature Method of Moments (DQMOM) represents the evolution of the aggregate size distribution using a small number of scalar values [17]. This allows for the possibility of modeling rheological structure under different flow conditions.

Modern rheometers are now coupling microscopy and light-scattering techniques with sensitive torque and speed sensors [18]. This allows scientists to obtain quantitative data on rheological structure and the resulting fluid rheology under a wide range of shear environments. The breakdown of rheological structure under high shear conditions often results in a "shear-thinning" flow curve where the viscosity of the slurry appears to thin or lessen with increasing shear rate. Understanding this interaction between rheological structure and fluid rheology can allow for fundamental correlations between these parameters to be obtained. If these correlations are used in the computational fluid dynamics framework discussed above, the following question can be addressed:

> *Question: Can advanced computational-fluid-dynamics techniques predict rheological structure and the resulting rheological behavior of complex fluids under varying flow conditions?*

Theme Area 3: Complex Solution Phase Phenomena in HLW Processing

Unraveling and predicting complex solution phase phenomena in both aqueous solutions and liquid glasses has been, and will continue to be, recognized as of prime importance in HLW processing. Such solution phase phenomena are fundamental to controlling the stability of the waste glasses, retrieving tank solutions, determining the leaching of tank sludges, and determining the long-term stability and corrosion of the waste tanks. They are key to developing separation strategies for radioactive and non-radioactive components. As well, the tank wastes are not in chemical equilibrium. Chemical and physical properties continue to change over time effecting storage, retrieval and processing. This theme area addresses the complex solution phase phenomena that dominates HLW behavior and the future scientific challenges needed to address HLW processing.

As an example of this theme area, one of the major science challenges centers on aqueous chemistry and the associated thermodynamics of concentrated electrolytes. Because of the near ubiquitous presence of water in virtually all HLW processing streams, the chemical behavior of dissolved solutes in aqueous solution has been a focus of process engineers and scientists, starting with the Manhattan Project and continuing today. During this time, much of the fundamental equilibrium chemistry of actinide elements, fission products, and many non-radioactive components has been elucidated, and we now know a great deal about the chemical behavior of these species in aqueous solutions over extended ranges of solution composition and temperature. This fundamental knowledge has, over the past two decades, been summarized in several thermodynamic data reviews and incorporated into predictive chemical models that have been used at all DOE HLW storage sites to analyze a wide range of issues. These issues range from HLW processing from predictions of the dissolution of waste sludges to the removal of radionuclides from process streams to line plugging in waste-transfer lines. The challenge now is to extend this successful equilibrium-based approach to non-equilibrium reactions and more extreme conditions in solvent properties. In this regard, it will be essential to address fundamental questions on the nature of solution phase reactivity.

> *Question: Can we predict the thermodynamics of concentrated electrolyte and mixed-solvent-electrolyte systems to very high concentrations?*

Theme Area 4: Chemical Recognition Phenomena in Environmental Applications

Lehn originally defined recognition in terms of selective binding connected with some purpose [19]. Binding a guest ion or molecule enables a separation or detection, and selectivity becomes the most important characteristic of the binding interaction. In the present context, the motivating purposes entail the core environmental needs for monitoring and analysis or for decontamination of waste, equipment, buildings, soil, groundwater, etc. This theme area includes the role of chemical recognition, the design of new reagents and materials, chemical recognition in separations, sensing and analytical methods, interactions at solid interfaces, and the recognition of specific contaminant species. Significant fundamental questions have been identified for research inquiry.

One major science challenge in this area is a more complete understanding of ionic bonding. The binding agent for a target species is referred to as a receptor or host, and it will be broadly considered here to mean molecular as well as solid-phase materials. In the vein of host-guest chemistry, the target species, referred to as a guest ion or molecule, can be a contaminant of interest, most often a radionuclide ion such as $^{99}TcO_4^-$ or $^{137}Cs^+$; a toxic metal, such as beryllium, mercury, or lead; a species that interferes with processing, such as sulfate in vitrification; or otherwise harmless species that contribute to waste volume, such as sodium and aluminum. A receptor structure whose shape and electronic characteristics are complementary to those of a guest species will bind selectively to the guest species if the binding interaction is sufficiently strong in the medium in which it occurs. The binding interactions from the receptor or host originate from collections of donor atoms held in space by a superstructure of linking groups. The superstructure may be a molecular framework constructed of all covalent bonds, but it can also involve self-assembled frameworks constructed partly from weak bonds, such as coordinative interactions, H-bonds, pi-pi stacking, and the like. If the target guest species is a cation, the donor atoms will be electron-rich ones, especially oxygen and nitrogen atoms. Likewise, anion receptors consist of an array of electropositive groups, especially hydrogen-bond (H-bond) donors and coordination sites on metal cations. Much of what is known about binding comes from research on coordination chemistry and supramolecular chemistry [19]. Still, we are not yet at the stage where the thermodynamics of ion binding can be predicted, leading to the fundamental question:

Question: Can the structure of complexes and the thermodynamics of complexation processes involving small donor molecules and ions be predicted in condensed media?

Technical Risks Facing EM

As described above, the challenges facing the EM cleanup mission require investments spanning fundamental discovery-based research up to applied demonstrations and deployments of existing technology. In Table II, we identify specific risks to the EM cleanup mission that require the investments in fundamental research we identify in this paper. These risks are divided into the seven strategic initiatives defined in EM's OET Roadmap [14]. The first five of these—Waste Storage, Waste Retrieval, Tank Closure, Waste Pretreatment, and Stabilization—are under the Waste Processing Program Area. The final two initiatives—Spent Nuclear Fuel and Challenging Materials—were recently added to the Roadmap. These program areas and the identification of the associated risks are still under development. Therefore, the risks in Table II for Spent Nuclear Fuel and Challenging Materials are preliminary, and associated science questions have not yet been developed. An Initiative Development Team organized by the EM OET with staff from several national laboratories, industrial partners, and academia are working on a more complete list of risks in these two areas.

Table II. Risks and Uncertainties Needing Applied Solutions. Fundamental research is needed to develop applied solutions in the following areas to reduce technical risk and uncertainty in the DOE-EM Waste Processing mission. These range from fundamental chemical and physical data to advanced theoretical and computational models to technology development, enabling transformational engineering solutions. Categories here are derived from the OET Roadmap.

Category	Risks and Uncertainties
Waste Storage	1. Low temperature in-tank sealing technologies compatible with waste chemistry and storage systems to enable tank repairs
	2. Mechanisms governing general corrosion, pitting, and stress corrosion cracking, including effects of waste aging and temperature with time to support tank life extension
	3. Reaction pathways in HLW slurries producing volatile components to mitigate the risks of headspace corrosion, tank failure, ventilation system failure, and occupational exposure
	4. Effects of storage conditions and aging on morphology and surface characteristics of salt and sludge waste, including the role of water on surface chemistry, as they affect continued storage, retrieval, and processing
	5. Effects of waste evaporation and blending operations on waste properties impacting retrieval, transport, and flammable gas safety basis
	6. Chemical and physical processes governing gas retention and release, including submerged bubble retention and gaseous floating layers impacting flammable gas safety and general tank operations
	7. Mercury compounds in waste systems and new monitoring technologies to mitigate impacts on processing and reduce personnel exposure
Waste Retrieval	8. Chemical and physical properties of dried wastes, including salt heels and annular sludge needed to support retrieval and waste acceptance at treatment plants
	9. Oxalic acid and other novel leaching agents interaction during heel removal to mitigate carbon steel tank corrosion and flammable gas generation rates
	10. Existing mineral phases, condensation of new minerals, and co-deposition of radionuclides on metal surfaces that increase source terms
	11. Chemical and physical properties of insoluble heels formed that will be generated during complex retrieval and blending operations in staging tanks to enable their eventual retrieval and disposal
	12. Physical properties of the tank waste to mitigate system failures, including line plugging, pumping failures, and feed variability
	13. Physical and chemical processes leading to foam, crust, and floating layer formation during retrieval to mitigate impacts on tank scaling and flammable gas safety
	14. Rheological characterization of wastes as well as mixing and transport designs to support homogeneous delivery of feeds to treatment plants
	15. Heel retrieval technologies and chemical models insufficient to ensure waste acceptance at treatment plants
	16. Models for saltcake draining and dissolution to predict solution chemistry, rates, dissolution methods, and radionuclide partitioning enabling the optimization of retrieval-system designs and operation
	17. Chemical properties of tank waste needed to support acceptance and process ability

Table II (Contd)

Category	Risks and Uncertainties
Tank Closure	18. Interactions of waste with the surrounding fill and near vadose zone to reduce the migration of waste that has already leaked or may leak during retrieval
	19. Heel chemistry and associated radiochemical source terms following retrieval activities, including modified sluicing to enable selection of appropriate tank fill materials
	20. Improved stabilization forms as alternatives to baseline grout and consolidated low-strength materials
	21. In-tank method to analyze residual materials, including components driving performance assessment (^{99}Tc, ^{79}Se, ^{129}I, and ^{237}Np) and waste acceptance (particle size, percent solids, etc.)
	22. Sensors for radionuclides in soil and groundwater at tanks will enable long-term monitoring.
	23. Sensors for *in situ* characterization of radionuclide content of tank heels will shorten retrieval times and inform decision-making.
Waste Pretreatment	24. Tank corrosion mechanisms that could impact safety during retrieval and processing
	25. Behavior of minor waste components that could result in currently unrecognized impacts to waste-processing flowsheets
	26. Statistical variability in waste composition to enable control strategy to run and optimize plant operations
	27. Chemistry of the secondary waste and recycle streams to mitigate potential impacts to start-up and plant operations
	28. Thermodynamics and kinetics of Al mineral precipitation, transformations, and dissolution to enable optimized leaching and substantial decreases in low-activity waste (LAW) glass production as well as reduce the risks of oversaturated conditions
	29. Behavior of chromium and Pu during oxidative leaching to enable optimization of leaching conditions and general operations
	30. Waste compositional and thermodynamic data to optimize blending
	31. Advanced reactive transport models supported by detailed thermodynamic and kinetic solution stability data to prevent line plugging and allow for a comprehensive strategy for recovering from line plugging
	32. Advanced multi-phase computational fluid dynamics models for time-dependent non-Newtonian fluids to predict and optimize mixer tank and filtration performance
	33. Advanced online capabilities for process monitoring to enable process optimization
	34. Improved in-tank and laboratory methods for solids characterization to optimize plant operations
	35. Separation methodology for removing sodium hydroxide from alkaline HLW for sludge washing and retrieval uses would reduce the volume of vitrified waste.
	36. Selective removal of sulfate, a vitrification poison, would enable reduction of glass production.
	37. Deeper understanding of Cs, Sr, and actinide separation processes being implemented at Hanford and the SRS would reduce technical risks associated with plant commissioning and long-term operation.

Table II (Contd)

Category	Risks and Uncertainties
	38. Chelation of Al and Cr could enable reduction of both HLW glass and LAW volume.
	39. Online monitoring of radionuclides in processes being implemented would reduce analytical costs and improve operational performance.
	40. Foam formation and destruction in process streams to reduce impacts to processing and improved flammable gas safety
Stabilization	41. Vault science and technology enabling improvements in performance assessment
	42. Alternative HLW glasses with increased waste loading needed to boost throughput and reduce canister count
	43. Grout curing and variations with formulations needed to ensure long-term performance and reduce the release of volatile components
	44. Alternative LAW and secondary waste forms to mitigate the impacts of low LAW melter throughput
	45. Cold cap chemistry, including flash reactions, off-gas, and overall melting reactions and rates to optimize throughput, minimize refractory corrosion, and reduce off-gas and recycle streams
	46. Liquidous-glass transition to model and predict the solubility of limiting components, enabling optimized formulations, and to increase waste loading, optimize melt rates, reduce melter temperature, and increase throughput
	47. Grout rheological and physical properties to support pumping operations and filling of ancillary systems, including transfer lines and cooling coils
	48. New approaches to reducing the content of waste components, such as aluminate, sodium, and sulfate, that determine glass volume to aid supplemental treatment
Spent Nuclear Fuel	49. U metal oxidation mechanisms and rates needed to reduce technical risks associated with selection and implementation of treatment options for U-metal-containing materials
	50. Technical basis at Yucca Mountain for acceptance of metallic uranium and other non-UO_2 fuels
	51. Thermodynamics and kinetics of water release from $Al(OH)_3$ required to address transportation of Al-clad fuels
	52. Long-term chemical behavior of decay products from activation and fission products as well as temperature histories to reduce uncertainties in fuel chemistry and electronic structure that is challenging container integrity and the validity of reactive transport models
	53. Mechanisms leading to degradation of DOE aluminum-clad spent fuels to ensure safe storage
	54. Alternative sealing technologies enabling advanced canister closures in high-radiation environments
	55. Advanced neutron absorbers performing over geological timescales to enable safe storage in national repository
	56. Fissile element redistribution during corrosion of DOE fuels to reduce conservatism in current design and associated cost
	57. Alternative treatment flowsheet for Fast Flux Test Facility Na and K bonded fuels to mitigate transport risks and waste acceptance risks to treatment at Idaho and/or direct

Table II (Contd)

Category	Risks and Uncertainties
	shipment to Yucca Mountain
	58. New technologies for nondestructive assay of plutonium and other isotopes in the high-radiation environments of spent fuels for wet and dry storage to enable flowsheet development, ensure safe storage, and improve accountability
Challenging Materials	59. Chemical and electronic structure changes arising from radiolytic decay in Cs, Sr, and other sealed capsules to assess long-term integrity and enable the development of disposal options
	60. Corrosion hindering long-term performance of 3013 containers
	61. Tritium absorption and desorption thermodynamics and kinetics in structural materials and components to support safety basis
	62. Transuranic (TRU) element adsorption and penetration of surfaces to enable development of improved decontamination technologies needed to reduce the volume of material sent to the Waste Isolation Pilot Plant (WIPP)
	63. Thermodynamic and chemical data on Pu-containing materials needed to support processing and stabilization
	64. Chemical and radiolytic hydrogen gas generation mechanisms to enable TRU transportation to WIPP
	65. Alternative waste forms and advanced melter technologies needed to stabilize excess nuclear materials, including Pu
	66. Reaction mechanisms driving gas generation in 3013 canisters and other long-term storage containers to safe storage
	67. Improved technologies to monitor the integrity and contents of 3013 canisters and other long-term storage containers to safe storage and accountability
	68. Advanced non-intrusive characterization technologies, including the measurement of chemical, physical, and radiological properties, to enable the development of treatment options and accountability

CONCLUSION

The overall intent of this paper is to foster a dialogue on how basic scientific research can assist the EM mission [12]. This paper presents an initial attempt to frame fundamental questions of importance for reducing technical risk in EM's long-term mission. As with all areas of fundamental research, this requires ongoing discussion as new discoveries are made, and new challenges are encountered. The authors encourage feedback from our colleagues in the community of scientists and engineers interested in nuclear chemistry, materials science, and associated fields. We look forward to an active dialogue on these important questions and others that may be posed.

REFERENCES

1. P. BREDT, A.R. Felmy, P.A. Gauglitz, D. Hobbs, S. Krahn, N. Machara, M. McIlwain, B.A. Moyer, A.P. Poloski, K. Subramanian, J.D. Vienna, B. and Wilmarth, "Scientific Opportunities to Reduce Risk in Nuclear Process Science," PNNL-17699, Pacific Northwest National Laboratory, Richland, Washington (2008).

2. National Research Council (NRC), "Building an Effective Environmental Management Science Program: Final Assessment," Washington, D.C., National Academies Press (1997). Available at: http://books.nap.edu/catalog.php?record_id=5557. Accessed November 10, 2008.

3. National Research Council (NRC), "Alternatives for High-Level Waste Salt-Processing at the Savannah River Site," Washington, D.C., National Academies Press (2000). Available at: http://books.nap.edu/catalog.php?record_id=9959. Accessed November 10, 2008.

4. National Research Council (NRC), "A Strategic Vision for Department of Energy Environmental Quality Research and Development," Washington, D.C., National Academies Press (2001). Available at: http://books.nap.edu/catalog.php?record_id=10207. Accessed November 10, 2008.

5. National Research Council (NRC), "Improving the Scientific Basis for Managing DOE's Excess Nuclear Materials and Spent Nuclear Fuel," Washington, D.C., National Academies Press (2003). Available at: http://www.nap.edu/catalog.php?record_id=10684. Accessed November 10, 2008.

6. National Research Council (NRC), "Improving the Characterization and Treatment of Radioactive Wastes for the Department of Energy's Accelerated Site Cleanup Program," Washington, D.C., National Academies Press (2005). Available at: http://books.nap.edu/catalog.php?record_id=11200. Accessed November 10, 2008.

7. National Research Council (NRC), "Tank Waste Retrieval, Processing, and On-Site Disposal at Three Department of Energy Sites," Washington, D.C., National Academies Press (2006). Available at: http://www.nap.edu/catalog.php?record_id=11618. Accessed November 10, 2008.

8. National Research Council (NRC), "Science and Technology Needs for DOE Site Cleanup: Workshop Summary," Washington, D.C., National Academies Press (2007). Available at: http://www.nap.edu/catalog.php?record_id=11932. Accessed November 10, 2008.

9. U.S. Department of Energy (DOE), "Environmental Management Strategic Plan for Science & Technology," DOE, Washington, D.C. (1998). Available at: http://www.p2pays.org/ref/14/13636.pdf. Accessed November 10, 2008.

10. U.S. Department of Energy (DOE), "Environmental Management Research and Development Plan: Solution-Based Investments in Science and Technology," DOE, Washington, D.C. (1998).

11. U.S. Department of Energy (DOE), "U.S. Department of Energy Strategic Plan," DOE, Washington, D.C. (2006). Available at: http://www.energy.gov/media/2006_DOE_Strategic_Plan.pdf. Accessed November 10, 2008.

12. U.S. Department of Energy (DOE), "Engineering and Technology Program Management Plan," DOE, Washington, D.C. (2008). Available at: http://www.em.doe.gov/pdfs/08N00100_72dpi.pdf. Accessed November 10, 2008.

13. U.S. Department of Energy (DOE), "Waste Processing Multi-Year Program Plan Fiscal Year 2008-2012," Washington, D.C. (2008). Available at: http://www.em.doe.gov/pdfs/MYPP%205.23.pdf. Accessed November 10, 2008.

14. U.S. Department of Energy (DOE), "Engineering & Technology Roadmap: Reducing Technical Risk and Uncertainty in the EM Program," Washington, D.C. (2008). Available at: http://www.em.doe.gov/pdfs/FINAL%20ET%20Roadmap%20_3-5-08_.pdf. Accessed November 10, 2008.

15. D.L. MARCHISIO, and R.O. Fox, "Solution of Population Balance Equations Using the Direct Quadrature Method of Moments," Journal of Aerosol Science 36(1):43–73 (2005).

16. E.E. BIBIK, "Rheology of Disperse Systems," Leningradsky Universitet, Leningrad (1981).

17. A.P. POLOSKI, R.C. Daniel, D.R. Rector, P.R. Bredt, E.C. Buck, J.C. Berg, and A.E. Saez, "Characterization and Correlation of Particle-Level Interactions to the Macroscopic Rheology of Powders, Granular Slurries, and Colloidal Suspensions," PNNL-16133, Pacific Northwest National Laboratory, Richland, Washington (2006).

18. E. DI COLA, T.A. Waigh, and R.H. Colby, "Dynamic Light Scattering and Rheology Studies of Aqueous Solutions of Amphiphilic Sodium Maleate Containing Copolymers," Journal of Polymer Science Part B: Polymer Physics, 45(7):774–785, (2007).

19. J-M. LEHN. 1973. "Design of Organic Complexing Agents. Strategies Towards Properties." In: Alkali Metal Complexes with Organic Ligands. JD Dunitz, Ed. Springer, Berlin, Volume 16 of the series Structure & Bonding 16:1–69.

20. G. WILKENSON, R.D. Gillard, and J.A. McCleverty (Eds.), "Comprehensive Coordination Chemistry," Pergamon Press, Oxford, Vols. 1–7 (1987).