DEPARTMENT OF ENERGY
UNITED STATES OF AMERICA

Nuclear Separations Technologies Workshop Report

Getting From Where We Are to Where We Want To Be in Nuclear Separations Technologies

July 27–28, 2011

TABLE OF CONTENTS

ACRONYMS AND INITIALISMS

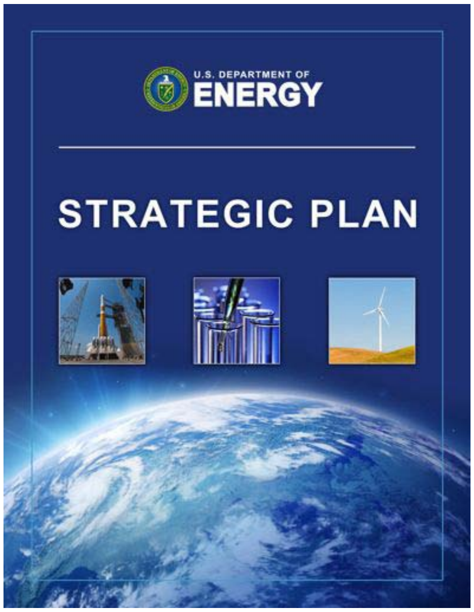
µm	Micrometer(s)
µM	Micromolar
3D	Three-Dimensional
Al	Aluminum
Am	Americium
AMEX	Amine Extraction
ASTM	ASTM International, formerly the American Society for Testing and Materials
ATR	Advanced Test Reactor
Be	Beryllium
BRC	Blue Ribbon Commission on America's Nuclear Future
BTP	Bis-Triazinyl-Pyridine
C	Carbon
Ca	Calcium
CaDTPA	Calcium Diethylenetriaminepentaacetate Complex
CEA	Commissariat à l'energie atomique
CFD	Computational Fluid Dynamics
CFR	Code of Federal Regulations
Cl	Chlorine
Cm	Curium
Co	Cobalt
CRESP	Consortium for Risk Evaluation with Stakeholder Participation
Cs	Cesium
CSEX	Cesium Extraction
CSSX	Caustic-Side Solvent Extraction
CST	Crystalline Silicotitanate (ion exchange)
DoD	Department of Defense
DOE	Department of Energy
DTPA	Diethylenetriaminepentaacetic Acid
DWPF	Defense Waste Processing Facility
EM	Office of Environmental Management
FCR&D	Fuel Cycle Research and Development (program)
FCT	Fuel Cycle Technologies
FP	Fission Product
GDP	Gaseous Diffusion Plant
GPO	Government Printing Office
GTRI	Global Threat Reduction Initiative
H	Hydrogen
HEU	Highly Enriched Uranium
HLW	High-Level Waste
HM	Heavy Metal
HOPO	Hydroxypyridinonate
I	Iodine
IAEA	International Atomic Energy Agency
IL	Ionic Liquid
In	Indium
Ir	Iridium
ITP	In-Tank Precipitation Process
IX	Ion Exchange
kg	Kilogram(s)
Kr	Krypton
LAW	Low-Activity Waste
LEU	Low-Enriched Uranium
LLW	Low-Level Waste
LWR	Light Water Reactor

M	Molar
MD	Molecular Dynamics
mm	Millimeter(s)
mM	Millimolar
Mo	Molybdenum
MOX	Mixed Oxide
Na	Sodium
NA-10	Defense Programs (NNSA)
NA-20	Office of Defense Nuclear Nonproliferation
NAS	National Academy of Sciences
NE	Office of Nuclear Energy
NIH	National Institutes of Health
NIS	Office of Nonproliferation and International Security
nm	Nanometer(s)
NNSA	National Nuclear Security Administration
Np	Neptunium
NRC	Nuclear Regulatory Commission
NSF	National Science Foundation
NSUF	National Scientific User Facility
O	Oxygen
PJM	Pulse Jet Mixers
Pd	Palladium
pM	Picomolar
Po	Polonium
POM	Polyoxometalate
Pu	Plutonium
PUREX	Plutonium/Uranium Refining by Extraction
QSAR	Quantitative Structure-Activity Relationship
Ra	Radium
R&D	Research and Development
RD&D	Research, Development and Demonstration
RDD	Radiological Dispersal Device (e.g., dirty bomb)
REDOX	Oxidation Reduction
S	Sulfur
SC	Office of Science
SCN^-	Thiocyanate
SNF	Spent Nuclear Fuel (as used in this report, equivalent to used nuclear fuel)
Sr	Strontium
SREX	Strontium Extraction
SS&T	Separation Science and Technology
SX	Solvent Extraction
TALSPEAK	Trivalent Actinide–Lanthanide Separation by Phosphorus Reagent Extraction from Aqueous Complexes
TBP	Tri-N-Butyl Phosphate
Tc	Technetium
THORP	Thermal Oxide Reprocessing Plant
TRA	Technology Readiness Assessment
TRL	Technology Readiness Level
TRU	Transuranic
TRUEX	Transuranic Element Extraction
U	Uranium
UNF	Used Nuclear Fuel
UREX+	Uranium Extraction Plus
WIPP	Waste Isolation Pilot Plant
WTP	Waste Treatment Plant
Xe	Xenon
Y	Yttrium
Zr	Zirconium

EXECUTIVE SUMMARY

The Department of Energy (DOE) sponsored a workshop on nuclear separations technologies in Bethesda, Maryland, on July 27 and 28, 2011, to (1) identify common needs and potential requirements in separations technologies and opportunities for program partnerships, and (2) evaluate the need for a DOE nuclear separations center of knowledge to improve cross-program collaboration in separations technology. The workshop supported Goal 3 of the DOE *Strategic Plan*[1] to enhance nuclear security through defense, nonproliferation, and environmental management. The Office of Environmental Management (EM), Office of Nuclear Energy (NE), and National Nuclear Security Administration (NNSA) jointly sponsored the workshop. The Office of Science (SC), which performs fundamental research in relevant areas, also participated. The workshop attracted 133 attendees from national laboratories, academia, industry, DOE oversight and advisory organizations, sponsoring offices and the international community.

Figure 1. The workshop supported Goal 3 of the DOE Strategic Plan.



The workshop included four breakout sessions with program-related topical areas covering a broad range of separations activities. The topics also span the range of DOE-defined Technical Readiness Levels (TRLs)[2] where the lower readiness levels are less mature technology (more basic research and development [R&D]) and the higher numbers are more mature (more deployable) technology (see Figure 2). The breakout session topics were as follows:

- Chemistry and Speciation of the Actinides and Key Fission Products (Cs, Tc, I)
- Design of Molecules and Materials with Selective Separation Properties
- Scale-up of Separation Processes from Bench-Top to Plant
- Interface Synergies between Separations, Waste Management, and Fuel Fabrication

Role of Nuclear Separations

Within DOE and its predecessor agencies, there has been a continuing need for new nuclear separations technologies over the past 70 years. DOE has multiple responsibilities that require the ability to separate nuclear materials for their direct use, future reuse or disposition:

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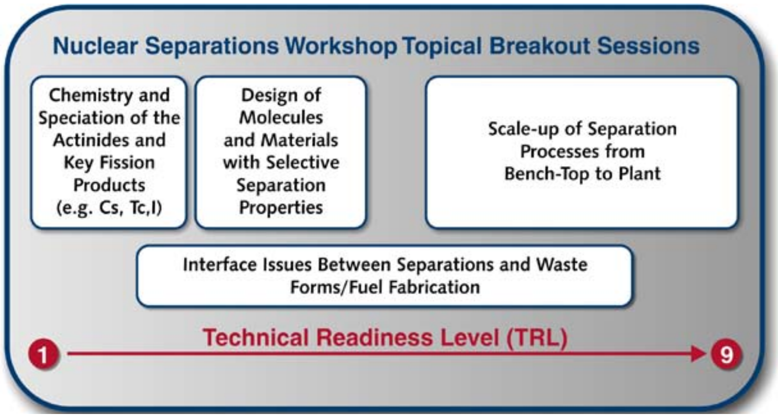
[1] U.S. Department of Energy. *Strategic Plan*. Washington: GPO, May 2011.

[2] ---. DOE Guide 413.3-4A, Technology Readiness Assessment Guide, September 15, 2011.

(1) nuclear weapons manufacture and maintenance, (2) technical aspects of nuclear nonproliferation, (3) cleanup of legacy defense-related nuclear facilities, (4) disposition of excess weapons plutonium, (5) research on advanced commercial fuel cycles, and (6) treatment and disposal of radioactive wastes including spent nuclear fuel (SNF). Of special interest in nuclear separations technologies are those related to capturing elements such as uranium and plutonium, other actinides such as americium, and selected fission products (FPs) such as technetium, iodine, and cesium.

Figure 2. The workshop included four breakout sessions with program-related topical areas.



Significant advances in separations technologies can be derived from industrial applications, as separations technologies are the backbone of the pharmaceutical, chemical, metal production, and fossil fuel industries. However, research, development and demonstration (RD&D) of nuclear separations technologies faces different challenges, such as the following:

(1) In the absence of a large commercial domestic market in nuclear separations, responsibility for developing these technologies falls to DOE. DOE should be capable of taking the necessary steps in behalf of our national interests to assure the technical capabilities exist to meet current and future nuclear separations needs.

(2) Nuclear separations RD&D requires highly specialized facilities, as many of the important species are radioactive and/or entail extensive safeguards and security. Preserving or developing specialized facilities for RD&D, and maintaining internal centers of excellence, will ensure required capabilities are available.

(3) The U.S. reservoir of trained professionals outside the DOE complex is small. Developing the next generation of young professionals to replace retiring staff is essential to maintain U.S. technical expertise in this important technology.

DOE nuclear separations challenges include:

- *Meeting our national needs*
- *Sustaining specialized capabilities/facilities*
- *Training and developing the workforce of the future*

Opportunities for Program Partnerships

Nuclear separations R&D addresses needs and requirements that cut across multiple DOE offices, as they share a common interest in the chemistries of actinides and FPs. For example, understanding radionuclides' transport in the environment and their subsequent recovery is normally considered part of the EM mission; however, NNSA needs similar chemistry to detect nuclear weapons activities, as does NE to model transport of radioactivity from disposal sites—including geological repositories.

Scientific breakthroughs have been successfully transferred from one DOE program to another; examples include the well-known transuranic element extraction (TRUEX) process for actinide separations and, for cesium removal from tank waste, the caustic-side solvent extraction (CSSX) and crystalline silicotitanate (CST) ion exchange processes. All three processes were based on scientific insights developed through DOE basic science programs, and the methods were applied in environmental cleanup of the weapons complex and development of advanced fuel cycle technology.

Figure 3. The CSSX ion exchange process, an innovation based on new molecules, resulted from cooperation across DOE offices.

In order to capitalize on opportunities for program partnerships, breakout session participants identified common needs and potential requirements in nuclear separations technologies. Recognizing the different mission requirements of the sponsoring programs, participants were able to identify areas with common uses and related applications, as discussed below.

Chemistry and Speciation of the Actinides and Key Fission Products (Cs, Tc, I)

Understanding the underlying physical and chemical properties of given materials is the basis for all separations. In addition, the area of nuclear separations involves the need to understand how these properties change in the presence of a radioactive environment. Also of great importance is understanding the properties of actinides which, relative to most other elements, have complex chemistries that are less well explored and more difficult to model.

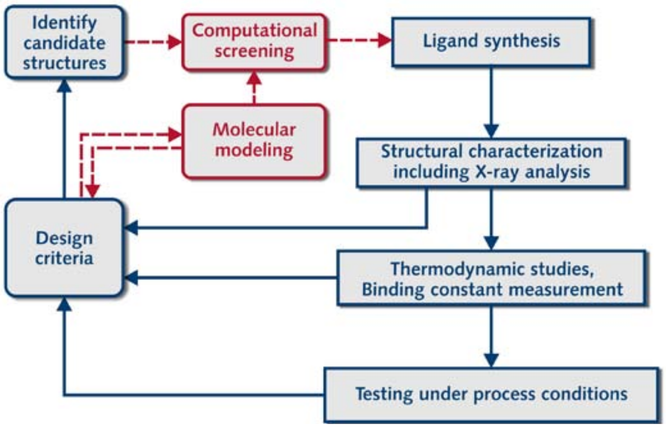
Of benefit to the sponsoring programs is understanding chemical properties, such as oxidation states and coordination environments, which can be adjusted to optimize partitioning and separation in multi-radionuclide systems. Better understanding actinide and FP chemistry will impact a variety of challenges facing DOE, such as monitoring actinides during processing and technetium volatilization in waste treatment. To help predict process performance and behavior, understanding the fundamental effects of radiolysis on solvents, ligands and other separations molecules will enable development of advanced models of radiation resistance, decomposition, and formation of radicals. In addition, advanced tools are needed to predict the molecular structure of actinides and FPs in extreme systems, ranging from ultra-low-concentration contaminants to complex environments at high temperatures.

Design of molecules with selective nuclear separations capability

The development of nuclear separations technologies has historically involved the empirical screening of chemical compounds for their ability to perform separations. The last decade has seen a maturity in the technology to synthesize molecules and materials for a specific function. Improved predictive science that couples experimentation with modeling and theory allows researchers to design molecules and materials that precisely target particular nuclear separations requirements. Breakthroughs of this type require a full-cycle, systematic approach by teams with diverse capabilities from molecular design to synthesis to chemical engineering (see Figure 4). Advancing this design approach supports multiple DOE separations needs.

While many nuclear separations processes are project-specific, others have applicability across the Department, such as selective co-separation of fissile and fertile materials. Current commercial SNF recycling processes allow for the separation of pure plutonium. Custom-designed molecules could make possible the co-separation of given mixtures of actinides while making production of pure plutonium difficult, changing the diversion risks encountered in these processes. Such separation systems could also be more economical because the product is suitable for direct fuel fabrication. In addition, to address nuclear accidents and radiological terrorist incidents more effectively, there is a need for the removal of radionuclides from a variety of host matrices, such as soils, concrete, and the human body.

Figure 4. Recent separations research, such as computer-aided ligand development, is largely aimed at design of molecules and materials and requires teams with diverse capabilities.

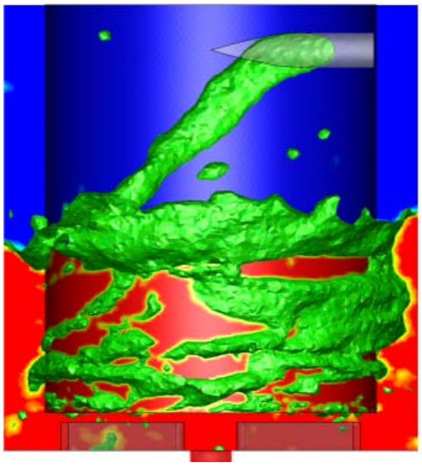


Scale-up to industrial capabilities

The history of transitioning nuclear separations processes from the laboratory to an industrial scale includes a number of failures and setbacks due to the unforecasted effects of radiation. Radiation affects the behavior of separations agents with time. Equally important, modifying a nuclear separations facility after it has begun operations requires time and money an order of magnitude greater than for a comparable non-nuclear chemical plant. Therefore, it is essential to recognize, and account for, the hazards throughout the process when scaling up nuclear separations facilities operated under high levels of radiation. All of the sponsoring programs will face these hazards when developing technology from the bench scale to the industrial scale. In order to ensure certainty in taking a technology from bench to industrial scale, programs will have to analyze and address the technology risks associated with each step in the scale-up process. An effective risk analysis calls for understanding the key physical and chemical properties affected, and the appropriate number of scale-up steps necessary, in order to properly consider risk, cost, and expected performance.

There is a need to develop methods to increase confidence when scaling up nuclear separations technology. Fundamental understanding of science coupled with advanced computational capabilities (see Figure 5) may increase the efficiency of scale-up testing, providing methods that supplement the traditional multi-step process (e.g., 1/1000 scale to 1/100 scale, 1/100 scale to 1/10 scale, etc.) to reduce risk, lower costs, and increase certainty. Collaboration with foreign partners with more recent experience in scale-up may also provide useful input and insight. Ultimately, reducing program risk in process scale-up will provide tangible benefits to the sponsoring programs.

Figure 5: Faster scale-up is possible with advances in modeling, such as this computer simulation of a solvent extraction separations process using a centrifugal contactor.



Interface synergies between nuclear separations, waste management, and fuel fabrication

Whether separating the contents of a high-level waste (HLW) tank for stabilization and disposition or separating SNF for fuel material recycling, the interface between the different processes and the waste forms that they produce is a critical consideration when reducing costs and optimizing the overall operation. Efficiencies in one area may lead to complications in other areas. A systems analysis approach is therefore essential to guide R&D.

Tools that capture functions and requirements of a process must be developed to improve synergies between the separations process and follow-on processes. For example, developing a separations technology commonly involves chemicals that function as complexing agents, such as iron. If subsequent steps in this process entail using borosilicate glass for waste disposal, the presence of iron will limit the ability to maximize waste loading, reducing efficiency and ultimately increasing the overall costs. Understanding the impact that each step has on the overall process and capturing interface synergies will result in improved overall performance and reduced costs.

Advantages of a Nuclear Separations Center of Knowledge

The participants of the workshop acknowledged that the focus of separations research has shifted from a primary mission involving weapons to supporting multiple DOE offices with potentially competing priorities. Scattering DOE resources among various R&D paths can dilute DOE’s potential to achieve its missions. Expanded and multiple emphases also make it more difficult for DOE to maintain a skilled workforce. Since the cold war, the NNSA production complex has downsized as missions have evolved, resulting in an aging workforce that is declining in numbers. In addition, it is more expensive to maintain facilities with radiological capabilities to support multiple missions.

A DOE center of knowledge for nuclear separations can:
- *Improve coordination across DOE programs*
- *Maximize the use of existing capabilities and facilities to best use available funding and resources*
- *Facilitate training researchers of the future*

To address these needs, a center of knowledge is proposed. Such an entity could assist DOE in taking full advantage of the synergies between programs, as well as fully exploiting resources—including technical expertise and experimental capabilities—across national laboratories, academia, and industry. In addition, establishing a center could contribute to developing a future skilled technical workforce. Such a center may be created initially as a coordinated virtual network of existing national assets, then evolve over time as experience informs a changing portfolio of functions and capabilities. Given the nature of this technology and the potential for multinational interactions, the center should account for international safeguards agreements and export control requirements.

Benefit

For DOE, going from one initial primary goal (weapons production) to multiple research, energy-production, and cleanup goals has resulted in a multi-dimensional set of technology needs. Those needs are defined by various offices and documented in dozens of different reports. There is no single big picture of needs, but there are significant overlaps representing important opportunities for research with broad impacts. Therefore, coordinated efforts can help weave seemingly disparate—even competing—needs into a coherent effort. Short-, medium-, and long-term needs and interface requirements should be concisely defined and assembled in a way that allows researchers and program managers to match needs with capabilities, identify solutions, enable synergies, and share changes as requirements evolve.

Establishing a center of knowledge for nuclear separations can initially be a virtual network connecting common work between programs

A DOE center of knowledge for nuclear separations technologies can:

(1) Improve coordination across multiple DOE programs, facilitating collaboration and technology synergies.

(2) Maximize the use of existing capabilities and facilities to ensure efficient and effective use of available funding and resources.

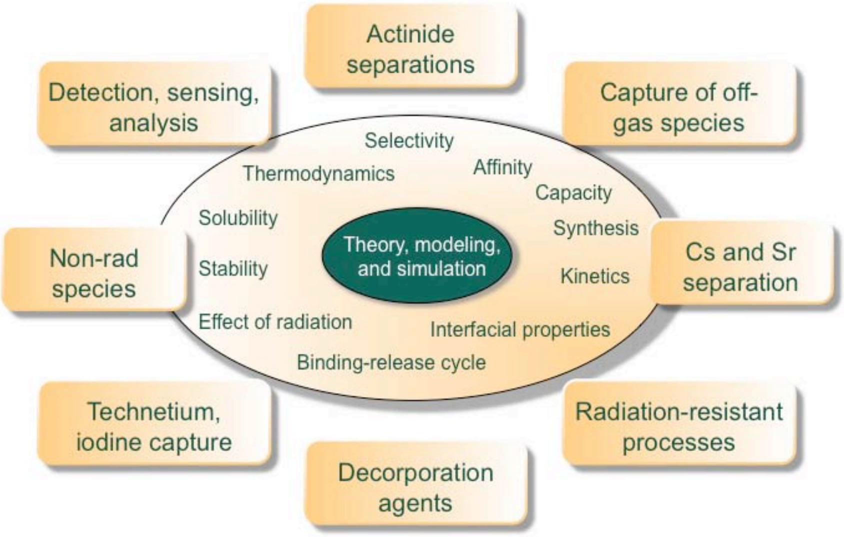
(3) Facilitate coordinated plans for developing and training the needed researchers and operators of the future to ensure the United States maintains a knowledge edge in expertise and experience.

Establishing a center of knowledge for nuclear separations technology and networking user facilities for R&D purposes will require detailed proposals and an implementation plan, as determined by the sponsoring programs.

Next Steps

The Nuclear Separations Technologies Workshop established a foundation of cooperation in this important area between EM, NE, NNSA and SC. More discussions and broad participation will be needed to advance the concepts and ideas introduced during the workshop and to ensure inclusive research scope.

Figure 6. The workshop found that partnership opportunities exist for all separations-related technologies.



Next steps resulting from this workshop are to be broken into three phases:

(1) Startup

(2) Growth

(3) Sustainable Program

The Startup phase includes preparation of a nuclear separations roadmap that would discuss technical issues, programs, and collaborations in the areas of separations necessary to achieve the goals of DOE program offices. Specifically, the nuclear separations roadmap will:

(1) Establish the plans and strategies necessary to develop the cooperation initiated at this workshop into a sustainable collaboration between the sponsoring programs, including the estimated scope, schedule, and costs associated with the Growth and Sustainable Program phases.

(2) Support the coordinated DOE response to the Blue Ribbon Commission on America's Nuclear Future (BRC) recommendations, expected in January 2012, as they relate to nuclear separations technologies.

(3) Refine the concept of a nuclear separations center of knowledge that responds to DOE needs, improves program partnerships, and supports the effective use of available funding and resources.

A nuclear separations center of knowledge may be a candidate for DOE's portfolio of new research efforts, such as the Innovation Hubs. A center would provide a mechanism to integrate multiple phases of nuclear separations RD&D across DOE offices and address the boundaries between science, engineering, and technology development.

1. INTRODUCTION

1.1 Overview

On July 27 and 28, 2011, DOE hosted a workshop to bring together scientists and engineers from the national laboratories, academia, and industry to set a course for moving from where we are to where we want to be in nuclear separations technologies. The technical goals of the workshop were to determine the path necessary to address the following technical challenges within the next three to five years:

- Enable the responsible deployment of civilian nuclear power and fuel cycle management by developing used fuel recycling technologies that are alternatives to plutonium/ uranium refining by extraction (PUREX) and that support waste minimization.
- Support environmental remediation of our legacy and active sites by developing next-generation waste treatment technologies that increase performance and reduce cost.
- Reduce global threats from nuclear materials by supporting technologies that reduce the risks of proliferation, such as alternative methods of medical isotope production that do not use highly enriched uranium (HEU).

The workshop presented two overarching programmatic objectives that support optimizing the path to resolve these technical challenges:

- Identify common needs and potential requirements in nuclear separations technology and opportunities for program partnerships.
- Evaluate the need for a DOE nuclear separations center of knowledge.

The workshop directly supported Goal 3 of DOE’s recently revised *Strategic Plan*: Enhance nuclear security through defense, nonproliferation, and environmental efforts.[3] Three DOE organizations jointly hosted the workshop: EM, NE, and NNSA. SC, which establishes basic research needs and funds fundamental science programs in relevant areas of actinide separations, also played an active collaborative role. More about these workshop sponsors can be found in Appendix E.

To ensure an appropriate mix of subject matter experts, participants were solicited through two methods: 1) DOE reached out to specific individuals to serve in appropriate breakout sessions, and 2) a broader invitation was issued encouraging interested parties to attend (contingent upon DOE approval). The workshop attracted 133 attendees including representatives from 8 national laboratories and 22 academic institutions. Also represented were industry partners, the Nuclear Energy Advisory Committee’s Subcommittee for Fuel Cycle Research and Development, the

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[3] U.S. Department of Energy, *Strategic Plan*. Washington: GPO, May 2011.

Nuclear Waste Technical Review Board, and three international organizations: the French Embassy, the French Commissariat à l'energie atomique (CEA), and the U.K.'s National Nuclear Laboratory.

The two-day workshop began with an introductory plenary session, summarized in Section 2 of this report, in which executives presented information about their respective organizations' backgrounds and viewpoints regarding separations issues. Workshop participants then divided into four breakout sessions organized to address specific technical challenges in the following areas:

- Chemistry and Speciation of the Actinides and Key Fission Products (Cs, Tc, I)
- Design of Molecules and Materials with Selective Separation Properties
- Scale-up of Separation Processes from Bench-Top to Plant
- Interface Synergies between Separations, Waste Management, and Fuel Fabrication

The workshop concluded with a summary plenary session in which each program breakout group reported session outcomes, including analyses and recommendations. The results of the breakout sessions are summarized in Section 3 of this report, with full session reports included in Appendices A through D. Appendices to this report also provide the workshop agenda and a complete participant list.

To prepare participants, advance reading materials were posted to the workshop website. The general reading list included agency plans and roadmaps, a report from the Massachusetts Institute of Technology on the nuclear fuel cycle, an EM document on separations technology challenges, and the executive summary from the Nuclear Regulatory Commission (NRC) white paper on SNF recycle facilities (NUREG 1909). These and other references directly related to the subject of RD&D associated with nuclear separations are found at the end of this report.

1.2 Background

As DOE's *Strategic Plan* articulates, the growing global demand for energy, coupled with increasing concerns about climate change, has accelerated deployment of nuclear power plants and fuel cycle facilities despite recent events overseas. Meeting this need, however, requires that a number of technological hurdles associated with the nuclear fuel cycle be addressed. Basic and applied research by the Department's predecessor agencies in the mid-20th century laid the foundation for modern nuclear power and fuel cycle technologies. A key element of nuclear fuel cycles is the use of separations technologies such as used fuel recycling, material stabilization, waste treatment, and isotope development and production. The need to develop these nuclear separations technologies cuts across a number of important Department organizations: EM, NE, NNSA, and SC. Therefore, these offices joined forces to host a workshop to set a course for moving from where we are to where we want to be in nuclear separations technologies.

The need for advances in this area is increasingly pressing. As EM notes in a recent report,[4] fifty years of nuclear weapons production, combined with activities supporting nuclear energy, have already left the United States with millions of gallons of highly radioactive waste, thousands of tons of SNF and special nuclear material, and enormous quantities of contaminated soil, water, and facilities. The cleanup effort currently covers over a million acres in thirteen states. The EM cleanup program, which has already been under way for twenty years, estimates several decades for completion. As energy demand grows, nuclear power will expand; and as nuclear power expands, SNF and HLW inventories will grow. The Nuclear Waste Policy Act of 1982 gave the U.S. government the mission to safely manage the SNF and HLW from these nuclear power plants. The responsibilities under this mission are science- and technology-intensive; several recent efforts have identified ongoing technical challenges.[5,6]

RD&D of sustainable nuclear fuel cycles and waste management activities is critical both to address existing inventories of SNF and HLW and to ensure a continued role for nuclear energy in the nation's clean energy portfolio. NE is currently supporting RD&D of three fuel cycles: once-through, modified open, and closed. For the current fleet of nuclear reactors, a once-through or "open" nuclear fuel cycle is employed. Used fuel from commercial light water reactors (LWRs) in the United States is currently stored at the reactor sites. The Nuclear Waste Disposal Act of 1987 mandated that the disposition for this used fuel was direct disposal in a geologic repository, which would complete the once-through cycle. Although minimal separations technologies are required, this cycle entails the greatest need to manage SNF and HLW. A modified open cycle entails some separations and fuel processing, reusing components of the initial discharged fuel to utilize more energy from the same amount of nuclear material while reducing the quantity of long-lived radiotoxic elements. DOE is also evaluating prospects for a cost-effective sustainable closed fuel cycle that eliminates much of the HLW, reclaiming the energy from used fuel by recycling the long-lived actinide elements continually through a nuclear reactor. In a full recycle (closed cycle) system, only waste products require disposal, not used fuel. A closed cycle would require extensive use of separations technologies. The present NE approach to RD&D has been described in a recent report to Congress.[7]

NNSA also has interest in separations to support its mission areas of nuclear nonproliferation and safeguards and security and for ongoing weapons complex operations. The NE RD&D roadmap[8] acknowledges the importance of minimizing the risks of nuclear proliferation and terrorism and

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[4] U.S. Department of Energy, Office of Environmental Management. "Environmental Management Separations Technology Challenges," July 21, 2011.

[5] National Academy of Sciences. *Waste Forms Technology and Performance: Final Report*, Washington, DC: National Academies Press, 2011.

[6] ---. "Advice on the DOE's Cleanup Technology Roadmap," Washington, DC: National Academies Press, 2009.

[7] U.S. Department of Energy, Office of Nuclear Energy. *Nuclear Energy Research and Development Roadmap: Report to Congress*, April 2010.

[8] U.S. Department of Energy, Office of Nuclear Energy. *Nuclear Energy Research and Development Roadmap: Report to Congress*, April 2010.

commits to working with organizations such as the NNSA, the Department of State, and the NRC in an integrated approach to assessing and implementing domestic fuel cycle technology.

The Department supports the President's call to work with other nations to "build a new framework for civil nuclear cooperation…so that countries can access peaceful power without increasing the risks of proliferation."[9] Technical aspects of this challenge are described in a 2009 National Academy of Sciences (NAS) report on the growing international character of the nuclear fuel cycle.[10]

Recognizing the critical need for clean energy and, hence, for solutions to nuclear fuel cycle challenges, the Administration recently established the BRC to guide decisions regarding nuclear energy waste management. Coincident with this workshop, the BRC issued a draft report. The report supported continued nuclear fuel cycle RD&D and reiterated the need for U.S. leadership in international efforts to address safety, waste management, nonproliferation, and security concerns.[11] These draft observations are consistent with the planning and deliberations of this workshop.

The Department is also implementing Secretary Chu's vision of using science to provide technological breakthroughs to solve all of the United States' grand challenges. DOE offices, including NE and EM, aim to utilize high-risk–high-payoff R&D, seeking revolutionary and transformational breakthroughs to accomplish agency objectives and, in this case, address difficulties inherent in the nuclear fuel cycle.

The Nuclear Separations Technologies Workshop is both result and forerunner of these commitments. As noted above, several offices joined to engage expertise across not only government offices but also U.S. industry, national laboratories, and universities. Together, these participants helped identify high-level R&D needed for innovative solutions to some of the most complex, pressing energy challenges facing our country: improving energy production and the use of nuclear fuel; assuring that safeguards and security needs are fully met; and reducing the volume, toxicity, and lifetime of waste streams.

1.3 Breakout Sessions

The above background dictates a need for a fundamental understanding of the separations chemistry of the contaminants of concern. At the fundamental chemistry level, challenges run the gamut of nearly infinitely dilute solutions to molten inorganic salts. Engineering and scale-up pose equivalent complications. As some elements must ultimately be disposed even after

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[9] The White House. Remarks by President Barack Obama. Hradcany Square, Prague, Czech Republic, April 5, 2009.

[10] National Academy of Sciences, *Internationalization of the Nuclear Fuel Cycle: Goals, Strategies and Challenges*, Washington, DC: National Academies Press, 2009.

[11] Blue Ribbon Commission for America's Nuclear Future, *Draft Report to the Secretary of Energy*, July 29, 2011.

successful separations, managing waste is inherently tied to other fuel cycle elements and presents comparable challenges. Breakthroughs in separations chemistry and engineering can effect significant improvements across the board: costs, schedules, environmental protection, resource management, and safety and security.

Successfully utilizing separations techniques necessitates a holistic vision of the fuel cycle; put simply, the front and back ends must inform each other. Workshop session topics were selected to examine the natural progression of the fuel cycle, ranging from fundamental science studies (actinide chemistry and speciation, and molecule/material design) to coordination and industrial implementation of these technologies (scale-up), as well as interfaces between processes.

For each session, DOE designated a chair, co-chair, organizer and federal coordinator. With their input, DOE also invited panelists and helped ensure diverse participant representation from laboratories, universities, and institutes. The preparatory reading posted to the workshop website included sets of questions developed jointly by the chairs and panelists that later served to drive discussion during the sessions.

Once the breakouts were under way, panelists provided relevant presentations in their areas of expertise, followed by discussion of the subject matter’s relevance to the session’s overarching questions. Chairs also dedicated portions of the sessions to soliciting input to the two overarching workshop objectives. Participants first identified crosscutting areas of research and program interest, noting that carefully coordinating research activities in these identified areas would leverage limited federal resources to maximize benefits. Facilitating such synergistic efforts and tracking results could be crucial functions of a separations center of knowledge. To achieve the final workshop objective, breakout session participants examined this concept, discussing its viability, roles, benefits, and features. Section 4 of this report provides session findings that evaluate and define a center of knowledge and indicate areas of interest that cut across disciplines, DOE programs, and federal agencies.

2. PLENARY

2.1 Keynote Address

Deputy Secretary Daniel Poneman gave the keynote address, describing this workshop as a first step towards overcoming “stovepipes” within the DOE complex, improving communication and cooperation between the offices involved in nuclear separations.

Since President Eisenhower’s “Atoms for Peace” program, U.S. nuclear nonproliferation policy has undergone several periods of change. For example, significant changes in U.S. policy followed India’s 1974 explosion of a nuclear device, which had been developed with technology acquired in Canada and the United States. In April 2009, President Obama outlined a new framework for international cooperation to support peaceful uses of nuclear energy. Among other changes, the Administration shifted program emphasis from near-term deployment of commercial-scale reprocessing facilities in favor of further research. A critical R&D area is separations technology, which is essential for developing alternatives to PUREX and to HEU for production of medical isotopes.

Advanced separations technologies are also critical for disposing of weapons-related material, as well as material from the back end of the nuclear fuel cycle. The tremendous scale of environmental cleanup at Hanford and Savannah River pose particular challenges, necessitating development of next-generation waste processing technologies to appreciably reduce the cost of cleanup. EM is further challenged by $25 billion liability and technical issues with dispositioning actinides in tank waste.

Additional challenges for separations (and other crosscutting) programs are posed by DOE’s annual budgeting process, which is focused on individual offices. Multi-year funding can provide greater continuity with the certainty that a project is funded for the long term.

The goal of this workshop was to propose viable, cost-effective solutions for the back end of the nuclear fuel cycle. Mr. Poneman noted that doing so is an imperative for the planet, adding that we have not inherited the Earth from our parents but are borrowing it from our children.

A question was raised regarding restrictions nuclear supplier nations impose on handling used fuel that was irradiated in other countries. Mr. Poneman said that it is incumbent on each supplier country to develop waste disposal methodology with sufficient provisions to support processing a relatively small additional amount for countries with less developed capabilities. Commercialization of the fuel cycle’s back end will provide another major incentive for development “once the ice is effectively broken.”

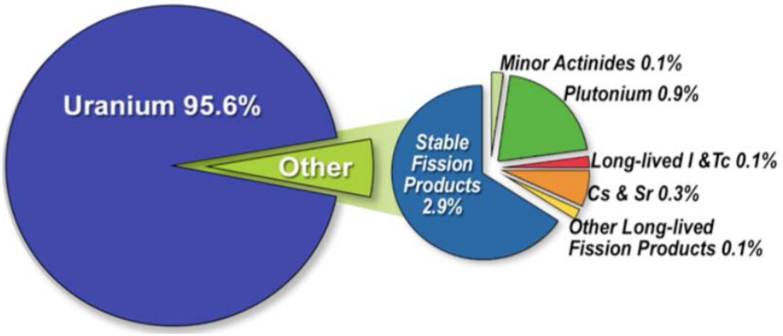
2.2 DOE Office Missions

2.2.1 Office of Nuclear Energy

Dr. Peter Lyons, Assistant Secretary, noted that as separations technologies are encountered throughout the nuclear fuel cycle, development of nuclear technology can greatly benefit from advancement in nuclear separations. He expected the workshop to influence U.S. separations research by identifying crosscutting technology needs across DOE and leveraging R&D to speed development.

The BRC's work has been heavily impacted by the events at Fukushima, highlighting in particular the need for interim storage facilities. The BRC draft report is intended to define a publicly acceptable national strategy for managing the back end of the nuclear fuel cycle that will guide DOE's overall fuel cycle R&D strategy. The report focuses on near-term improvements to LWR safety, including technologies for storage and disposal of SNF and HLW, and long-term efforts to develop "game-changing" fuel cycle technologies.

Figure 7. Isotopic distribution of used nuclear fuel



From Dr. Lyons' presentation: Figure can be found in the 2010 NE R&D Roadmap.

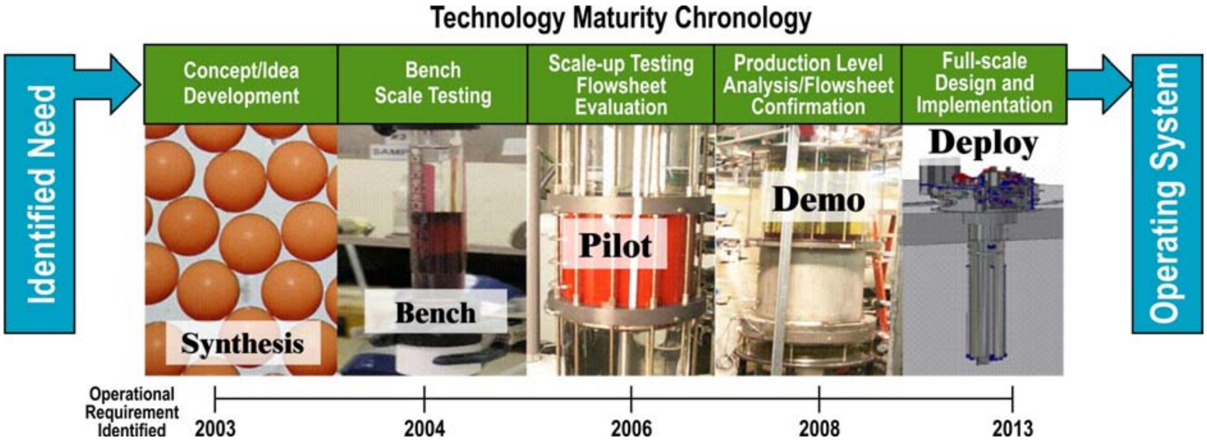
DOE's approach towards separations will rely heavily on modeling and simulation and small-scale experimentation, with systems engineering principles guiding technology selection. By the year 2013, NE expects to complete a systems engineering evaluation of three nuclear fuel cycle approaches: once-through cycle, modified open cycle, and full recycle. The most promising set of technologies will be researched, followed by engineering-scale experiments to enable deployment by mid-century. Grand challenges to overcome include development of interim storage facilities, fuel conditioning processes, and the full recycle methodology. The ultimate goal is to develop technologies that are superior alternatives to the PUREX process.

2.2.2 Office of Environmental Management

Chief Operations Officer Cynthia Anderson presented EM's mission: to safely transform the environmental legacy of the Cold War into useful assets by completing quality cleanup on schedule and within cost. At the start of the cleanup project in 1989, there were 110 legacy sites in 35 states occupying a total of 3,125 square miles. This year, the contaminated area will be only 350 square miles and, by 2015, only 90 square miles. An important lesson learned from

DOE's experience is to consider how to dispose of waste from the start of a project, e.g., tailings from mining and milling operations in countries developing uranium mines. Key challenges facing EM are 1) treatment of 90 million gallons and 600 million curies of tank waste remaining at three sites, 2) reduction of the lifecycle costs and legacy footprint, and 3) disposition of the remaining 52,000 cubic meters of transuranic waste.

Figure 8. Scale-up progression from R&D to deployment



EM faces a number of separations challenges, including technetium removal and immobilization, radionuclide removal from tanks, separation of non-radioactive compounds from HLW, mercury and chromium remediation, and sub-surface contamination. Addressing these challenges requires developing mature technologies from today's R&D programs within the next five to ten years. Ms. Anderson expected the workshop to help identify needed laboratory R&D, noting that a DOE roadmap for separations would help in carrying out workshop objectives.

2.2.3 National Nuclear Security Administration

Mr. Mark Whitney, Acting Principal Assistant Deputy Administrator for NNSA's Office of Defense Nuclear Nonproliferation (NA-20), described the three offices within NA-20 that deal with separations technologies: the Global Threat Reduction Initiative (GTRI), the Office of Nonproliferation Research and Development (R&D), and the Office of Nonproliferation and International Security (NIS). GTRI is responsible for reducing the risk of HEU in civil applications (medical isotopes and research reactors), while the Nonproliferation R&D office and NIS develop sensors to detect proliferation. NIS works closely with NE to carry out its mission of curbing the spread of sensitive fuel cycle technology and would both evaluate threats and implement safeguard measures for a separations facility. Factors to consider in developing safeguards for this facility include the nature and volume of material streams. However, quantifying proliferation risk is challenging.

2.3 Nuclear Separations Program Overviews

2.3.1 Office of Nuclear Energy

Dr. Monica Regalbuto, Deputy Assistant Secretary for Fuel Cycle Technologies, identified the following challenges: accelerated worldwide deployment of reactor and fuel cycle facilities, continuing build-up of nuclear waste from both commercial reactors and DOE, and lack of a comprehensive waste management strategy. NE has learned a key lesson from U.S. separations history and is incorporating waste management into the development process, which was not done for decades after pioneering the development of PUREX separations.

NE is working towards an integrated, science-based approach that will address the entire fuel cycle, optimized through systems analysis and engineering. Criteria are being developed to address waste management, resources, proliferation, safety, security, economics, and the environment. Improved management of SNF is the near-term goal, while better resource utilization is being pursued for the long term. NE seeks partnerships with other agencies and the international community to develop and down select fuel cycle alternatives.

2.3.2 Office of Environmental Management

Dr. Mary Neu, Chief Scientist for EM, described the centrality of separations to nuclear areas, including EM’s mission. Cleaning up the legacy of the Manhattan project, the cold war nuclear build up, and nuclear research to the 1980s involves separations and partitioning. Restoring sites and processing enormous amounts of materials and waste can be more effectively completed by innovation and developing new technologies. EM has successes that used the technology development pipeline to provide separations solutions, from fundamental research begun in SC through applied research and technology concepts in EM, and technology maturation at sites in partnership with national laboratories and federal contractors. EM’s remaining portfolio is technologically demanding. Separations and partitioning advances are needed, for example, in the following: technetium in waste, groundwater, and soil; non-radioactive species in HLW; and mercury in groundwater and soil. EM sees multi-office and agency partnership opportunities to meet crosscutting research needs, including stabilization, reuse and disposition of nuclear materials, under effective safeguards and security measures and in a manner that minimizes waste. Dr. Neu states that the desired outcomes of this workshop were 1) to identify applied research for further development into useful technology and 2) to provide the foundations of a DOE separations roadmap.

2.3.3 National Nuclear Security Administration

Dr. Marc Humphrey, Physical Scientist for the Office of Nonproliferation and International Security, identified two hypothetical proliferation paths: 1) diversion, in which a host state removes small amounts of material over time, and 2) facility misuse, in which a host state modifies a declared facility (either clandestinely or overtly after abrogating treaties) to produce separated plutonium. Challenges are present in protective actions: material accountancy, process

Figure 9. H-Canyon Separations Facility at Savannah River

monitoring, surveillance to prevent tampering, and verification/detection of clandestine misuse. Advanced technologies are being developed for accurate accounting of plutonium and transuranics in SNF and reprocessing plant streams. Development of vastly improved separations technologies requires corresponding improvements in measurement capabilities. Electrochemical separations (non-aqueous methods) requires an entirely different safeguards approach, as those for traditional aqueous methods are not applicable to pyroprocessing. A feasibility study is under way to use H-Canyon at Savannah River, the only operational industrial-scale separations facility in the United States, as a test bed for emerging safeguards technologies. Dr. Humphrey stressed that since any separations processes will ultimately need to be under safeguards, new processes should be developed with safeguards considerations in mind.

2.4 Closing Remarks

In closing, Dr. Regalbuto noted that limited resources require cooperation between the agencies. Workshop results, as documented in this report, should serve as a catalyst for future funding, as the workshop sends a strong message advocating for separations technology. Moving forward requires articulating a plan for the future, developing a budget, identifying key problems, and formulating a plan to address those problems. She challenged participants to think beyond their own organizations in developing these next steps.

Dr. Steven Schneider of EM reiterated Dr. Poneman’s charge to break down internal DOE stovepipes. By working together, investments can be effectively leveraged towards a common separations program goal. This workshop set DOE on the right track and achieved the desired outcomes.

3. BREAKOUT SESSIONS

3.1 Chemistry and Speciation of the Actinides and Key Fission Products (Cs, Tc, I)

CHAIR: **Wolfgang Runde**, Los Alamos National Laboratory
CO-CHAIR: **Ken Czerwinski**, University of Nevada, Las Vegas
FEDERAL COORDINATOR: **Jim Bresee**, Office of Nuclear Energy
ORGANIZER: **Al Sattelberger**, Argonne National Laboratory

3.1.1 Background Information

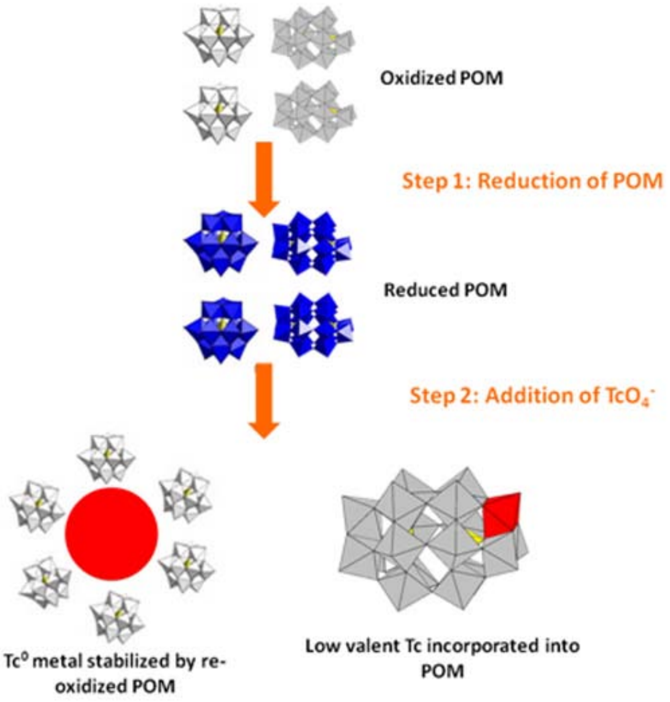
Early efforts at separating plutonium and other actinides from irradiated nuclear fuel focused on acidic conditions for the fuel's dissolution and the recovery of uranium and plutonium. PUREX uses nitric acid and separates radionuclides by exploiting the differences in the actinide and FP chemistries without detailed knowledge of their speciation. Although significant improvements in process efficiency, safety, and cost reduction have been achieved, a detailed understanding of actinide and FP chemistry and speciation has not been fully integrated. New separations processes have been developed using ion exchange, precipitations, and solvent extraction to separate radionuclides under high-pH, high-ionic-strength conditions.

Large-scale separations of plutonium from irradiated nuclear fuel have left behind enormous volumes of legacy wastes; Hanford and Savannah River contain the majority of DOE tank waste inventory with over 90 million gallons of highly alkaline supernates, saltcake, and precipitated solids. A large number of inorganic and organic constituents combine to form a high volume of waste with diverse radioactive elements, high radiation fields, and complex chemistry, posing significant cleanup challenges. Past waste management policies are unacceptable by modern standards, with leakage releasing waste to the environment at both Hanford and Savannah River. Speciation under environmental conditions, with lower concentrations and near-neutral pH conditions, occurs mainly via ion exchange or sorption onto natural surfaces or by precipitation—noticeably different from aqueous-based fuel separations processes.

Disposition of legacy waste requires incorporation into durable forms such as borosilicate glass. Understanding and controlling the radionuclide chemistry during these processes can produce efficiencies and cost reductions that would greatly enhance DOE's ability to remediate and close sites.

Throughout the different compositions—from acidic PUREX solutions to near-neutral natural environments to alkaline tank wastes—the valence state is the key property that governs the behavior, speciation, and coordination chemistry of radionuclides in solution, solid state, and the gas phase. The actinide elements uranium through americium can exist in multiple oxidation states that dictate their chemical behavior, a property that has been exploited for separation. Some FPs also exhibit significantly different behavior when changing oxidation states. Understanding and predicting the speciation, coordination, and chemistry of the actinides and FPs are paramount to fully utilizing existing separations and developing new processes. Advanced technologies need to take advantage of scientific discoveries made during the last fifty years and may include non-acidic aqueous processes, novel solvents (organic or ionic liquids), volatility, or designer ligands to target individual radionuclides or to enable group separations.

Figure 10. Strategy for reduction of pertechnetate, $^{99}TcO_{4^-}$, in An-polyoxometalate (POM)



3.1.2 Grand Challenges

Key to improving all separations efforts is accurately understanding the targeted radionuclide species’ oxidation states and coordination environments. Likewise, a detailed understanding of the speciation of the key radionuclides in waste forms is essential for building a convincing and defensible basis for their long-term immobilization. Three principal grand challenges have been identified:

- Molecular chemistry of actinides and FPs in media of inherent complexity
- Effects of radiation chemistry in separations processes
- Advanced analytical and computational tools

Molecular chemistry in complex media

While complexation of actinides and FPs in PUREX is limited to a few ligands, tank waste is inherently complex with a multitude of inorganic and organic ligands. Understanding these reactions and exploiting the resulting product species would be extremely valuable. The species found in tank wastes have not been extensively investigated and would be expected to be quite different from those in near-neutral or acidic conditions. Thermodynamic properties are not available for elevated temperatures and complex salt mixtures, and high concentrations of non-radioactive metal cations (aluminum, sodium) can alter composition and stability, leading to poor predictive capabilities.

Effects of radiation chemistry

An intense radiation field can profoundly alter speciation and chemistry of solutions and solid phases by attacking chemical bonds, degrading molecules and forming new species. The ability to accurately predict speciation requires a detailed understanding of such radiation-induced reactions as metal ion reduction, decomposition of solvents and organic ligands, radiolysis in aqueous systems, and alteration of solid phases.

Advanced analytical and computational tools

Present models cannot accurately predict the speciation of radionuclides in highly non-ideal systems such as high-level nuclear waste tanks or the multiphase systems present in solvent extraction. The imprecision causes significant problems for the treatment and partitioning of wastes into high- and low-activity waste streams. Access to advanced speciation tools is vital to the scientific communities working with radioactive materials. DOE synchrotron radiation light source user facilities have revolutionized the speciation of radioactive materials and have become an essential investigational tool. However, access to experimental time and expert infrastructure is insufficient.

It should also be understood that the complex interactions implicit in nuclear fuels processing and waste management must be broadly considered: at the molecular and supramolecular levels and from static (limits of thermodynamic stability) and dynamic (rates and mechanisms) perspectives. A broad array of analytical methods must be available for application to address these complex interactions. Because many of the species of concern are radioactive, facilities with key functions (e.g., nuclear magnetic resonance or mass spectrometry) must be readily accessible in locations suited to their applications. The Atalante facility at Marcoule, France, provides an example whose design could be considered in the context of advanced analytical chemistry.

Advanced analytical and spectroscopic methods have enabled analysis of speciation on a molecular scale. X-ray-related spectroscopic methods, for example, have directly revealed the coordination environments of actinide complexes, while advances in x-ray scattering techniques probe the dimensions of colloidal species in solution. Development of new analytical technologies is critical to detect, speciate and monitor actinides and FPs in such extreme environments as nuclear fuel and waste streams.

3.1.3 Proposed Solutions

Molecular chemistry of actinides and FPs in media of inherent complexity: Transition from binary mixtures to complex multi-component systems

There is a critical need to comprehend the nature and properties of actinide and FP species in extreme environments—high radiation, concentrated salt mixtures, extremes of pH, multi-radionuclide and multi-ligand systems—and to be able to predict behavior of these species. Chemical properties such as oxidation states and coordination environments can be adjusted to optimize partitioning and separation from multi-radionuclide systems. Solvation and inner-sphere complexation can be tuned to design organic molecules that target specific radionuclides. Similarly, understanding the structural factors of ion exchange materials that lead to site specificity will guide the production of new materials with increased selectivity. The open literature provides thermodynamic data of actinides and FPs in complex mixtures; evaluating these data will help identify additional needs for experimental studies and model development in concentrated electrolytes.

Understanding actinide and FP chemistry will impact a variety of challenges that both EM and NE are facing:

- How can actinides be monitored during processing in complex mixtures? (NE)
- Why does ^{237}Np not partition in solvent extraction steps as predicted in UREX+? (NE)
- How can technetium volatilization be minimized, prevented, or otherwise exploited? (EM, NE)
- What are the technetium species in Hanford tank wastes, and how can they be partitioned in-tank to minimize volatilization of technetium during vitrification in waste treatment plants? (EM)

Effect of radiation chemistry on speciation and separation efficiency

Understanding radiolysis' fundamental effects on solvent, ligands and other separations molecules will enable development of advanced models of radiation resistance, decomposition, and the formation of radicals to predict process performance. Radiolysis in highly complex mixtures must be understood to enable the design of radiation-resistant, selective molecules to achieve tailored separations. Isotopes with different half-lives and radiation fields must be available to enable radiation studies. Finally, it is essential to train the next generation of experts in radiation chemistry and regain U.S. expertise in this field.

Advanced analytical tools to meet the challenge of measurement and detection

Advanced tools are needed to speciate actinides and FPs in extreme systems, ranging from low-concentration contaminants to complex environments at elevated temperatures. Direct determination of speciation at picomolar (pM) concentrations is needed, along with advanced capabilities to determine the speciation of radionuclides in high-radioactive matrices at moderate concentrations (mM to µM) in the presence of closely related chemical elements. These new tools can also be applied to the direct, real-time measurement of radionuclide concentration and speciation for process control and nonproliferation monitoring.

Expanded synchrotron radiation capability is essential, along with nuclear scientists to provide front-line user support and develop new methodologies and techniques. Broader use and application of advanced spectroscopic tools could be fostered by transitioning speciation tools from rare, large facilities (light sources, neutron sources) to laboratory-based devices.

Radiological facilities equipped with more conventional analytical measurement devices must also be maintained.

Development of rapid throughput combinatorial methods would meaningfully assist in evaluation of actinide and FP speciation under a range of conditions.

3.2 Design of Molecules and Materials with Selective Separation Properties

CHAIR AND ORGANIZER:	**Bruce Moyer**, Oak Ridge National Laboratory
CO-CHAIR:	**Kenneth Nash**, Washington State University
FEDERAL COORDINATOR:	**Stephen Kung**, Office of Nuclear Energy

3.2.1 Background Information

Advanced processing of irradiated nuclear fuels will require a new stream of separation agents that enable solutions to a variety of technical problems that stand in the way of maximizing the safety, security, reliability, and performance of nuclear technologies (from electricity production to weapons stockpiles to Navy nuclear propulsion), while at the same time reducing the possibility of nuclear terrorism. Managing radioactive waste and cleaning up environmental contamination pose significant obstacles to the expanded application of nuclear power, leaving significant opportunity for expanded R&D and implementation and demonstration efforts. Advanced processing of irradiated nuclear fuels will require a new stream of separation agents that enable solutions to these diverse challenges while at the same time reducing the possibility of nuclear terrorism.

There is a substantial need for new molecules and materials in nuclear separations technologies. A variety of methodologies for radionuclide separations in select applications have been developed over the course of the last century. More than 50 years of research and process experience have produced robust and familiar hydrometallurgical processes such as AMEX (AMine EXtraction) for uranium extraction from ore leach liquors using simple fatty amines and PUREX for aqueous reprocessing of irradiated uranium and SNF using tributylphosphate (TBP). However, when separations goals move beyond recycling uranium and plutonium, new molecules and materials to capture and detect target species must be developed. A new generation of materials and molecules will offer acceptable and cost-effective technical solutions for the wide range of separations needs in both the nuclear fuel cycle and the clean-up of legacy sites.

In finding alternative methods or in moving beyond recycling uranium and plutonium, new molecules and materials to capture and detect target species must be developed. New applications and increasing demand for selective separations drives a new generation of research—a new generation of materials and molecules—that will offer acceptable and cost-effective technical solutions for the wide range of separations needs in both the nuclear fuel cycle and the cleanup of legacy sites.

Advanced processes will target the recovery of actinides individually or as a group and will reinvent the disposition and disposal of currently problematic fission products like ^{135,137}Cs, ^{90}Sr, ^{99}Tc, ^{129}I, noble gases (Xe and Kr) and the lanthanides. For example, new separation processes will allow species such as the minor actinides to be fabricated into targets and recycled to a reactor and the lanthanides to be dispositioned. Isolation and transmutation of actinide elements significantly reduces the overall hazards of the remaining material.

3.2.2 Grand Challenges (including identified capability gaps)

Confounding advances and improvements are a variety of technical challenges that will require innovative solutions (summarized in Section 3.2.3). Several significant challenges are summarized below. Solving these, among other, issues will enable the development of new separations technologies applicable to a wider range of nuclear fuel cycle and waste management applications.

Molecular modeling and simulation and other prediction approaches: Realize the vision of molecular-designed separations processes

The ability to predict chemical and physical parameters as a function of composition and operating conditions has the potential to dramatically decrease development costs for new separations systems, while also optimizing system performance and reducing technical risk. As such, a grand challenge is to develop high-throughput screening systems that can predict the chemical and physical selectivity characteristics of materials or molecules in order to efficiently identify and rank highly selective molecules/materials for use in targeted separations or detection schemes. Computational tools must evolve to draw together molecule generation capabilities on computers, scoring algorithms, code development, and experimental data. Significantly improved modeling and simulation capabilities will enable more efficient molecular design and optimal property prediction and will streamline and shorten the R&D timeline across the basic discovery, development, and implementation phases of new separations applications.

Improvements need to be made in scoring or ranking candidate molecules/materials with better methods, including using molecular modeling to understand binding affinities, selectivities, and macroscopic properties such as the physical properties of the phases (e.g., viscosity, heat capacity, vapor pressure) and the distribution of species between phases. Understanding the molecular dynamic processes of separation, including solvation at the quantum level and transport processes at interfaces, will also be required to make possible the deliberate design of processes using separating agents with desired chemical and physical properties. It is important that modeling progress in connection with synthesis and experimental characterization studies, enabling validation of both computational methodologies and performance of ideal compounds and materials.

Actinide-lanthanide separation: Develop efficient transmutation processes to achieve significant reduction in long-term radiotoxicity of fission residues

The three options for managing byproduct wastes of nuclear fission (open, modified open, and closed fuel cycles) offer very different time scales for geologic isolation of the radiotoxic byproducts and for composition of the disposal package. The closed fuel cycle option seeks primarily to minimize the potential impact of long-term radiotoxicity through transmutation of minor actinides in fast reactors. This option would offer advantages versus subnational threats if the fissile material is sufficiently diluted. The breakout session panel primarily addressed separations to support actinide burning of long-lived radionuclides. However, advanced actinide–lanthanide separations may also enable separate disposal of long-lived radionuclides (minor actinides, americium, curium, neptunium) by borehole or other techniques while creating a closed fuel cycle without pure plutonium. (It should be noted that the BRC draft report—which was issued the day after this workshop took place—included recommendations relevant to actinide–lanthanide separations.[12])

This “ultimate” (transmutation) solution to transuranic management is most efficiently accomplished in the absence of lanthanides. Decades of research on this subject have produced several wet and dry options for accomplishing this separation, but no clear technology that is considered ready for industrial-scale application. Separating the minor actinides from the lanthanides involves some of the most difficult challenges in separation science[13]: chemical similarity of americium/curium to FP lanthanides; high specific activity of americium, curium and select lanthanides; high neutron capture cross sections of several important lanthanides that interfere with actinide transmutation efficiency. It has been established that this group separation is most efficiently accomplished through the application of ligand donor systems containing N- or S-donor chelating agents or other soft donor anions (Cl^-, SCN^-). A decade-long ligand design effort conducted largely in Europe has produced new extractants through multiple investigator studies involving most of the European Community. In the United States, this separation has been addressed primarily through characterization and modification of the TALSPEAK process, in which the actinide-selective soft donor reagent is water-soluble.

As this separation has not been resolved, the system is a natural target for focus in the computationally linked ligand design effort. This system would also be significantly assisted by development of new actinide speciation tools described in the speciation breakout panel section of this report (see Appendix A). Another potential ligand design option for actinide–lanthanide separations would be to develop reagents that promote creation of a master blend of plutonium, uranium, and possibly other radionuclides for recycling plutonium back into reactors. A separations agent that could be used to create a multi-actinide transmutation target while

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[12] BRC. *Draft Report to the Secretary of Energy*. July 29, 2011.

[13] D. R. Peterman, et al. “Separation of Minor Actinides from Lanthanides by Dithiophosphinic Acid Extractants,” Report No. INL/CON-07-13474. Idaho Falls, ID: Idaho National Laboratory, September 2008.

rejecting lanthanides and other FPs could provide advantages versus subnational threats while reducing associated costs.

Such advanced separations could open pathways to two waste management options. The process could provide the feed to fuel fabrication plants to efficiently recycle and transmute transuranic isotopes, thereby reducing the proportion of long-lived radioactive isotopes, thus reducing the toxicity, that fission residues contain. Alternatively, selected transuranic radionuclides could be disposed of via advanced technologies such as borehole disposal,[14] which is several kilometers deeper than traditional repository disposal, providing potentially superior waste isolation capability. This advanced technology would impose restrictions on waste volumes and thus is best utilized only after targeted separations have isolated products for long-term disposal.

Interface properties: Understand the properties of interfacial systems to address interfacial problems that deter scale-up

In addition to the kinetics and selectivity problems often caused by the transfer of mass to or across phase boundaries during separations, interfacial problems contribute to the fouling phenomena that, despite the best attempts at design, can deter or halt progress in scaling up chemistry in process equipment. Understanding the unique transport, reactivity, and structural properties of fluid–solid interface and fluid–fluid interface systems will be required to overcome the challenges posed by interfacial phenomena. New experimental techniques and computational methods will enable quantitative, fully dynamic, and chemically realistic descriptions of the interactions of electrons, atoms, and molecules that give rise to macroscopic interfacial properties. This new information will encourage progress in a range of separations science applications such as solvent extraction, crystallization of mineral phases from supersaturated solutions, selective sorption of ions or gases on solid surfaces, selective transport of ionic and molecular species, and controlled formation of large molecular clusters, ions, and particles for separation.

Other major challenges

- *Environmentally mobile and volatile species: Overcome the challenge of capturing gaseous/volatile FPs using advanced separation agents and stable waste forms for long-term disposal.* The separation and containment of gaseous and volatile FP species (such as iodine, xenon, krypton and technetium isotopes) from fission residues represent a unique challenge. These species are highly mobile and prone to easy dispersal and may be difficult to contain owing to the natural dilution associated with the solid–liquid–gas phase transfer process, and complicated by the low- to non-reactive nature of select target species (e.g., noble gases).

  Developing suitable processes to capture and contain these species in stable waste forms will allow removal of isotopes of comparatively low specific activity, reduce long-term

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[14] BRC. *Draft Report to the Secretary of Energy*. July 29, 2011.

radiotoxicity of radioactive wastes, and enhance predictability of repository performance, thereby improving safety margins.

- *Fission products ^{90}Sr and ^{137}Cs: Develop new methods for separation of these species in a variety of types of media including tanks, soil, groundwater, and building materials.* Binding agents and solid-ion exchange materials have successfully been used in straightforward separations of the fission products ^{90}Sr and ^{137}Cs. However, the emergence of new problems (e.g., soil contamination in Japan) has revealed a need for more efficient methods that can be used in a range of media types.
- *Decorporation agents: Design new effective, selective, orally active, non-toxic, and cost-effective decorporation agents for removing internally deposited radionuclides.* Accidental or inadvertent intake of radionuclides from occupational/environmental exposure represents a significant health risk and, as such, is a clear area of emphasis for EM, NE, and NNSA. To date, only a few standard treatments are available for certain radionuclide intakes. New interventional therapies to mitigate the health effects of exposure to radionuclides are needed to increase the range and effectiveness of the United States' ability to protect humans from radiation effects associated with internally deposited transuranic radionuclides.

  Advanced therapies will address the current barrier of prolonged treatments, such as chelation therapy using pentetate calcium trisodium (CaDTPA), resulting in depletion of biological metal ions and other toxicity side effects, while at the same time achieving minimum levels of efficacy, including high levels in immediate post-contamination treatment.

3.2.3 Proposed Solutions

A range of separations issues drives discovery and development of new processes and materials. A number of proposed solutions to FP separations were put forward during the workshop. A summary of these solutions follows.

Inorganic ion-exchange materials: Develop inorganic ion-exchange materials with high selectivity that result in economical processing into durable waste forms.

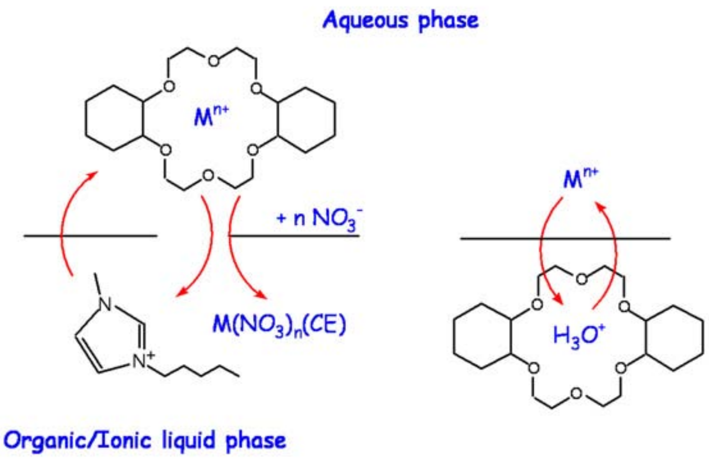
Inorganic crystalline oxide materials (e.g., zeolites, molecular sieves, clays) have chemical, mechanical, and thermal stability characteristics that support their widespread use in products to be used in environmental cleanup, commercial fuel reprocessing and detection/sensing systems for NNSA applications. Examples of target ions and molecules include cesium, strontium, volatile FPs ($^{129}I_2$, ^{85}Kr, $^{14}CO_2$, ^{3}H) and minor actinides. Understanding structure–property relationships in nanoporous materials that are selective for certain ions and molecules will enable development of materials that have high selectivity with high capacity. Such materials would likely also have high repository performance (i.e., durability) as waste forms (e.g., natural mineral analogs).

Inorganic membrane materials: Design a high-flux–high-selectivity membrane for separation of radiological ions from aqueous ion mixtures.

New technologies with high flux and high selectivity for ion separations in aqueous solutions will allow cost-effective separation of radiological ions from ion mixtures in commercial processes. Research on inorganic zeolite and/or clay membranes may yield efficient and improved membranes with ion selectivity in water with a wide range of salt concentrations that also have good thermal and mechanical stability, chemical inertness, and shape tunability—characteristics that are highly desirable for long-term separations applications.

Polymer-supported complexants: Design and synthesize ion-selective polymers that can be applied in highly dilute metal ion separations applications.

Figure 11. Metal ion extraction by ionic liquids



Achieving targeted separation of actinides and rare earths in large scale or highly dilute solutions requires ion-selective agents and effective platforms to deploy them. Polymer-supported metal ion complexants offer a potential solution to this problem. Ion-selective ligands are bound onto polymer supports; these ion-exchange resins—cross-linked polymer networks—are insoluble during remediation. After contact with the ion-containing solution, the resin—now selectively loaded with metal ions—is separated by filtration. Once loaded, it is highly desirable that the polymer be easily stripped of its metal ions using an aqueous-based eluent. This characteristic would ensure that the polymer-supported complexant is regenerable, re-usable, and environmentally compatible.

To design materials with rapid loading rates that meet DOE needs for targeted separations in select environments, new ligands and platforms to deploy the final polymer must be identified. The ligands must be easy to prepare; using diphosphonic acids as ion-selective ligands should be explored. New platforms (such as devising novel methods of functionalizing polypropylene) must not alter the binding of the target species.

Neoteric media: Develop extractants that do not display decreased utility in large-scale aqueous two-phase system separations processes.

There has been growing recent interest in using separations processes exhibiting both high efficiency and selectivity *and* minimal environmental impact—a combination of characteristics not readily obtained with traditional extraction systems, which are frequently characterized by the use of toxic, volatile, or flammable diluents. Neoteric solvents, specifically supercritical fluids such as SC-CO_2, and ionic liquids offer a non-traditional approach to actinide FP separations.

In order to be viable at a large scale, these solvents must achieve adequate solubility of extractants and extracted metal complexes, while at same time maintaining reasonable process characteristics (e.g., temperatures or pressures). Developing novel extractants with attractive extraction efficiencies and manageable system complexities will require understanding 1) the solubilization mechanism of metals into supercritical fluids, 2) the behavior and performance of ionic liquids as separations media, and 3) interactions between extractants and surfaces.

Decorporation agents: Perform research to understand metal ion transport in biological systems and use knowledge to improve design and selection of decorporation agents with high selectivity for the species of interest and high stability under biological conditions.

Molecules that typically survive in biological systems are extremely complex, as are the systems in which they operate. Therefore, a more complete understanding of mechanisms of metal ion transport phenomena in biological systems will be required to improve the design of desirable and successful decorporation agents. Areas of study comprise quantification of binding affinities and selectivities, behavior and stability of metal ion radionuclides in living organisms—including absorption rates, solubility in biological fluids, and transport by blood to organs—and other characteristics of potential chelation agents (metabolites of such agents). The information gained from these studies will enable more accurate prediction of agent toxicity and design of successful decorporation agents.

3.3 Scale-up of Separation Processes from Bench-Top to Plant

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3.3.1 Background Information

NE, EM, and NNSA face a variety of scale-up issues as they advance separations technology from the laboratory “bench-top” to plant scale in order to achieve their mission goals. Conceptually, scale-up is relatively simple: engineering principles are applied to a chemical or physical process to increase its throughput to achieve a desired plant capacity. However, these organizations deal with very complex chemical matrices and physical processes that are not all yet fully understood. Further, new technologies coupled with existing technologies may result in unexpected behaviors in the interaction from one process to the next.

As a result, scale-up presents itself as a very complex process that must be tailored to a specific situation, where no one standard approach fits every application. This section outlines the various challenges that the organizations face in regards to scale-up, as well as proposed solutions in order to move towards accomplishing their mission goals. Table 1 below provides an overview of separations technology scale-up needs by each of the three DOE organizations.

Table 1. Overview of Separations Technology Scale-up Interests

Technology	NE	NNSA	EM
Mixing	X		X
Melter	X		X
Solid / Liquid Separations	X	X	X
Off-Gas Separations	X	X	X
Extraction Processes	X	X	X
Liquid / Solid Transfer	X	X	X
Testing Sensors on Scaled System	X	X	X
Instrumentation, Analytical	X		X

3.3.2 Grand Challenges

Office of Nuclear Energy

NE's Fuel Cycle Research and Development (FCR&D) program focuses on science-based, engineering-driven research to better understand potential separation processes and identify transformational technologies that could potentially reduce the cost and complexity of advanced processing facilities. The FCR&D program is looking towards a long-term solution for recycling SNF, perhaps a decade or two in the future. As such, there is currently little effort focusing on equipment scale-up until some reference processes are identified, with the anticipation for greater future scale-up testing. Thus, the main issue is that the processes and equipment that will be used are somewhat unknown at this point. Nevertheless, as advanced separation technologies are developed, the scale-up of specific processes will be required. For example, there is a certain likelihood that future used-fuel separations

Separations Progression

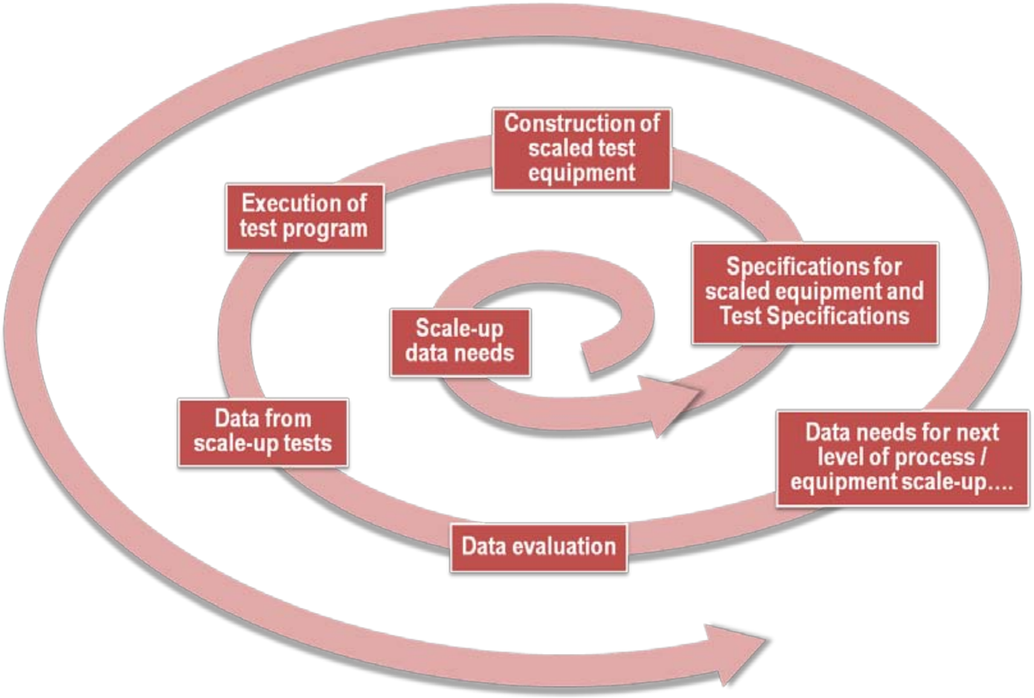
Process development
- Lab-scale tests of chemical/physical behavior
- Chemical models
- Equipment design and testing

Process demonstration
- Extended tests of flowsheets and instrumentation

Simulation and modeling
- Extraction and E-chem processes
- Unit operations
- Interfacial and molecular-level

Engineering-scale
- Equipment design and testing
- Process implementation
- Control systems

Figure 12. Scale-up process



facilities to process LWR fuel will incorporate solvent extraction processes to some degree, necessitating appropriate scale-up, regardless of whether pulsed columns, mixer-settlers, or centrifugal contactors are chosen. Further, prototypic equipment and processes with less industrial experience, such as voloxidation, will require specific equipment scale-up testing.

National Nuclear Security Administration

Rather than scale-up, the stockpile mission of NNSA may be more impacted by scale-down issues affecting component refurbishment and dispositioning tasks. Scale-down is reflected not only in downsizing existing equipment and facilities, but also in converting continuous processes to batch operation—and in the need to address potential changes in performance (particularly separations) that may result. Thus, the problem is essentially the same as that of scale-up, only solved in reverse. The need is still the ability to determine or predict the transferability of performance data between facilities of two specific scales.

In safeguarding any process development activities at engineering scale or above, avoiding nuclear criticality and protecting fissile material such as plutonium or HEU are very important considerations. Sensors, data acquisition and interpretation systems, and computer modeling are essential for material accountancy. In terms of nonproliferation and safeguards missions, key components include detection of fissile material processing activities, evaluation of unconventional (non-industrial) technologies and processing pathways, and characterization of materials generated by these alternative technologies. These include speciation of products, formation of byproducts, interaction of reagents and products with process and environmental contaminants, and transient behavior.

Office of Environmental Management

EM is focused on near-term implementation of separations technologies to support cleanup of their facilities, even though these technologies will be employed over subsequent decades. Many processes and equipment pieces require testing and scale-up, with some at several levels of scale-up. Further, as EM's facilities are first-of-a-kind, there is less opportunity for learning from previous plants, and each tends to be somewhat unique with different waste streams based on the specific site history. The scale-up needs are confounded by the wide variety of materials and physical and chemical properties that must be addressed. This makes designing processes and scaling them up complex because of the wide variability in the streams to be processed and the potential need to test more variations for feeds in the lab in order to simulate what is going to happen. Consequently, meeting scale-up needs will require a very ambitious program. For the present purpose, no attempt has been made to address the very large programmatic commitments, time involved, and budget requirements for meeting the scale-up needs.

3.3.3 Proposed Solutions

Office of Nuclear Energy

In dealing with the scale-up of solvent extraction processes, data relative to throughput, efficiency, and hydrodynamic behavior of the solutions will be required using engineering-scale equipment, at a minimum. Specific scale-up testing of prototypic equipment and processes could involve engineering-scale testing with simulants and/or actual solutions, as well as mockup testing of full-scale equipment. Implementing transformational technologies, significantly different from current processing technologies, will likely require a more rigorous effort to evaluate and understand scale-up issues. Ultimate implementation relies on an industry that leans toward conservatism, deploying evolutionary improvements to proven technologies. Industry's adoption of any new and innovative approach is only likely once a compelling business case can be made based on sound research, development, and successful scaled-up demonstrations.

National Nuclear Security Administration

To avoid nuclear criticality and protect fissile material, it is essential to incorporate, test, and establish adequacy of sensing equipment and computer data acquisition and interpretation steps in scaled-down operations. Aspects of material accountability are well established, but bringing new and perhaps radically different processes on-line may necessitate re-evaluating existing safeguards approaches, systems and equipment. Computer modeling of the systems, with respect to both individual process steps and integrated systems, is an essential and well-established approach to maintaining accountancy.

As for scale-down efforts for nuclear nonproliferation and safeguard missions, the chief consideration to be applied is the same as that for any chemical process: a reduced-scale process must produce results that are representative of the facility of concern. Therefore, issues to be considered in scaling include fidelity of materials transfer operations (e.g., hydraulics), chemical reaction kinetics (including mass transfer operations involving speciation), and use of materials (reagents, materials of construction, and likely contaminant sources) identical to those present in the facility of concern. Owing to the wide variety of chemistries and the range of possible equipment types involved, determination of scale is a function of both the specific unit operation and type of data desired.

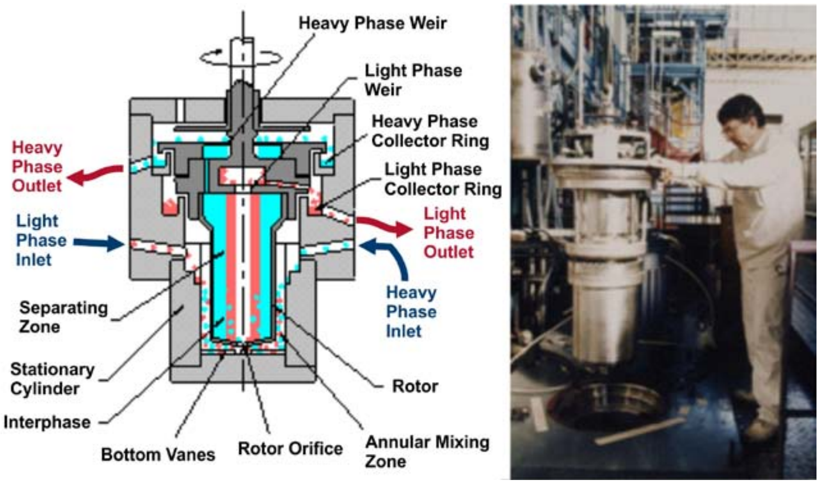
Office of Environmental Management

Several processes that require scale-up are under consideration for use in EM's cleanup effort: pulse jet mixing, next-generation melters, solids filtration, pretreatment plant processes, and transfer line plugging. Pulse jet mixing has been used elsewhere for mobilization wastes that include heavy sludges. In these sludges, avoiding selective sedimentation of suspended solids is of special importance because selective sedimentation of plutonium oxide could pose a criticality problem. Therefore, it is important to carry out tests at adequate scale on representative solids. Current melters could be replaced by next-generation melters of different types and/or sizes, requiring their testing and scale-up. Cross-flow filtration is proposed for the filtration of a very wide variety of solid suspensions because of its resistance to plugging and fouling. Testing on several scales on solids representative of the solids to be filtered will be required. In pretreatment plants, testing at several scales of the individual process steps and of the processes integrated to study process interactions will be required. Examples of processes include removal of aluminum and separations of actinides. Finally, methods of unplugging transfer lines between waste tanks, process tanks, and process equipment will need to be studied in prototypic systems at several scales using appropriate simulants to test for transfer characteristics and adequacy in representative pumping and piping equipment.

Recent Experience – International and Domestic

The breakout session participants discussed scale-up processes used for several foreign and domestic nuclear chemical processing facilities, along with insights from the Technology Readiness Assessment (TRA) process used to evaluate the maturity of technologies prior to deployment.

Figure 13. Centrifugal contactors qualified by CEA at La Hague



- CEA presented the following steps in their development process: basic and applied laboratory studies (scale 1/100000), laboratory-scale scientific feasibility (scale 1/10000), engineering-scale technical feasibility (scale 1/1000), pilot-scale demonstration (scale 1/100 to 1/10), and industrial-scale test (scale 1). Detailed discussion was provided of the nature of data that were collected at each stage, how they supported later development stages, and the nature of their impact on the design effort. The group introduced insights from recent CEA design, development and construction efforts, including installation of centrifugal contactors in the plutonium purification cycle at the LaHague plant. Not all steps would necessarily have to be used; for example, for adaptations to existing flowsheets, fewer steps would be utilized.

- An example of a project that was an adaptation of a previous flowsheet (PUREX) is the design, development and construction of THORP; during the entire design–build cycle, another processing plant was operating at industrial scale on the same site, so significant process knowledge could be transferred. The THORP development work was divided into "hot," "warm" and "cold" efforts. Hot testing was reserved for very small-scale efforts to maximize flexibility, enabling flowsheet changes. The principal "hot" rig was the highly active miniature pilot plant with processing throughput capability of 1 kg(HM)/day irradiated fuel (1/6250 compared to THORP). It confirmed the complete chemical flowsheets for several fuel types. For the full chemical separations flowsheet and controls, the majority of R&D experimental work was performed using miniature and engineering-scale pulse column equipment with various "warm" feeds (e.g., uranium, HNO_3, TBP/OK and/or selected components of neptunium, plutonium, technetium, non-radioactive FP simulants). This work—supported by hot testing but still uncertain for full scale—was carried out iteratively in conjunction with modeling studies. Mechanical components and subsystems were "cold" tested.
- Development of the caustic-side solvent extraction (CSSX) process started with basic laboratory-scale testing using simulants. This led to batch contact testing using actual solutions in the proposed salt flowsheet under extraction, scrub and stripping conditions. Radiolysis testing was then performed using a five-centimeter centrifugal contactor with cesium-spiked solution. The following complete flowsheet testing with actual waste used laboratory-scale (two-centimeter) centrifugal contactors. Performing the tests with laboratory-scale contactors minimized the amount of feed solutions needed and the amount of waste generated. These tests resulted in construction and operation of a pilot-scale separation process for operation of the CSSX process with actual tank waste solution; the scale of this pilot plant was determined by an actual mission need to process a certain type and volume of HLW. The breakout session group also discussed lessons learned from the use of a one-third-scale, non-radioactive melter system in the design and development effort for the Defense Waste Processing Facility (DWPF).
- DOE has adopted the TRA process to evaluate the maturity of technologies prior to deployment. The TRA process uses descriptions of development stages similar to those discussed by the CEA (above), in part, to provide definitions of the technology readiness levels (TRLs) that are determined/defined as part of TRAs. As part of the TRA process,

however, it is understood that different types of technologies may require adjustments to definitions and questions used in TRA evaluations of TRLs. EM has tailored and used the TRA process to evaluate nuclear waste processing technologies, and work has been performed previously to tailor the TRA process to NE's needs.

3.3.4 Overall Findings and Recommendations

The scale-up methods used in several foreign and domestic nuclear chemical processing facilities can serve as models in development of separations scale-up processes and are generally consistent with DOE's TRA process.

The following is a summary of common scale-up considerations applicable across the EM, NE and NNSA. The full report (Appendix C) provides more in-depth discussion.

- Common process improvements to explore in the near term include:
    - Solid–liquid separations processes
    - Off-gas systems
    - Evaporation systems
    - De-nitration systems
    - Melter/immobilization/stabilization systems
- Scale-up—whether of unit operations, integrated processes, engineering demonstrations, pilot plants, or full-scale demonstrations—must be considered very carefully with respect to scale-up goals. Goals may be of the following types:
    - Demonstrate unit operations on the appropriate scale, which can be a fraction of full scale or, when necessary, at full scale.
    - Demonstrate that integrating a separation process' component parts can be functional and seamless.
    - Demonstrate that a scaled version of an engineering process is of an adequate size to meet not only the immediate process objective but also the goals of other programs that may rely on output from the process demonstration.
    - Establish the utility of simulants or surrogates to reproduce the desired characteristics of feeds to the process being investigated.[15]

Figure 14. Pilot-scale integration testing for CSSX flowsheet scale-up

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[15] ASTM International. Standard ASTM C1750 - 11 "Standard Guide for Simulant Development, Approval, Validation, and Documentation," West Conshohocken, PA.

  - Demonstrate appropriateness and efficacy of process monitoring and control instrumentation.
  - Demonstrate the validity of fissile materials accountancy instrumentation or other equipment related to recording, evaluating, and informing fissile material flow and handling irregularities.
  - Provide verification and needed improvement to computer models of the process.
- As the scale-up cycle progresses, ensure that the development team carefully considers specific scale-up goals that are reflected in design specifications for construction of test equipment at each step of the scale-up process.
- Provide for flexibility in the scaled-up process to study process upsets and off-normal events, as well as accommodating unexpected difficulties.
- Within the DOE complex exists a significant body of knowledge, expertise, and separations capabilities that must be preserved. An effort should be undertaken to define the appropriate functions of a possible center for separations knowledge, as well as inventorying the facilities that could be used to support separations scale-up over the next five to twenty years.
- Ancillary issues include the need for a broad-based, solid foundation to maintain and advance these issues in the United States.

3.4 Interface Issues between Separations and Waste Forms/Fuel Fabrication

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CO-CHAIR:	**Bob Sindelar**, Savannah River National Laboratory
FEDERAL COORDINATOR:	**Jim Marra**, Office of Environmental Management
ORGANIZER:	**Bill Wilmarth**, Savannah River National Laboratory

3.4.1 Background Information

Crucial to all nuclear fuel cycles—whether closed, open, or modified—are the interfaces of separations processes. In a closed nuclear fuel cycle, considerations regarding the need for waste forms involve radioactive wastes generated from the start of uranium mining through its conversion and enrichment, fuel fabrication and conditioning, as well as those wastes from post-separations waste streams associated with potential fuel recycling options. Fuel fabrication in a closed cycle considers purities of recycled uranium and the need to include burnable actinides either as an integral part of the fuel or as a separate target in a reactor core. A modified open fuel cycle would also require waste forms and disposal pathways for actinides and FPs removed during the minimal reprocessing (see Section 1.2 of this report for a brief discussion of the three fuel cycles under DOE-supported study). While the fuel cycle for nuclear power dominates separations R&D discussions, it is also important to plan for disposition of materials and wastes generated from other reactor cycles, such as the production of molybdenum-99 for medical uses.

Therefore, a holistic vision must be given to any nuclear fuel cycle to ensure that the selected alternatives for each of the major parts of the cycle would mesh with each other prior to their specification. This section presents a listing of the various challenges involved with addressing interfaces of separations to waste forms/fuel fabrication in the nuclear fuel cycle, as well as recommended solutions.

3.4.2 Grand Challenges

To identify transformational technology opportunities, fuel cycle components—fuel design, waste form specification, repository selection, etc.—should be considered comprehensively and with an eye towards the present U.S. reactor fleet and near-term additions to the fleet with advanced LWR designs. The following are specific challenges and capability gaps that need to be addressed when considering separations interfaces in the nuclear fuel cycle:

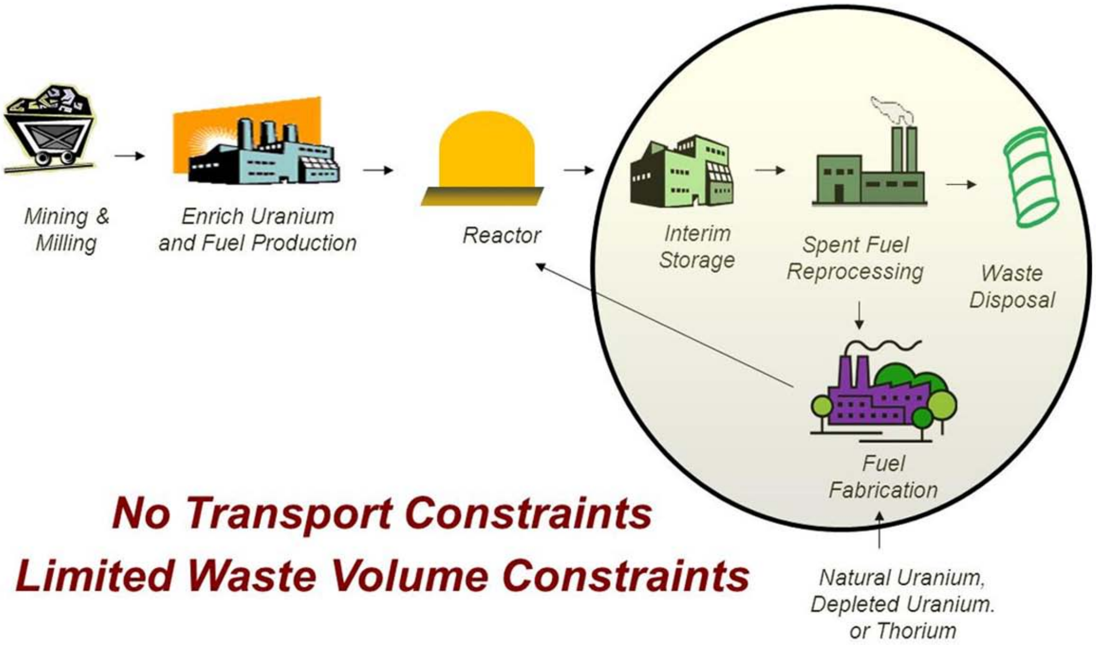
1. Establish a baseline fuel cycle(s) with well-defined meshed fuel cycle components.
2. Establish an approach to down select fuel cycle components.
3. Establish a prioritization for technology development for an overall “weak” component of the nuclear fuel cycle (e.g., waste form for a volatile species) and for further technology development among the leading candidates (e.g., “zeolite 1” versus “zeolite 2” for the volatile species waste form).
4. Develop technology with low programmatic risk, which necessitates that demonstration facilities be available for an RD&D approach to development and ultimate deployment.
5. Identify management strategies for used fuel storage to allow for radioactive decay, etc.
6. Strengthen the nuclear workforce in the United States.
7. Better define the separation/waste form and then waste form/repository interfaces.
8. Cultivate a broad base of support, as necessary and appropriate, for facilities in the nuclear fuel cycle (e.g., a separations facility).
9. Strengthen approaches for safeguarding and securing nuclear material, especially in separations systems.
10. Obtain NRC licenses for facilities for commercial nuclear fuel cycle components.

3.4.3 Proposed Solutions

With respect to interfaces between separations and fuel fabrication and used fuel management, the overarching conclusion is the need for a systems analysis approach to guide needed R&D. Such an approach must be cognizant of and inform essential national policy decisions regarding fuel cycle configurations to be developed (i.e., open, closed or modified), the role and timeframes for used fuel storage, and repository selection for final waste disposal. In regards to fuel cycle components, development of specific technologies should follow a prioritized approach that considers alternatives under the systems approach so as to enable selection of the "best" cycle(s) that are risk-informed, with explicit cost-benefit information. For example, development and implementation of a risk-informed waste classification system is central to defining radionuclide and materials segregation strategies, waste disposition pathways, and waste forms. The following presents proposed focused studies that specifically parallel the ten identified challenges described above (Section 3.4.2):

1. For a baseline fuel cycle, a reference set of plausible fuel cycle configurations should be established based on major driving criteria (economics, safety, environment, etc.). Included would be high-level definitions of timeframes and primary options for each stage of each selected fuel cycle, including reactor type, fuel form, storage of used fuel, extent of recycling, waste forms, and waste disposition environments.
2. For the down selection of fuel cycle components, systems models should be developed for each selected fuel cycle option that include initial estimates of mass and energy balances, considering both existing and to-be-generated SNF. All major primary and secondary waste streams should be identified. The potential benefits and risks of co-locating major backend components of the fuel cycle (i.e., storage, recycling, fuel fabrication, and disposal) should also be evaluated. These systems models should serve as the basis for identifying major knowledge gaps and what research will have the greatest impact on decision making. The systems evaluation should include development of implementation models that define options for private sector participation: roles and

Figure 15. Proposed combination of backend nuclear fuel cycle facilities



economic drivers. Caution must be exercised in the use of “bounding” assumptions and models to prevent today’s assumptions from becoming future constraints that are orders of magnitude too limiting compared to evolving science and engineering knowledge. The commercial nuclear industry, for example, is taking advantage of greatly improved analytical techniques by removing excess conservatism from safety analyses, thereby gaining hundreds of megawatts of additional generating capacity through power uprating of existing plants.

3. Prioritization in technology development should be driven by a process that is transparent to interested parties, with a defined set of published objectives, and informed by the outcomes of systems modeling. Recognizing timeframes for implementing potential fuel cycle options is important for distinguishing urgency in basic and applied research, as well as the demonstration of different components of fuel cycle options. A joint national laboratory, university, and industry advisory committee would ensure consideration of the full development pipeline, from basic research through full implementation. Research planning should also leverage international partnerships and investments.
4. Test beds, including cold and hot facilities from bench to engineering demonstration scale, will be essential to the success of separations R&D. Pathways and funding for access to hot experimentation by university researchers need to be established. Potentially available and needed facilities (e.g., glove boxes, hot cells, flexible engineering-scale demonstration facilities) should also be identified. Implementation of hot testing should be timely in the R&D cycle of the waste form (if implemented too early in the R&D process, negative data results may inhibit materials optimization or improvement). Early use of the facilities should consider NE, EM, and NNSA needs.
5. Regarding fuel storage management, further evaluation is needed for the potential role of used fuel conditioning prior to storage that includes separation of major components and constituents. This is a new concept in response to the potential for intermediate storage options prior to subsequent recycling or permanent disposal, which may be needed to maintain materials stability for 100–200 years and facilitate later (and potential unknown) management options.
6. In terms of strengthening the nuclear workforce, the existing NE university program should be expanded to include subject areas of nuclear chemical engineering, nuclear environmental engineering, nuclear chemistry, radiochemistry, actinide chemistry and materials sciences. These are essential components to the future of nuclear energy, yet they have almost been extinguished because of the lack of investment necessary to sustain the necessary academic programs, faculty engagement, and student interest. Nuclear energy must realize that it is competing with other exciting, high-tech fields for the best and brightest available minds. DOE and NRC should provide greater assistance in establishing (or re-establishing) nuclear engineering programs in U.S. universities.

7. When defining the waste form/repository interface, development and maturation is needed for new and alternative waste forms that can be used to manage the full range of recycling waste streams (liquid, solid, and gas) and are consistent with planned disposal environments.
8. Research on the social science and communications aspects of implementing future nuclear fuel cycles should be a component of the emerging R&D plan. Ultimately, public and policymaker understanding and engagement will be central to future decision making and the selected path forward.
9. Safeguards and verification needs, as well as monitoring and instrumentation needed for process control, require research that should evolve in concert with process development. (Note: There is a similarity of needs for remote observation with respect to environmental remediation.)
10. Part of the planning process should involve NRC’s evaluation of R&D needed to for licensing and oversight evaluations.

An overarching paradigm for prioritization of recommended programs and activities is that LWR technologies are near-term (vis-à-vis the advanced burner reactor). In addition to DOE and NNSA programs, common needs and program information sharing with international partners is recognized as critical to enable cost-effective, technically sound selection of nuclear fuel cycle components that serve U.S. energy needs.

4. CROSSCUTTING RESULTS

As noted in the introduction to this report, the workshop provided participants with two overarching programmatic objectives:

- Identify common needs and potential requirements in separations technology and opportunities for program partnerships.
- Evaluate the need for a DOE nuclear separations center of knowledge.

While Section 3 provided breakout session findings specific to their respective topics, this section focuses on crosscutting results that support these objectives.

4.1 Overarching Themes

During the broad range of technical discussions that occurred during the workshop, several themes were consistent across the various sessions. These themes were based on the participants' understanding of DOE separations needs as presented by the sponsoring program offices. Therefore, a logical place to begin the dialogue concerning overarching themes is a short summary of these needs.

4.1.1 Summary-Level Program Office Needs

The needs of the various program offices build on the same fundamental separation sciences; however, the offices have what can be described as differing mission timeframes and scales:

- To support their near-term mission of environmental cleanup, EM has large-scale and near-term needs, especially in the area of waste processing; there is the potential for longer-term efforts to support the area of groundwater and soils remediation.
- NE is looking towards a long-term solution to the recycle of SNF, demonstrating technology by the middle of the next decade with commercialization by mid-century. The challenge is that the specific processes that will be used may be fundamentally different from current technology.
- While NNSA has near-term and long-term needs and has taken actions to transform their Defense Program (NA-10) infrastructure to meet program needs, NNSA faces many challenges in terms of processes and equipment development. These challenges include making the best use of existing R&D infrastructure, converting continuous processes to batch processes, working with the smaller amounts of materials associated with forensics and monitoring functions, and evaluating sensors or remote monitoring tools for scenarios that might be encountered in undeclared or misused facilities.

Because of these differing foci, the offices may identify different priorities in the advancement of separations science, technologies and projects. The processes put in place to implement the insights gained through this workshop will need to be sensitive to these differing program foci. Roadmap strategies, for example, should be inclusive and flexible enough to account for alternate R&D pathways within a topic area. As discussed below, the approach to separations R&D must be comprehensive in scope, covering not only various program needs but also all phases and aspects of the fuel cycle.

Table 2. Target species for separations processes

Area of Interest*	Program				
	EM	NE	NNSA	DOD	SC
Actinides: U, Np, Pu, Am, Cm	X	X	X		
Volatiles: I, Tc, Cs, Xe, Kr, C, ^{3}H	X	X	X		
Human body contaminants: U, Pu, Ra, ^{90}Sr, ^{129,131}I, ^{137}Cs, ^{60}Co			X	X	X
Pyroprocessing/molten salt: U, TRUs, FPs	X	X	X		
^{99}Tc and ^{129}I as ubiquitous contaminants/risk drivers	X	X	X		
Mercury in groundwater, soil, building materials	X				X
Cr(VI) in groundwater	X				
^{137}Cs, ^{90}Sr in tanks, soil, groundwater, building materials, off-gas	X	X			
Non-rads Al, Na, S, Cr, HNO_3, Be, Zr, Pd	X	X			
^{60}Co in groundwater, equipment, RDD cleanup	X	X			

*Note: After the workshop, gallium was also identified during the report development as a possible area of interest.

4.1.2 Need for a Comprehensive Vision of and Approach to Separations RD&D—Informed by Modeling and Simulation

The sessions dedicated to actinide chemistry and molecule design both described a need to develop understandings that spanned the range from atomic-/molecular-scale insights to processing system improvements. For example, in discussing interfacial systems, it was noted that new techniques will enable quantitative, fully dynamic, and chemically realistic descriptions of the interactions of electrons, atoms, and molecules that give rise to the macroscopic interfacial properties. Additional dialogue centered on the need to understand the properties and behavior of materials and reagents in the extreme environments associated with SNF and HLW. The need for in-depth understanding of important phenomena, and the environments in which those phenomena occur, exists side by side with the need for systems-level models that describe the entire nuclear fuel cycle—from mining to placement in appropriate waste disposal facilities—in addition to the need for improved subsystem models of separation processes. A holistic vision must be given to any nuclear fuel cycle to ensure that selected alternatives work well in tandem prior to their implementation. These challenges will require development and continued refinement of modern modeling tools to simulate and analyze important problems.

4.1.3 Need for Ready Access to Appropriately Scaled and Capable Facilities

Workshop participants described the need for both larger- and smaller-scale facilities for RD&D—paralleling NNSA's programmatic needs for smaller-scale solutions and EM's larger-scale requirements. Two examples of smaller-scale needs are the transition of synchrotron radiation light sources from large facilities to laboratory-based devices and pathways for access to hot experimentation by university researchers. One breakout session group received detailed briefings on how staged development of separations processes—from bench scale to engineering scale—in the United Kingdom, France, and the United States had substantially contributed to the successful implementation of new separation processes over the past two decades. Consistent with the above discussion of a comprehensive vision and approach, this discussion of facility scale was complemented with dialogue regarding the need to match project or experimental goals and objectives to the design and specification of apparatus, regardless of size.

4.1.4 The Need for Contributions from a Broad Spectrum of Disciplines

Throughout the dialogue at the workshop, there was an understanding that the progress in separations science and technology would require the contribution of a broad spectrum of disciplines. Clearly traditional technical skill sets are crucial—from radiochemistry through nuclear chemical engineering—but the social sciences can also provide insights. On the topic of technical areas of expertise, concern was expressed regarding the continued challenges that exist in attracting and retaining quality people in the areas of nuclear chemistry, radiochemistry, nuclear materials science and nuclear chemical engineering. Several workshop participants voiced the importance of training the next generation of experts and strengthening the U.S. nuclear workforce, especially to develop the next generation of separations science discoveries. DOE is likely to achieve the best results working in concert with universities and national laboratories, with possible industry input. Consistent recognition of the need for environmentally acceptable options was also evident. For example, one session noted that polymer-supported metal ion complexants should be designed to be not only effective but also regenerable, reusable and environmentally acceptable. One session identified the need for a more complete understanding of metal ion transport phenomena in biological systems. Participants also noted that separations solutions needed to be developed with an eye towards compliance with NRC regulations. Such insights point to the need for a broad spectrum of experts assisting in the development and execution of separations RD&D.

4.2 Shared Disciplines/Areas of Interest

The following sections highlight RD&D disciplines and areas of interest that cut across the four breakout session topic areas. Although each topic area is characterized by its own barriers and requires its own solutions, commonalities extend across a variety of research efforts.

4.2.1 Computational Modeling and Simulation

Across the different areas of separations RD&D exists the common need for advances in computational modeling and simulation. For example, for scale-up of separation processes, these tools can help to design and optimize separations processes and equipment; elucidate scale-up issues; and provide information on product and waste stream volumes, radioactivity content, and nuclear criticality potential. On a more fundamental level, modeling can predict actinide and FP speciation, guide separations agent design, predict chemical and physical selectivity characteristics, and enable methods to efficiently identify and rank highly selective molecules/ materials for use in targeted separations or detection schemes. Sophisticated modeling and simulation methods make it possible to streamline and shorten the R&D timeline across the basic discovery, development and implementation scale-up phases of new separations applications.

4.2.2 Experimental Validation

Currently available predictive capabilities do not always agree well with actual behaviors in real-world settings. For example, the composition of tank wastes affects actinide oxidation state stability and solubility; in these environments, predictions may be less accurate or unreliable. Therefore, in addition to advances in computer models, appropriate experimental validation across a range of levels of applications is also needed. Appropriate facilities and easy access to such facilities will be required to gather the necessary data to support computer model code development, validation, and implementation.

4.2.3 Radiochemical Diversity

The diversity of radionuclides of potential concern complicates efforts to understand speciation, design separations agents, scale up processes, and understand interfaces between waste forms and the fuel cycle. Chemical elements may be closely related or may occur in disproportionate levels—e.g., small amounts of transuranic elements in the presence of a large excess of uranium. New tools will be needed to provide real-time measurement of radionuclide concentrations and speciation; and consideration of these diverse elements incorporated into separations process development and scale-up methods.

4.2.4 Challenging Environments

Actinides and FPs are found in a range of environmental conditions. These environments may be characterized by low concentrations of radionuclides, high or low ionic strengths, extreme temperatures, complex chemistries, large volumes, high radiation fields, etc., which complicate theory, experimental approaches, and model development—not to mention design and maintenance of RD&D facilities. To ensure that advances lead to a range of real-world applications, RD&D planning needs to provide appropriate attention to the challenges presented by environmental conditions.

4.2.5 National Policy, Regulatory Requirements and Other Considerations

Regulatory and national policy risks invariably affect the future success and impact of new technological advances. As an example, methods to prioritize new and further technology development among leading candidate materials or processes should be made with respect to the best available knowledge of planned disposal environments. To better plan and carry out new research, dedicated efforts should be made to understand the most plausible set of realities based on current and pending policies and major policy-driving criteria (e.g., economics, safety, environment).

4.2.6 Nonproliferation

A commonality across separations RD&D is the need to prioritize safeguards and security concerns and insights. For example, research on monitoring and instrumentation is needed not only for process control, criticality safety, and waste management, but also for material accountancy, safeguards, and remote detection needs. Research supporting safeguards and security concerns should be pursued in concert with that supporting process development and waste management.

4.3 Advantages of a Center of Knowledge for Nuclear Separations Technologies

The participants in this workshop were asked to identify the attributes that they deemed desirable in a center of knowledge for nuclear separations technology, if established. Their thoughts and comments can be broadly grouped as follows.

4.3.1 Definition of RD&D Needs

Participants identified several attributes of a potential center of knowledge that support the identification and further refinement of RD&D needs.

- **Information sharing system:** A virtual information system or platform will offer a range of information, help minimize duplicative efforts and support the definition of RD&D needs. Examples of knowledge that should be captured include:
    - *Information and data:* Open literature, formal reports and studies, non-classified government reports
    - *Demonstration projects and other experiential lessons learned:* Experience from demonstrations that resulted in critical advances in capabilities, such as those with value as test beds for future scale-up operations and those addressing training new personnel

  - *Knowledge management:* Capturing, retaining, and sharing past experience and existing expertise to ensure its availability for future generations
  - *International resources:* Links to other resources, including work done by international organizations (e.g., Actinet, Japan Atomic Energy Agency, IAEA)

- **Inventory of facilities to support separations scale-up:** Efforts should be made to identify promising facilities that can support implementation and demonstration of new scale-up processes over the next five to ten years. As the scale-up design process progresses for a given new process, identifying candidate facilities will streamline the design cycle.

- **Resources to build the workforce:** Building a workforce of qualified individuals, mainly PhDs and scientists, will require opportunities for research funding, access to the facilities and information a center could provide, and a communication structure that facilitates information sharing and profitable linkages between DOE lab centers, academia, and industrial partners. Sample capabilities of the center could include:
  - *Mentoring program:* Such a program could draw promising candidates into the field and compete for the brightest minds available.
  - *Training for process engineering, radiochemistry, nuclear chemical engineering, etc.:* Although such opportunities do exist at universities, they are difficult to find and often not well promoted. The expertise at the center could provide a platform for furthering such training.

4.3.2 Coordination and Integration of Separations RD&D

One strength of a center of knowledge will come from the coordination of activities, involvement of both industry and academia, and clear methods to evaluate and prioritize research opportunities. In addition, the center should preserve the knowledge, experience, and lessons learned during demonstrations and implementation processes. The participants summarized their desired attributes as follows:

> **System for prioritizing and evaluating separations technology R&D activities:** An efficient pooling of resources and expertise requires a clear system for prioritizing and evaluating R&D needs. This evaluation process will enable optimal synergy in research efforts for the strongest possible impact. The process must be detailed with a mechanism for application and buy-in across DOE programs and researchers.

4.3.3 Establishment of a Scientific User Facility for Separations RD&D

A number of comments addressed the need for facilities to perform RD&D on radiochemical and nuclear chemistry topics—a facility that could provide access to researchers from academia and potentially industry. While it is recognized that program funding constraints would limit development in this area, the ideas discussed are summarized below.

- **Improved/upgraded test bed facilities for validating approaches:** Appropriate facilities for handling radioactive materials and testing approaches could provide the experimental data required for validating results of computational modeling. A range of conditions (e.g., a wide range of concentrations, hot-cell facilities, etc.) will need to be tested; appropriate facilities will enable such testing and validation of advanced methods. Related activities include:
    - Coordinating access to facilities from the bench to engineering demonstration scale.
    - Identifying needed facilities and equipment (e.g., glove boxes, hot cells, flexible engineering-scale demonstration facilities).
- **Connection to the academic community:** Rapid advances have been made in such fields as molecular modeling, while the number of U.S. PhD graduates in relevant fields is increasingly limited. Therefore, the center would be most beneficial if it had a clear tie to the academic community.
- **A cadre of nuclear scientists closely associated with the center:** A select group of scientists with specific expertise needs to be available (i.e., associated with the center) to serve as domain scientists and provide front-line user support to aid in efforts around the world to develop new methodologies and techniques.

It should be noted that the last three attributes address a core problem. DOE is presently the primary customer of actinide and FP separations; thus, there is not the complement of university and industrial research normally found in other areas of science and technology (where there are large commercial applications). If DOE wishes to take advantage of university and industrial research capabilities, a new mechanism, such as a scientific user facility, is a method that has been used by the Department in the past. There are several models on which to build. Within DOE, NE has established a scientific user facility, centered at the Advanced Test Reactor, that focuses on research requiring reactor, post-irradiation examination or "beamline" (i.e., particle, synchrotron, x-ray radiation) facilities. Internationally, experience can be drawn from the Institute of Transuranic Research operated by the European Community.

It is envisioned that a scientific user facility for separations would support development of trained manpower and more fully utilize university and private resources by removing a major barrier: the paucity of laboratory facilities, especially glove boxes and hot cells—facilities with the capability to handle high contamination and high radiation environments. The national laboratories have such facilities, but these are dedicated to specific missions—including defense missions with restricted access. The experience is that such facilities do not provide the easy, assured access required to support university graduate programs or industry. It should also be understood that radiotracer studies represent a viable pathway to development of new materials and processes, enabling advances in this technology that are not hindered by the absence of "hot" facilities; such investigations are readily enabled in an academic environment with considerable economy and minimal penalty in information gained. The NNSA decision to identify "Centers of

Excellence" in plutonium and uranium to retain proper capability (including nuclear separations competence) as part of its nuclear weapons complex transformation should be examined for lessons learned.[16]

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[16] DOE/EIS-0236, National Nuclear Security Administration, Final Complex Transformation Supplemental Programmatic Environmental Impact Statement, Complex Transformation, Volume II, Chapters 5-15 and Appendices A-G, October 2008.

5. CONCLUSIONS AND NEXT STEPS

The July 2011 workshop was successful in establishing a foundation of cooperation between EM, NE and NNSA in nuclear separations technologies. Examples of common areas of programmatic cooperation include molecular design targeting specific material separation and stabilization, scale-up methods for the rapid deployment of technology with reduced risk, and improved understanding of nuclear separations approaches and their relationship with related waste form production.

The workshop also highlighted opportunities for improved technology maturation. SC may identify specific separations technologies, explored in the field of basic science, that may be ready for development in the applied programs of EM, NE, and NNSA. Better cross-program integration and communication will support improved technology “hand-off” between DOE offices.

Such interconnection could be facilitated through a nuclear separations center of knowledge, which workshop participants concurred was a candidate for DOE's portfolio of new research efforts, such as the Innovation Hubs. A center would provide a mechanism to integrate multiple phases of nuclear separations RD&D across DOE offices and address the boundaries between science, engineering, and technology development.

Next steps will build on the foundation established during the workshop to initiate these advances in integration and communication. Appropriate actions need to establish this cooperation in practice, and follow-on actions will optimize available resources and grow the programmatic relationships in a manner that accomplishes the greatest good in the shortest time. The path forward should initially emphasize high-probability activities that establish the organizational relationships. The established network can then mature in parallel with the scope and complexity of activities that advance nuclear separations technologies.

The progression of activities to initiate and develop this collaboration is broken into three phases: Startup, Growth, and Sustainable Program.

Startup Phase

Within the first month of the approval of this report, EM, NE, and NNSA will conduct a programmatic summit to:

- Identify specific initial scope for cooperation in FY 2012.
- Identify initial funding levels.
- Establish lead staff and national laboratory assignment of roles and responsibilities.

- Establish initial functions of a nuclear separations center of knowledge and a path forward for a possible national user facility.

Within three months, follow-on workshop(s) will be scheduled to explore additional areas or dive deeper into specific subjects identified during the July 2011 workshop. These areas may include:

- Near-term EM and NE interests concerning technetium and iodine recovery and stabilization.
- NE and NNSA interests concerning process instrumentation.
- Developing advanced modeling capabilities in common support of near-term and longer-term interests of EM, NE, NNSA, and SC.

This phase would also involve preliminary planning for a DOE separations roadmap that would discuss technical issues, programs, and collaborations in the areas of separations necessary to achieve the goals of DOE program offices. Specifically, the nuclear separations roadmap will:

- Establish the plans and strategies necessary to develop the cooperation initiated at this workshop into a sustainable collaboration between the sponsoring programs, including the estimated scope, schedule, and costs associated with the Growth and Sustainable Program phases.
- Support the coordinated DOE response to the Blue Ribbon Commission on America's Nuclear Future (BRC) recommendations, expected in January 2012, as they relate to nuclear separations technologies.
- Refine the concept of a nuclear separations center of knowledge that responds to DOE needs, improves program partnerships, and supports the effective use of available funding and resources.

Establishing a center of excellence for separations technology and an associated user facility for R&D purposes will require a detailed proposal and implementation plan. As the facility might be open to foreign researchers and cooperating foreign parties, the proposal/plan must ensure that the implementation approach will be consistent with and meet the requirements of all applicable U.S. nonproliferation-related policies, laws, treaties and agreements, and export control regulations.[17]

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[17] These include, *inter alia*, the Atomic Energy Act, United States Agreements for Cooperation in the Peaceful Uses of Atomic Energy (Section 123 agreements) with foreign State partners, applicable U.S. government export control laws and regulations (including DOE controls on the transfer of nuclear technology in 10 CFR 810), and the United States-IAEA Agreement on the Application of Safeguards in the United States (INFCIRC/288) (and the Additional Protocol).

Growth Phase

This phase will include confidence-building actions that begin in FY 2013 and continue for approximately five years (as determined by the roadmap) to expand the scope, increase the complexity, and maximize the impact on the applied programs of EM, NE, and NNSA. Growth Phase steps will:

- Determine the process to identify new scope (e.g., focused solicitation, proposal development, programmatic review).
- Initiate activities that support objectives as established in the DOE separations roadmap.
- Consider expanded or adjusted DOE staff and national laboratory roles and responsibilities.
- Consider evolving functions of a nuclear separations center of knowledge.

Sustainable Program Phase

The steps in this phase will depend upon the preceding actions taken to form and build the cross-program cooperation. Sustainable Program Phase activities will be tailored toward balancing the resources available with continued beneficial cooperation for the foreseeable future.

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Appendix A. Breakout Session Report: Chemistry and Speciation of the Actinides and Key Fission Products

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Introduction

Since the 1940s, plutonium (Pu) and other actinides and fission products (FPs) have been separated from irradiated nuclear fuel using a variety of methods including precipitation, solvent extraction, electrochemistry, and ion exchange. In early days of actinide science, research and technology development efforts focused on acidic conditions appropriate for the dissolution of irradiated nuclear fuels and the recovery of uranium and plutonium. The commonly used large-scale PUREX separations process dissolves used fuel in hot, concentrated nitric acid; separations of radionuclides are achieved by exploiting the differences in the chemistries of the actinides and FPs. Solvent extractions are utilized in the PUREX process without detailed knowledge of the speciation of actinides and FPs. Understanding chemistry at the molecular level within the process was not necessary to achieve target processing/production goals. Process difficulties and conditions that could result in process disruption, such as third phase formation, were overcome through engineering modifications, typically using an Edisonian—or trial and error—approach. Oxidation and reduction reactions control valence state, complexation, and solubility, and hence play a central role in the separations. Over time, incremental changes/modifications have led to significant improvements in process efficiency, safety, and cost reduction. However, a detailed understanding of actinide and FP chemistry and speciation has not been fully integrated to optimize and further improve separations.

The historic large-scale separations of plutonium from irradiated nuclear fuel have left behind enormous volumes of legacy wastes at several DOE sites. The underground tank farms at the Savannah River Site and at the Hanford Reservations contain the majority of the DOE tank waste inventory, with over 90 million gallons of highly alkaline waste stored as concentrated supernates, saltcake, and precipitated solids—referred to as sludges. Tank wastes are complex alkaline mixtures containing a large number of inorganic and organic constituents that can affect the chemistry and speciation of actinides and FPs in solution and in the precipitated solids. Cleanup of the tank waste inventory is a grand challenge because of the large volume, diversity of radioactive elements, high radiation fields, and complex chemistry of the wastes. The disposition strategy for the tank waste is to separate the major remaining radionuclides from the bulk of the waste and incorporate the separated nuclides into a durable waste form such as borosilicate glass. New separations processes have been developed using ion exchange, precipitations, and solvent extraction to separate radionuclides under high-pH, high-ionic-strength conditions.

Past waste management policies allowed for radioactive waste disposal practices that are unacceptable by modern standards. Leaks in the storage tanks released waste to the environment at both the Hanford Site and the Savannah River Site. The radionuclide and hazardous metal speciation under environmental conditions, with lower concentrations and near-neutral pH conditions, noticeably differs from those occurring under aqueous-based fuel separations and pretreatment of tank wastes. In the environment, separations of radioactive contaminants can occur naturally or be fostered by engineered barriers. Natural retention and separation of actinide and FP species occurs mainly via ion exchange or sorption onto natural surfaces or precipitation. Engineered barriers can be injected into soil and sediment fractures, relying on those principles for contaminant separation from the aquifers.

Disposition of the legacy DOE high-level waste (HLW), as well as residues from nuclear fuel separations, requires incorporation into durable waste forms such as borosilicate glass. The behavior of actinides and FPs during waste form processing (e.g., removal of water and high temperatures) will be different from that during pretreatment of tank waste and spent fuel processing. For example, vitrification of radioactive waste occurs at about 1200˚C, conditions where the speciation of actinides and FPs remains relatively unexplored. Understanding and controlling the radionuclide chemistry during these processes can produce efficiencies and cost reductions that would greatly benefit the DOE’s ability to remediate and close sites.

Despite the different compositions of waste and processing streams—from acidic PUREX solutions to near-neutral natural environments to alkaline tank wastes—some properties and reaction mechanisms are common drivers for the behavior of radionuclides. Separations processes rely on small differences in the chemical characteristics of radionuclide properties to achieve successful partitioning and separation. The key property that governs the behavior, speciation, and coordination chemistry of radionuclides in solution, solid state, and the gas phase is the valence state. In particular, the actinide elements uranium through americium can exist in multiple oxidation states, and their chemical behavior is dictated by the oxidation states and coordination environments around the metal ion. Trivalent and especially tetravalent actinides have markedly lower solubilities than the highly oxidized forms of the actinides in their hexavalent and particularly the pentavalent oxidation states. The different chemical behavior of actinides in their different oxidation states has been exploited for separations. As an example, the redox control of plutonium in the PUREX process accounts for the extraction of Pu(IV) into the organic phase and back extraction of Pu(III) into the aqueous phase.

Some FPs also exhibit significantly different behavior when changing oxidation states. As one of the most problematic FPs in Hanford tank waste, technetium (Tc) can be extremely soluble and mobile as TcO_4-, yet is insoluble as TcO_2; the volatile binary oxide Tc_2O_7 is generated under processing conditions which causes about 75 percent of technetium to escape retention in low-activity waste (LAW) glass which then must be captured in the off-gas. In their different oxidation states, the actinides and FPs demonstrate quite different coordination chemistries. While the actinides in their III, IV and VI oxidation states show a great affinity to complexation with hard donor ligands even at low pH, complexation of pentavalant actinides is less pronounced and requires higher pH or higher ligand concentration. The coordination of actinides can result in the precipitation of low-solubility phases, but can also lead to increasing solubility or the stabilization of actinides in solution. As an example, hydroxides of Pu(IV) have solubilities below 10^{-10} M, while the presence of carbonate, sulfate, or nitrate can significantly raise the soluble concentration by the formation of inner-sphere complexes. Understanding and predicting the speciation, coordination, and chemistry of the actinides and FPs are paramount to fully utilizing existing separations and developing new processes.

Separation and partitioning of actinides and FPs are central to a variety of technologies ranging from intentional separation of radionuclides in irradiated nuclear fuel and partitioning of targeted radionuclides in tank waste, to the natural or engineered retention of contaminants in sediments and mineral fractures. The speciation of actinides and FPs provides the scientific basis to any separation process and can be tuned to take full advantage of the chemical differences for best separation performance. Ion exchange, solvent extraction and precipitation are common separation processes in natural environments, and engineered technologies and the nature of solution and surface complexes and solid phases will determine separation efficiencies. There are great opportunities to improve the performances of currently used separations technologies and to develop the next generation of advanced separations technologies to meet future challenges. Advanced technologies need to take advantage of scientific discoveries during the last fifty years and may include non-acidic aqueous processes, novel solvents (organic or ionic liquids), volatility, or designer ligands to target individual radionuclides or to enable group separations.

1.0 Grand Challenges

Key to improving all separations efforts is the critical need to understand accurately the nature of the targeted radionuclide species. Despite the large differences in characteristics, the fundamental separations mechanisms rely on common principles that utilize the different chemical properties of the actinides and FPs. Whether the separation involves used nuclear fuel, tank waste, or environmental contamination, improving processes in a rational manner requires a detailed description of the oxidation states and coordination environments of the key radionuclides. Likewise, a detailed understanding of the speciation of the key radionuclides in waste forms is essential for building a convincing and defensible basis for their long-term immobilization.

Although the chemical behavior and speciation of actinides and FPs is determining the performance of any separations technology, three principal grand challenges have been identified:

- Molecular chemistry of actinides and FPs in media of inherent complexity
- Effect of radiation chemistry in separations processes
- Advanced analytical and computational tools

The chemistry of inherently complex process and waste streams must be understood to advance the current state of knowledge and technology. The fundamental chemical reactions in bulk (complexation, precipitation) or on surfaces (ion exchange, sorption) occur based on the preponderant chemical conditions. These reactions are dictated by temperature, solution characteristics, surface chemistry, radiation levels, and presence of ligands. Dissolved actinides and FPs can coordinate with ligands to form soluble or insoluble species during separation and in waste and process streams. While complexation of actinides and FPs in the acidic solutions of PUREX is limited to few ligands, tank waste is of inherent complexity with a multitude of inorganic and organic ligands present in the various waste types. Historically, the behavior and speciation of actinides in solution and solid phases has been developed with simplistic, well-characterized systems with a single actinide and one or two complexing ligands. The synergistic effects of multi-ligand, multi-actinide, alkaline systems of high ionic strength remain ambiguous. Understanding these reactions and exploiting the behavior of the resulting actinide and FP species would be extremely valuable for fully exploiting current separations and developing next-generation tunable, selective separations methods.

While complexes most important to the near-neutral conditions of natural settings have been reasonably well characterized, speciation of actinides and FPs relevant to the different steps of the PUREX process remains poorly understood. In addition, the species found in tank wastes have not been extensively investigated and would be expected to be quite different compared to those in near-neutral and acidic conditions. Under near-neutral conditions, the behavior of actinides is largely explained with binary species; the large concentrations of inorganic salts in tank wastes likely cause the actinides to coordinate with multiple ligands to form ternary complexes. Thermodynamic properties of actinides and FPs are available for binary complexes with very limited extension to elevated temperatures and complex salt mixtures. In addition, high concentrations of non-radioactive metal cations (e.g., aluminum [Al] and sodium [Na]) can alter the composition and stability of solid actinide phases with different solubility behavior. The composition of tank wastes affects actinide oxidation state stability and solubility and, consequently, soluble concentrations do not always agree well with currently available predictive capabilities.

The presence of a multitude of highly radioactive isotopes in solutions of dissolved used nuclear fuel and tank wastes creates an intense radiation field. The radiation can have a profound impact and alter speciation and chemistry of solutions and solid phases, attacking chemical bonds, degrading molecules, and forming new species. Common chemical reactions induced by radiation are metal ion reduction, decomposition of solvents and organic ligands, radiolysis in aqueous systems, and alteration of solid phases. The ability to accurately predict speciation in these systems requires a detailed understanding of radiation interactions. Radiation chemistry, the study of the chemical effects induced by radiation, is a critical part of any evaluation of actinide and FP speciation in separations processes.

Modeling efforts for understanding actinide and FP speciation, chemistry, and coordination need to be improved for separations. For a given oxidation state, current thermodynamic modeling is effective for predicting actinide and FP speciation in aqueous solutions, to some degree as a function of ionic strength. These models are also useful for understanding surface complexation, which limits migration of radionuclides in the environment. Similar processes occur at the solid–liquid interfaces during ion exchange. At present, these models cannot accurately predict the speciation of radionuclides in highly non-ideal systems, such as high-level nuclear waste tanks or the multiphase systems present in solvent extraction. This lack of knowledge hampers development of new separations schemes as well as the rational improvement of existing ones. In addition, the inability to accurately predict when an actinide or FP species is present in tank waste has caused significant problems for the treatment and partitioning of these wastes into high- and low-activity waste streams. Furthermore, the coupling of advanced computations on the molecular and electronic levels with relevant actinide and FP speciation is lacking. Modeling improvements are expected to benefit existing and future separations.

Access to advanced speciation tools is vital to the scientific communities working with radioactive materials. Knowledge of fundamental speciation is a key tenet for the development and implementation of rational processes, from basic research to the evaluation of a final separations process and for the accurate assessment of environmental consequences. A major set of capabilities and tools that has led to a revolution in the speciation of radioactive materials, and in fact has become an essential component of many contemporary investigations, has been developed at and made available by DOE synchrotron radiation light source user facilities. However, the momentum established more than a decade ago has been blunted as access to experimental time and expert infrastructure supporting experiments at these facilities for front-line speciation is insufficient to support world-class efforts necessary to address current challenges. Furthermore, the development and implementation of new speciation techniques relevant to this field at light sources has decreased in the United States, resulting in a loss of leadership in this area.

The development of advanced analytical and spectroscopic methods to probe highly radioactive systems has enabled significant progress to analyze the speciation of actinides on a molecular scale. As an example, time-resolved fluorescence spectroscopy can measure the spectroscopic features of a few actinides in selective oxidation states (U(VI), Cm(III)) at low concentration levels. With the availability of x-ray-related spectroscopic methods to study radioactive materials, the coordination environments of actinide complexes in solution, solid state or at interfaces have been revealed directly. More recently, advances in x-ray scattering techniques enabled scientists to probe the dimensions of colloidal species in solution. Continuous development of advanced analytical technologies at the frontier of science is critical to provide the analytical tools to detect, speciate, and monitor actinides and FPs in extreme environments such as nuclear fuel and waste processing streams.

2.0 Proposed Solutions

A separations technology program must advance the current understanding of actinide and FP behavior in extreme environments and develop the next generation of analytical tools to probe species under these challenging environments, such as low concentrations, high and low ionic strengths, and high radiation fields. Developing the speciation of key radionuclides and identifying and characterizing the dominant reaction paths will take time. Concerted, short-term and long-term speciation efforts will support and drive tank waste processing, separations developments and remediation efforts over the next decades. A set of short-term and long-term goals will bridge this time gap and will be beneficial to users and stakeholders. Advanced computational tools will better predict the behavior of actinides and FPs in waste and process streams. Expertise in actinide and FP speciation exists across the DOE complex and at various universities. Teaming of users, stakeholders, experimentalists, and theorists is essential to accelerate progress on high-priority objectives in advanced speciation and to support grand scientific challenges beyond the current rate.

1. ***Molecular chemistry of actinides and FPs in media of inherent complexity: Transition from binary mixtures to complex multi-component systems***

   The inherent complexity of environment, fuel processing, or tank waste makes it very difficult to obtain a complete understanding of all chemical species and reaction pathways associated with the separation and incorporation of radionuclides. However, understanding this complexity is essential for the optimization of current processes and development of the next generation of advanced separations processes. Comprehending the nature and properties and the ability to predict the behavior of actinide and FP species in extreme environments of high radiation, concentrated salt mixtures, multi-radionuclide and multi-ligand systems is a great challenge and critical to this endeavor. As an example, the design of organic molecules to coordinate with actinides and FPs for separation is based on the nature (molecule size, charge) of the targeted (charged or neutral) species. Solvation and inner-sphere complexation can be tuned to meet the need for a separation designed to target specific radionuclides. Similarly, understanding the structural factors of ion exchange materials that lead to site specificity will guide chemists and material scientists to produce new materials with increased selectivity.

Information on the behavior of actinides and FPs in complex mixtures will enable scientists to improve predictive capabilities extending the thermodynamic database from binary complexes to ternary complexes (and beyond) in highly concentrated systems. As an ultimate outcome, the gained information will bridge the gap from electronic structure to thermodynamics of species in complex systems. A robust and critical evaluation of thermodynamic data available in the open literature will identify additional needs for experimental studies and model development in concentrated electrolytes.

Understanding the chemistry of actinides and FPs will impact a variety of challenges facing both the DOE Office of Environmental Management (EM) and the Office of Nuclear Energy (NE):

- How can actinides be monitored during processing in complex mixtures? (NE)
- Why does ^{237}Np not partition in solvent extraction steps as predicted in UREX+? (NE)
- How can technetium volatilization be minimized, prevented, or otherwise exploited? (EM, NE)
- What are the technetium species in Hanford tank wastes, and how can they be partitioned in-tank to minimize volatilization of technetium during vitrification in the waste treatment plant? (EM)

Non-conventional separations technologies can be developed only by understanding oxidation state stabilities, coordination environments, or electrochemical properties. Chemical properties such as oxidation states and coordination environments can be tuned to optimize partitioning and separation from multi-radionuclide systems. It is imperative that a separations technology program advance the current understanding of actinide and FP behavior in extreme environments and develop the next generation of analytical tools to enable scientists to probe species under these extreme environments.

2. *Effect of radiation chemistry on speciation and separation efficiency*

In order to predict the efficiency of separations processes in high radiation fields, the effects of radiation on actinide and FP speciation must be understood. Understanding the fundamental radiolysis effects on solvents, ligands, and other separation molecules will enable development of an advanced modeling capability to predict process performance. Radiation resistance, decomposition, and formation of radicals can be modeled. Radiolysis in highly complex mixtures must be understood to enable design of radiation-resistant, selective molecules and exploit the resulting chemistry to achieve tailored separations. Isotopes with different half-lives and suitable external radiation fields must be made available to enable radiation studies. This implies access not only to equipment but also to suitable isotopes, which would greatly benefit the actinide research community. Understanding and predicting radiation-induced changes in speciation are of great importance for any advanced technology using non-conventional solvents to dissolve or separate the actinides and FPs.

Studies on the radiation chemistry in separations-related systems were performed early on to assist in development of the PUREX process. Radiation studies involved organic solvents, extractants, and actinide oxidation state stability. With an aging workforce, the knowledge in radiation chemistry is disappearing, which will create a problem in the near term. It is essential to emphasize the scientific research needed in radiation chemistry and regain the expertise by training the next generation of experts. The development of next-generation separations technologies will enable us to evaluate the radiation resistance of solvents and solutions to be applied in future separations technologies.

3. *Advanced analytical tools to meet the challenge of measurement and detection*

Analytical and spectroscopic methods are the tools to characterize actinides and FPs in environment and process/waste streams. Some of the most important needs that would have great impact on specific scientific objectives and priorities require advanced tools to speciate actinides and FPs in extreme systems, ranging from low-concentration contaminants to complex environments at elevated temperatures. Currently, low concentrations of radionuclides limit speciation in the environment or in cleaned tanks, and analytical capabilities need to be improved to enable the direct determination of speciation of radionuclides at relevant concentrations down to picomolar (pM) concentrations. The presence of a multitude of radionuclides complicate speciation in processing and waste streams, and advanced capabilities could determine the speciation of radionuclides in high-radioactive matrices at moderate concentrations (millimolar [mM] to micromolar [μM]) in the presence of closely related chemical elements. This will enable speciation of small amounts of transuranic elements in the presence of a large excess of uranium. These new tools can also be applied to the direct, real-time measurement of radionuclide concentration and speciation for process control and nonproliferation monitoring.

Re-establishing and supporting a larger world-class synchrotron radiation capability and infrastructure for this field is essential to provide access to advanced speciation tools that span the activities in the nuclear separations community. A cadre of nuclear scientists at and/or closely associated with the user facilities needs to be available that can serve as domain scientists to develop new methodologies and techniques with an explicit mission of supporting the prioritized efforts of the scientific community and to provide front-line user support. These efforts should be accompanied by a similar emphasis on and support of complementary specific laboratory-based capabilities.

To successfully make advanced tools and capabilities available to this scientific community on a regular basis and to ensure solid scientific foundations based on speciation while regaining preeminence in the field, selective major re-investment in the infrastructure that makes current and future advanced speciation of highly radioactive materials possible is required. For development of rapid throughput, combinatorial methods would meaningfully assist in evaluation of actinide and FP speciation under a range of conditions. Broader use and application of advanced spectroscopic tools could be fostered by transitioning speciation tools from rare, large facilities (light sources, neutron sources) to laboratory-based devices. Although such laboratory-based instruments most likely will not reach the power of the larger synchrotron facility, they can be a venue to study more concentrated actinide and FP materials.

Appendix B. Breakout Session Report: Design of Molecules and Materials with Selective Separation Properties

CHAIR AND ORGANIZER: **Bruce Moyer**, Oak Ridge National Laboratory
CO-CHAIR: **Kenneth Nash**, Washington State University
FEDERAL COORDINATOR: **Stephen Kung**, Office of Nuclear Energy

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Spiro Alexandratos, Hunter College of the City University of New York
Joseph Birdwell, Oak Ridge National Laboratory
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David DePaoli, Oak Ridge National Laboratory
Mark Dietz, University of Wisconsin, Milwaukee
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1. INTRODUCTION AND BACKGROUND

1.1 Why do we need new molecules and materials in nuclear separations technologies?

In over a century of accomplishment in the development of methodologies for radionuclide separations, the steady progress in this field has been enabled by a stream of new separation agents. New separations materials have specifically enabled solutions to many types of problems—from isolating radionuclides from ores through separations of actinides from irradiated nuclear fuels to the daunting challenges of defense waste treatment, environmental restoration, and contaminant immobilization.[1,2] At first, simple materials were used, including readily available neat solvents and natural ion-exchange materials, but the appearance of

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[1] Choppin, G. R., M. K. Khankhasayev (Editors) 1998. “Chemical Separation Technologies and Related Methods of Nuclear Waste Management: Applications, Problems, and Research Needs.” NATO Environmental Security – Volume 53. Klumer Academic Publishers, Dordrecht, The Netherlands.

[2] NAS, 1999. “Groundwater and Soil Cleanup: Improving Management of Persistent Contaminants.” Commission on Geosciences, Environment and Resources (CGER). The National Academies Press, Washington.

selective solvent extraction (SX) reagents from analytical laboratories and synthetic ion exchange (IX) resins from industry opened the door to a range of new separations technologies and problem solving. In the mid-20th century, the exploding demand for selective separations arising both from the Cold War and the burgeoning nuclear industry drove innovation of many new materials and methods. A host of now-familiar processes were developed, such as AMEX (amine extraction) to extract uranium from ore leach liquors using simple fatty amines and PUREX (plutonium–uranium reduction extraction) for aqueous reprocessing of irradiated uranium and used nuclear fuel using tributylphosphate (TBP). Chelating extractants and resins provided further progress, as discovered mainly through enlightened empirical research. The advent of macrocyclic extractants and the corresponding era of molecular recognition in the 1970s created a new paradigm for the design of new molecules and materials, enabling solutions to previously intractable problems in separations of f-elements and fission products (FPs).[3,4,5,6]

While a few processes, such as PUREX, have been deployed on an industrial scale, the continuing development of separation agents has yielded a number of new processes that either have been successfully deployed for specific tasks or have been developed to the point of readiness in advanced nuclear fuel cycles (e.g., TALSPEAK for separation of trivalent actinides and lanthanides[7,8]) and for cleanup of legacy sites (e.g., caustic-side solvent extraction for cesium removal from tank waste[9]). While many separation materials developed in the past decades have proven economical and powerful for their varied purposes, the current generation of materials has not yet enabled the solution to more challenging separation problems posed by needs for closing the nuclear fuel cycle, cleaning up environmental contamination, treating Cold War wastes, and enhancing national security. Based on the record outlined above, it is projected that new molecules and materials will open new doors to addressing these persistent issues, as strongly echoed by a number of predecessor workshop reports and independent

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[3] Waste Forms Technology and Performance: Final Report ISBN 978-0-309-18733-6, The National Academies Press, Washington, D.C. 2011.

[4] Wilmarth, W.R., G.J. Lumetta, M.E. Johnson, M.R. Poirier, M.C. Thompson, P.C. Suggs, and N.P. Machara. “Waste Pretreatment Technologies for Remediation of Legacy Defense Nuclear Wastes,” *Solvent Extr. Ion Exch.*, 29(1), 1–49 (2011).

[5] Choppin, G. R., M. K. Khankhasayev (Editors) 1998. Chemical Separation Technologies and Related Methods of Nuclear Waste Management. Applications, Problems, and Research Needs. NATO Environmental Security – Volume 53. Klumer Academic Publishers, Dordrecht, The Netherlands.

[6] NAS, 1999. “Groundwater and Soil Cleanup: Improving Management of Persistent Contaminants.” Commission on Geosciences, Environment and Resources (CGER). The National Academies Press, Washington.

[7] Weaver, B., F.A. Kappelmann.”Preferential extraction of lanthanides over trivalent actinides by monoacidic organophosphates from carboxylic acids and from mixtures of carboxylic and aminopolyacetic acids.” J. Inorg. Nucl. Chem., 1968, *30*, 263-272.

[8] Nilsson, M., K. L. Nash. Review Article: “A Review of the Development and Operational Characteristics of the TALSPEAK Process.” *Solvent Extr. Ion Exch.* 25(6), 665-701 (2007).

[9] Moyer, B. A.; J.F. Birdwell, Jr., P.V. Bonnesen, L.H. Delmau. “Use of Macrocycles in Nuclear-Waste Cleanup: A Real-World Application of a Calixcrown in Technology for the Separation of Cesium.” *Macrocyclic Chemistry—Current Trends and Future*; Gloe, K., Ed. Springer: Dordrecht, 2005: pp 383–405.

assessments.[10,11,12,13,14,15,16,17,18] However, it is also clear that most if not all of the "low-hanging fruit" has already been gathered and that new techniques for designing new molecules and materials, synthesizing them, and predicting their properties will be needed.

This appendix addresses the specific needs for new molecules and materials and the challenges and questions that must be addressed in future research. Parallels are drawn and overlaps in programmatic needs identified to help uncover potential program partnerships within the Department of Energy (DOE) and with outside entities. Finally, this appendix presents suggestions for proposed solutions to designing new molecules and materials in a sustained program referred to as a DOE center of knowledge.

1.2 What molecules and materials are of interest for selective separations?

Although SX and IX have been the workhorses in the nuclear industry for selective separations and are likely to remain strong in this capacity, new molecules and materials are needed in a far greater range of separations techniques. To identify where new opportunities for design lie, types of molecules and materials relevant to effecting selective separations may be categorized for discussion purposes as ligands, reactive solids, media, reagents, and catalysts. Ligands can be, for example, SX reagents, aqueous complexants, decorporation agents, functional groups tethered to resin backbones, functionalized linkers in 3D metal-organic frameworks, precipitation agents, flotation agents, and membrane carriers. Reactive solids include solid sorbents, inorganic and organic ion exchangers, membranes, and electrodes. Media are fluid phases such as solvents, supercritical fluids, gases, and ionic liquids (ILs); they can also be structured fluids such as emulsions. Reagents are all types of molecular species added to enhance or enable separations, for example, solvent modifiers, filter aids, coagulants, and de-emulsifiers. Catalysts are needed

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[10] Noble, R. D., and R. Agrawal. "Separations Research Needs for the 21st Century," *Ind. Eng. Chem. Res.*, 2005, *44*, 2887-2892.

[11] Robinson, S., J.S. Watson, J. Harness, D. Melamide, I. Tasker. "Separations Technology Roadmap For DOE Environmental Management," Proc. WM 2003 Conference, February 23-27, 2003, Tucson, AZ.

[12] Bredt, P.R., 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. Wilmarth. "Scientific Opportunities to Reduce Risk in Nuclear Process Science," PNNL-17699; July 2008.

[13] DOE-EM. *Engineering & Technology Roadmap Reducing Technical Risk and Uncertainty in the EM Program*; March 2008.

[14] DOE BES. *Technology and Applied R&D Needs for Advanced Nuclear Energy Systems*: Proceedings from Workshop on Basic Research Needs for Advanced Nuclear Energy Systems, July 31 – Aug 2, 2006. June 2006.

[15] DOE. "The Path to Sustainable Nuclear Energy: Basic and Applied Research Opportunities for Advanced Fuel Cycles," Sept 2005.

[16] ORNL. *Basic Research Needs To Assure a Secure Energy Future*, Feb. 2003.

[17] Sandia National Laboratories. "Proceedings of the Basic Research Needs for Countering Terrorism Workshop." Gaithersburg, MD, Feb 28 – Mar 1, 2002.

[18] National Research Council. "Research Needs for High-Level Waste Stored in Tanks and Bins at U.S. Department of Energy Sites," Environmental Management Science Program. National Academics Press, 2001.

for kinetic enhancements to many processes, which could include crystallization, phase transfer in SX, and redox at electrode surfaces.

Table 1 shows the applicability of these molecules and materials in various separations techniques organized by the phases involved. The table serves to emphasize the breadth of potential impact of design of new molecules and materials not only for nuclear separation technologies, but also across the spectrum of industrial separations.

Table 1. Role of new molecules and materials in selective separations

Phases	Method	Applicable molecules and materials				
		Ligands	Reactive Solids	Media	Catalysts	Reagents
Solid–liquid	Filtration	×	×	×		×
	Crystallization/precipitation	×		×	×	×
	Dissolution/leaching	×		×		×
	Ion exchange	×	×	×		×
	Membranes	×	×	×		×
	Zone refining					
	Electrochemical separations	×	×	×	×	×
	Magnetic filtration	×	×			
Gas–solid	Adsorption	×	×		×	
	Membranes	×	×		×	
	Volatilization/sublimation					×
Liquid–liquid	Solvent extraction	×		×	×	×
	Liquid membranes	×		×	×	×
	Extraction chromatography	×		×	×	×
Gas-–liquid	Flotation	×				×
	Distillation					×
	Evaporation					×
	Sorption	×		×		×

1.3 What is meant by "design" of molecules and materials?

While the word “design” describes many types of human creative endeavor, chemists and chemical engineers have enthusiastically appropriated the term not only for development of new chemical processes, but also for the materials on which the new processes depend. Judging by tens of thousands of publications annually, newly synthesized molecules and materials are more often than not said to be “designed.” Although the wondrous molecular structures emerging from the realm of supramolecular chemistry[19,20] lend credence to such pretensions that chemists have a degree of mastery over matter, methods of molecular design in fact remain fairly primitive. Often design amounts to logical extensions of new synthetic reactions and resulting families of new chemical structures, and there is some truth to the saying that such molecules “go looking for a purpose.” In the present context, the purpose in the end lies in new chemical separation processes to fill technology gaps, which will be described in the next section. In fact, the molecular design must target a conceptual process whose desired characteristics may already be known, and thus, molecular design and process design are closely linked.

Working backward from process needs, designed materials must fulfill a set of specific properties, the most important of which are collected in Table 2. The table shows that the selective binding of a new separation agent is only the starting consideration of design, in harmony with Lehn’s definition of molecular recognition as binding combined with function.[21]A candidate separation agent will fail if it does not bind rapidly enough, for example, or if it does not release the bound species efficiently. Separation materials must also be reasonably stable and resistant to fouling, and the technology must be compatible with up- and downstream processing, minimize secondary waste, and be easy and safe to use. Design therefore implies predictability of a multitude of performance characteristics. The goal is that diverse molecular properties of candidate molecular structures resulting from design can be reliably and quantitatively forecast from molecular to bulk scales.

Based on the assumption that selectivity resides in selective binding of guest species by a host structure, present methodology has only begun to address relative affinities. Given that thermodynamics of chemical processes are still predictable only in the gas phase, it is clear that the full meaning of design remains more of an aspiration than a reality. Methods toward pursuing this aspiration will be addressed in the final sections of this appendix.

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[19] Long, J.R., and O.M. Yaghi. *Chem. Soc. Rev.* 2009, *38*, 1213.

[20] Lee, J., O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp. *Chem. Soc. Rev.* 2009, *38*, 1450.

[21] Lehn, J.M. “Design of Organic Complexing Agents. Strategies Towards Properties,” *Alkali Metal Complexes with Organic Ligands*; Dunitz, J. D., Eds. Springer-Verlag: New York, Vol. 16, pp. 1-69, 1973.

Table 2. Technical requirements for successful separations agent development

Category	Required Property
Basic functionality	Adequate selectivity
	Adequate strength (affinity)
	Solubility
	High capacity
	Rapid kinetics (throughput)
	Reversibility, recyclability
Technology viability	Good stability
	Low loss rate
	Resists fouling, easy recovery
	Phase integrity
	Good interfacial behavior
	Robust to feed variation
	Predictable behavior
	Equipment-compatible
	Availability
	Minor components manageable
Industrial suitability	Low cost
	Real and perceived risk minimal
	Upstream/downstream compatible
	Standard equipment
	Ease of operation
	Safe
	Little secondary waste
	Environmentally friendly

1.4 Technology Needs for New Molecules and Materials in DOE Applied Programs

1.4.1 Office of Nuclear Energy

The development of closed-loop nuclear fuel cycles had its origins in the Manhattan Project nearly 70 years ago. Activities at the Hanford site in Washington State came into operation in an incredibly short period of time and resulted in the first large-scale production of man-made elements and ultimately in the site cleanup challenges left behind. The first hydrometallurgical separation in this application was based on co-precipitation of the target plutonium with $BiPO_4$, a process that was developed in the lab on the few micrograms of the isotope that was then available. The process was sufficiently robust to allow the isolation of kilogram amounts of plutonium from the complex matrix of irradiated nuclear fuel within a period of less than three years from the first ground-breaking at Hanford.

In the post-World War II environment that ultimately evolved into the Cold War, the advantages offered by liquid–liquid contacting led to SX as the preferred method for plutonium production. It was thereby possible to recycle uranium, increase throughput, increase quality of the final product and reduce the volume (and complexity) of waste byproducts.

The $BiPO_4$ process was supplanted first by the REDOX process in which plutonium and uranium were extracted by methyl(isobutyl)ketone (a.k.a., hexone) from $Al(NO_3)_3$ solutions with adjustment of oxidation states. The third iteration for plutonium production in the U.S. weapons program was the shift from the REDOX process to the PUREX process. In PUREX, the hexone extractant solution was replaced by a solution of TBP in odorless kerosene. Today, PUREX is used for commercial fuel reprocessing in France, the United Kingdom, Japan, and Russia and is continuously being improved. At each stage of this evolution, waste volume and complexity decreased. Because the priority during the Cold War was producing plutonium for weapons, waste management procedures were given less emphasis, and a system of subsurface waste tanks for storage of (predominantly) alkaline residues was established as the most expeditious strategy for managing byproducts.

At the beginning of the 21st century, the nuclear energy and weapons landscape changed. There are currently at least nine nuclear weapons nations, though the possibility of nuclear terrorism may have become a greater threat than that of a nuclear exchange between nations. More than 400 nuclear electricity generating units are in operation globally, generating approximately 17% of the total electricity that is consumed planet-wide. Though a geologic repository operates in the United States for defense wastes contaminated with transuranic elements (the Waste Isolation Pilot Plant [WIPP]), there are *no* operational geologic repositories for the permanent disposal of either used nuclear fuel or high-level wastes from reprocessing anywhere in the world. Concerns about the global climate have arisen, spurring demand for energy production approaches that release smaller amounts of greenhouse gases into the atmosphere (for which fission-based nuclear power is well suited). Demands for primary energy by rapidly industrializing/ modernizing countries like China, India, Brazil, and Russia are increasing. Each of these factors is a central consideration in establishing future directions for fuel cycle development.

The still incompletely resolved issue of managing radioactive waste is a significant obstacle to the expanded application of nuclear power. Upon removal of used fuel from the reactor, the short-lived FP radioactivity dominates the dose for the first decade or so. The isotopes that represent the longer-term risk for radiotoxicity include alpha-emitting transuranic elements (neptunium, americium, plutonium), intermediate-lived FPs like ^{137}Cs and ^{90}Sr and mobile species like the moderately long-lived ^{99}Tc, ^{135}Cs, and ^{129}I isotopes. Radiotoxicity of used fuel is dominated from a few years after discharge from the reactor until about 300 years by ^{137}Cs and ^{90}Sr. From 300 to about 4,000 years, the radiotoxicity of intact fuel is dominated by ^{241}Am, from 4,000 to 70,000 years by plutonium isotopes, and from 70,000 to about 2,100,000 years by ^{237}Np. In a closed fuel cycle in which plutonium is recycled (removing it from the waste stream), the toxicity of the high-level wastes is dominated by ^{241,243}Am isotopes from several hundred to 70,000 years and by ^{237}Np from 70,000 to at least 2,000,000 years. If all transuranic elements are removed and transmuted, the radiotoxicity of the residue returns to that of uranium ore when the ^{137}Cs and ^{90}Sr have decayed to benign levels (300 years). A significant “advantage” gained in the full-recycle approach is increased confidence in prediction of repository performance. Keeping the actinides in the fuel cycle with transmutation accrues advantages against subnational threats while extending the energy potential through recycle of fissile materials.

Today, France, China, the United Kingdom, Japan, and Russia use the PUREX process in closed-loop recycling (in DOE parlance, current recycling has most in common with the “modified open” fuel cycle). The recovered reactor-grade plutonium is recycled once as mixed oxide (MOX) fuel through a light water reactor. The PUREX process is robust, has enjoyed the benefit of more than 50 years of research and process experience, and undergoes continued refinement. If the goal of fuel processing remains recycling uranium and plutonium, PUREX (or a PUREX-like replacement that does not produce a pure plutonium stream) will suffice as an acceptable technological solution. However, nuclear fuel cycle reprocessing research being conducted around the world is addressing various possible options for advanced processing of irradiated nuclear fuels. Advanced processes specifically target several options for recovery of actinides individually or as a group. Problematic FPs such as ^{135,137}Cs, ^{90}Sr, ^{99}Tc, ^{129}I, noble gases (xenon and krypton), and the lanthanides are targets for developing separations processes to aid in their disposition and disposal (or in the disposition and disposal of actinides).

During the past several decades, the separations research effort in the United States has focused on developing processes and reagents to support cleanup of the former weapons complex. This focus has led to the development of the SREX (strontium extraction), CSEX (cesium extraction), and TRUEX (transuranic element extraction) processes and reagents that enable them; isotope-specific solid sorbents have also been developed. During the same period, the French-led

European program has focused on the development of CHON (carbon, hydrogen, oxygen, nitrogen) reagents for actinide management in advanced fuel processing. This research has led to the development of diamide extractants (and the DIAMEX) process, a class of compounds based on bis-triazinyl pyridine and bipyridine ligands. New dithiophosphinic acid extractant molecules and approaches to their use have also been proposed.

Each of these research efforts has been enabled by the search for new reagents and material design.

Following are several separation issues that still drive the discovery of new processes:

- Recovery and recycle of fissile/fertile components (uranium/plutonium isotopes) without producing a pure plutonium product. The challenges arise from the multiplicity of "stable" plutonium oxidation states that enable easy chemical manipulation to isolate plutonium if desired. The opportunity is to keep plutonium in the fuel cycle, either producing energy or being associated with FPs.
- Minor actinide (neptunium, americium, curium) management, which in a closed loop recycling system with transmutation requires isolation of americium/curium from the FP mixture (or even better, selective isolation of americium) with moderately efficient separation of americium/curium from FP lanthanides. A variety of options exist for neptunium management within a dedicated uranium/neptunium/plutonium recycle system (it should be noted that neptunium is also a potentially valuable byproduct as source material for ^{238}Pu production for space applications). The challenges arise for americium/curium/lanthanides from the chemical similarity of the two classes of elements; the high specific activity of americium, curium, and selected lanthanides; the high neutron capture cross sections of all members (which interferes with transmutation efficiency of americium/curium); and the elevated spontaneous fission half-lives of some curium isotopes. The opportunity that drives interest in this separation is considerable reduction in radiotoxicity of fission residues that is gained by transmuting americium).
- Prevention of the release of gaseous/potentially volatile species (iodine, xenon, krypton, technetium isotopes). The challenge arises from the ease of dispersal and difficulty of containment of volatile radioactive species and the non-reactive nature of noble gases. The opportunity is that the containment of these isotopes removes comparatively low specific activity, environmentally mobile radioactive components from effluents and so improves safety margins.
- The development of suitable waste forms for ultimate disposal of environmentally mobile byproducts, neptunium, technetium, iodine, xenon. The challenge arises from the low charge of neptunium and technetium oxidized species, iodine in all oxidations states, and the non-reactivity of xenon. The opportunities driving the development of new materials for these targets are reduced long-term radiotoxicity of radioactive wastes and increased predictability of repository performance.

While progress has been made in global research efforts to address some of these problems, this work continues, as preferred solutions have not yet emerged, though strong candidates exist in some areas.

1.4.2 Office of Environmental Management

The DOE clean-up inventory[22] includes 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 cleanup approach $350 billion and could take an additional 50 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 from 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 as well as development of suitable waste forms[23] can effect significant improvements to reducing the technical risks involved in the EM cleanup and significantly reduce life cycle costs and schedules.

The radiological risk drivers at the various low-level and high-level waste disposal (LLW and HLW, respectively) sites across the DOE complex are remarkably similar even though their inventories, site conditions, mode of immobilization, and modeling assumptions vary considerably. Table 3 presents the key risk drivers calculated from performance assessments for a wide range of different radiological facilities. Note that ^{99}Tc, ^{129}I, and ^{237}Np are common drivers for LLW, tanks, and HLW.

Table 3. Risk drivers identified for a wide range of different radiological facilities

Site	Facility	Risk Driver	Source
Hanford	LLW Integrated Disposal Facility	^{99}Tc, ^{129}I, U, ^{126}Sn, ^{237}Np	Mann, F. M., R. J. Puigh, S. H. Finfrock, R. Khaleel, M. J. Wood. “Integrated Disposal Facility Risk Assessment.” RPP-15834. CH2M Hill Hanford Group, Inc., Richland, WA, 2003.
SRS	E-Area LLW Facility	^{99}Tc, ^{129}I, ^{14}C, ^{3}H	Washington Savannah River Company. “E-Area Low-Level Waste Facility DOE 435.1 Performance Assessment, Volume 1.”

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[22] DOE-EM. “Report to Congress: Status of Environmental Management Initiatives to Accelerate the Reduction of Environmental Risks and Challenges Posed by the Legacy of the Cold War,” DOE/EM-0001, Washington, DC, 2009.

[23] NAS. “Waste Forms Technology and Performance: Final Report ISBN 978-0-309-18733-6.” The National Academies Press, Washington, DC, 2011.

Site	Facility	Risk Driver	Source
			WSRC-STI-2007-00306, Rev. 0. Aiken, SC, 2008.
SRS	Tank 19	^{99}Tc, ^{129}I, ^{237}Np	Department of Energy – Savannah River. Section 3116: "Determination for Closure of Tank 19 and Tank 18 at the Savannah River Site," DOE-WD-2005-002, Rev. 0. Aiken, SC, 2005.
SRS	Tank 18	^{237}Np	Ibid
INL	Remote Handler-LLW Facility	^{99}Tc, ^{129}I, ^{14}C, ^{238}U, ^{226}Ra	Idaho National Laboratory. "Assessment of System Wide Features Incorporated into the RH-LLW Disposal Facility Providing Protection of Human Health and the Environment (Draft)." INL/EXT-10-19385, 2011.
YM	Yucca Mountain	^{99}Tc, ^{129}I, ^{237}Np and Pu	Hornberger, G. M. "Total System Performance Assessment – Site Recommendation." Letter to Richard A. Meserve. NRC. 2001. http://www.nrc.gov/reading-rm/doc-collections/acnw/letters/2001/1290175.html

Examples of separations research areas related to the EM mission where new molecules and materials have potential for significant impact are described below.

Technetium chemistry, removal, and immobilization: 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. There are critical needs for technetium separation and materials development at several steps within the nuclear cycle, many of which have unique chemical environments. Some of these needs are as follows.

Technetium is primarily present in alkaline tank waste at the Hanford and Savannah River sites. A substantial portion of the technetium in tank wastes will partition into low-level activity waste. Technetium 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. Procedures and materials are needed to clean up these process systems/pipelines. Also, understanding the chemical adsorption or desorption and separation processes are needed for technetium on metal waste streams. Technetium is a key contaminant in meeting regulatory requirements for near-surface land disposal performance, including reducing cementitious materials, owing to the large inventory of technetium to be disposed in low-activity or secondary waste streams. Within the DOE complex, there are 16 subsurface technetium plumes.[24] An acceptable baseline technology for remediating technetium in subsurface environments does not exist. There is a need for a sorbent that is inexpensive and will remain effective for an extended duration that can be used in the vadose zone.

Fundamental studies that enable understanding of the chemistry occurring across the range of conditions described above, along with comparisons of non-radioactive surrogates (e.g., ReO_4^-), 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 IX media or precipitation agents could enable substantially simplified removal processes.

Mercury chemistry, removal, and immobilization: Historic uses of mercury at Oak Ridge 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 ecological and bio-geochemical interactions. Additionally, deactivation and decommissioning 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 Oak Ridge, mercury contamination is or will be problematic throughout the complex.

Cost-effective technical solutions are needed for waterborne mercury remediation and soil treatment. 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 on 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: Chromium 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 and for

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[24] Hazen, T. C., B. Faybishenko, and P. Jordan. “Complexity of groundwater contaminants at DOE sites.” LBNL-4117E. Lawrence Berkeley National Laboratory, Berkeley, CA, 2008.

plutonium oxidation state adjustment in the REDOX process. Hanford, Oak Ridge, and other DOE sites also possess groundwater and soil contaminated with chromium above regulatory limits. Refinements to chromium separation processes are needed to reduce dependence on 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: Iodine-129 is one of the most difficult contaminants to address in the DOE complex because of its complex chemical behavior (including volatility), limited long-term retention in immobilization processes, and high mobility in subsurface environments. There is limited understanding of the behavior, speciation, and mobility of iodine in sedimentary environments associated with past co-disposal of waste streams and the impacts on environmental remediation. Improved remediation technologies for groundwater are needed to provide long-term solutions. Potential technologies that could be applied include organic sequestering agents, inorganic sequestering agents (including silver-based), additives, or selective absorbents. Development of selective IX 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: 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. Improving removal of these constituents from the sludge and partitioning them into the aqueous waste would reduce the volume of HLW 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.

Materials are needed to achieve a more effective separation of constituents by 1) removing species that limit waste loading in high-level glass, 2) removing constituents that may limit or bound the operating conditions of other processes (e.g., phosphate), and 3) developing additives to stabilize aluminum solubility or developing improved prediction tools and control of aluminum solubility. 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 IX process at Hanford or the SX system at Savannah River would reduce the amount of sodium hydroxide added. Therefore, it would be helpful to develop materials that would either enhance aluminum solubility or prevent aluminum species from precipitating at an inappropriate process point.

Removal of key radionuclides for tank closure: Tank closure is currently achieved by filling the emptied and cleaned tanks with grout. Determining the readiness of the emptied tank for closure is not straightforward from technical and regulatory perspectives. Significant cost and schedule savings can be achieved through a combination of new separation 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. 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: Many of the subsurface contamination problems at legacy nuclear weapons sites currently have no practical remedy. 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.

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. There is a particular need for inexpensive sorbent materials to remove groundwater technetium that is not based on REDOX transformations and would last hundreds to thousands of years.

A key issue related to long-term stewardship of radiological disposal sites is: How does deterioration of the waste package influence rate of release? Laboratory, pilot-scale studies, and analogue field studies are needed to develop conceptual and input values for models.[25,26] A specific example demonstrating this question would be: What is the process by which slag-containing cements re-oxidize?

Contaminants of concern during demolition and disposal: Current decommissioning methods are costly, with significant potential risk to personnel. New *in situ* approaches, such as entombment, are being investigated to facilitate decommissioning. A scientific basis for entombment is needed not only in the development of these new approaches but also in the fate of decommissioned facilities. There is a need for new decontamination agents that can extract contaminants from

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[25] Miller, W., R. Alexander, N. Chapman, I. McKinley, J. Smellie. “Natural Analogue Studies in the Geological Disposal of Radioactive Wastes, Studies in Environmental Science.” 57, Elsevier, Amsterdam, 1994.

[26] Wang, L., E. Martens, D. Jacques, P. DeCanniere, J. Berry, D. Mallants. “Review of sorption values for the cementitious near field of a near surface radioactive waste disposal facility.” 2009.

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.

1.4. DOE National Nuclear Security Administration

The mission of the National Nuclear Security Administration (NNSA) comprises four components:

1) To maintain and enhance the safety, security, reliability, and performance of the U.S. nuclear weapons stockpile without nuclear testing.
2) To reduce the global danger from weapons of mass destruction.
3) To provide the U.S. Navy with safe and effective nuclear propulsion.
4) To respond to nuclear and radiological emergencies in the United States and abroad.

Separations needs in the performance of each of these mission areas vary significantly. The processes used in the performance of weapons production and refurbishment are well established and highly developed. The conversion of 34 metric tons of excess weapons plutonium to MOX fuel in the plant under construction at the Savannah River site will require a head-end purification operation that is based on PUREX chemistry. Due to the value and relative scarcity of the materials involved, stringent product specifications and safety requirements, and the large capital investments that have been made in existing plants (or those under construction), changes to these separation processes require large advantages to justify to DOE and the facility operators. In spite of this, changes to separation processes can result in substantial improvements that are implemented. For example, the conversion to calcium chloride (from NaCl-KCl mixtures) for electrorefining operations at Los Alamos will reduce operational and waste costs. Also, new separations operations are under consideration such as re-establishment of ^{238}Pu production, ^{241}Am recovery for use in neutron sources for industry, and ^{234}U recovery from ^{238}Pu operations.

With respect to nuclear proliferation concerns, there are several mission needs that require detailed knowledge of separations technology or would benefit from design of molecules and materials to capture and detect target species. The first mission need is the detection of nuclear separations operations performed using known processes or closely related processes and established chemistries. This includes detection of degradation products and emissions generated during operations. A closely related aspect is the evaluation of safeguards for advanced fuel cycle separations. A second need requires the capture of species of interest that may be present at extremely low concentrations. This application calls for separations media that have strong affinities for target species and high selectivity for them. Collection media that are also designed to signal uptake of a target species (through fluorescence, for example) would be of particular value. Very high reliability for a positive signal is a key concern. As deployment may be in remote locations and for long exposure times, durability of the separation material and platform are important. A third area of interest is the design of chemical markers for tagging chemicals that could be used in materials processing or in weapons components, as a means of tracking supply chains. Finally, improved separations technology is under development to provide economic alternatives to the use of highly enriched uranium in research reactors for medical isotope production. The goal is to allow conversion of all research reactors from highly enriched uranium to low-enriched uranium.

An additional need that is not specific to NNSA activities is the development of separations systems for the decontamination of surface waters, infrastructure, surfaces (such as soils, buildings, etc.) and personnel in the aftermath of an accidental or intentional dispersal event, be it chemical, biological, radiological, or nuclear. Effectiveness, ease of disposal, and the ability to manufacture large quantities of the decontamination system at reasonable cost are key factors.

2. TECHNICAL CHALLENGES, GAPS, AND QUESTIONS

2.1 Challenges in the Design of Separation Materials for DOE Technology Needs

Towards addressing the technology needs for selective separations in DOE programs, new molecules and materials are expected to lay the foundation for the processes of the future. The corresponding grand challenge is the question of design itself. Namely, what basic science and tools are required for the design of new molecules and materials, and how can they be applied to real problems? For given types of separation methods, what are the specific technical gaps that stand in the way of progress? This section explores these cross-cutting questions in greater detail, in turn suggesting opportunities for productive program partnerships to be presented in a subsequent section.

2.2 The Grand Challenge—Learning How to Design Separation Materials

Current experimental approaches to process development starting from molecular concepts consume 15–20 years in basic discovery, development, and implementation phases. Nearly half that time involves risky, empirical, expensive testing of many candidate separating agents, and progress tends to stop with the first usable candidate rather than the optimum one. Further, unanticipated deficiencies in the molecular system as discovered in scale-up or pilot testing are often mitigated with inefficient work-arounds adopted under schedule pressure vs. finding more functional molecular alternatives. The result is a long, expensive R&D timeline and (the path to a successful plant has many potential pitfalls) a plant that is unnecessarily, and possibly prohibitively, expensive to build and operate. Thus, there is incentive to improve both the discovery and selection of candidate separation materials and the prediction of their various properties that determine their performance under complex and even extreme conditions.

The magnitude of this challenge can be appreciated by the number of disparate properties and performance characteristics that must be anticipated in the development of a new separation agent and corresponding process, as listed in Table 2. Given that none of the required properties currently can be predicted except qualitatively, the challenge of predicting the overall performance of a candidate separation agent is staggering. The real problem is further compounded by the essence of design in being the identification of an optimal molecular structure from an initially specified set of target properties. Thus, the challenge qualifies as "grand" and may be stated as follows: How can highly selective separation materials be designed with predicted characteristics that can be applied to targeted separations and detection schemes?

Opportunity: Predicting the chemistry associated with separations represents an area where modeling and simulation, conducted in concert with focused experimental development, have potential for a large return on investment. When coupled with large molecular databases (cheminformatics) or *in silico* molecular generators (de novo design), the ability to predict chemical and physical parameters as a function of composition and operating conditions provides the means for identifying new separating agent candidates on the computer prior to any synthesis and testing. This capability would dramatically decrease development costs for new separations systems, optimizing performance and reducing technical risk.

Where we are: The ability to predict chemical and physical properties makes possible the deliberate design of separating agents with desired chemical and physical properties. Computer screening of candidate molecules through electronic structure and force-field models has been validated by experiment and has been highly valuable in significantly reducing the experimental effort needed.[27] Candidates for screening can be derived from chemical intuition or from databases of known molecules.

The past decade has seen the development of computer-aided design software, in which candidate separating agents are generated on the computer from molecular fragment libraries and then ranked using high-throughput screening methods.[28,29,30] This software is currently used to facilitate the discovery of host molecules in projects currently supported by the DOE Office of

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[27] Lumetta, G. J., B. M. Rapko, B. P. Hay, R. D. Gilbertson, T. J. R. Weakly, J. E. Hutchison. "Deliberate design of ligand architecture yields dramatic enhancement of metal ion affinity," *J. Am. Chem. Soc.*, 124, 2002: 5644-5655.

[28] Hay, B. P., and T. K. Firman. "HostDesigner: a program for the de novo structure-based design of molecular receptors with binding sites that complement metal ion guests," *Inorg. Chem*. 41, 2002: 5502–5512.

[29] Hay, B. P., A. A. Oliferenko, J. Uddin, C. Zhang, T. K. Firman. "Search for improved host architectures: application of de novo structure-based design and high throughput screening methods to identify optimal building blocks for multidentate ethers." *J. Am. Chem. Soc.* 127, 2005: 17043–17053.

[30] Hay, B. P., T.K. Firman, G.J. Lumetta, B.M. Rapko, P.A. Garza, S.I. Sinkov, J.E. Hutchison. "Toward the computer-aided design of metal ion sequestering agents." *J. Alloys Comp.*, 374, 2004: 416-419.

Basic Energy Sciences (receptors for anions and contact ion pairs, building blocks for self-assembled anion receptors), the Defense Threat Reduction Agency (receptors for chemical warfare agents), and the DOE Office of Nuclear Energy (receptors for An(III)/Ln(III) separation, receptors for uranyl from sea water). The software has recently been parallelized for use on high-performance computers.

Molecular modeling and simulation can be used in scoring by calculating binding affinities, selectivities, and macroscopic properties such as the physical properties of the phases (e.g., viscosity, heat capacity, and vapor pressure) and the distribution of species between phases. Continuum solvation models, incorporated in electronic structure codes, allow the accurate prediction of free energies of solvation for a wide variety of solutes and solvents, providing an approach for predicting partitioning equilibria between phases. Molecular dynamics (MD) simulations predict properties, such as viscosity and vapor pressure, to within experimental accuracy for a variety of neat solvents. There is also precedent for the use of MD simulations to predict solute free energies and complexation equilibrium constants. Grand canonical Monte Carlo simulations have been shown to be effective in screening metal–organic frameworks for selective separations in complex gas mixtures relevant to off-gas streams from nuclear processes.[31]

In addition to molecular modeling approaches, QSAR (Quantitative Structure-Activity Relationship) methods, widely used in the pharmaceutical industry, can often be adapted for property prediction. These methods quantitatively correlate calculated physicochemical properties for a molecule (volume, density, dipole moment, surface area, etc.) with known chemical reactivity or physical properties. Well-known examples include boiling point prediction, pKa prediction, the Hammett equation, and the Taft equation. When experimental data are lacking, molecular modeling, either with electronic structure or force-field methods, can be used to obtain the physicochemical properties for such correlations.

<u>What needs to be done</u>**:** Computer-aided molecular design involves generating possible molecular structures followed by high-throughput screening to rank them with respect to a targeted property. Although much progress has been made, further research is needed to attain molecule-generating algorithms that achieve a complete coverage of synthetically accessible chemical space for small (≤ 200-atom) compounds. Accurate ranking of computer-generated molecules with respect to a given property will require improved property prediction. Scoring capability must be prioritized based on need and cost effectiveness, identifying areas where modeling and simulation can now make useful predictions and areas where further theoretical development is needed.

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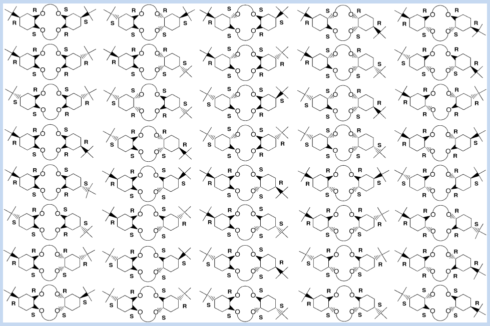
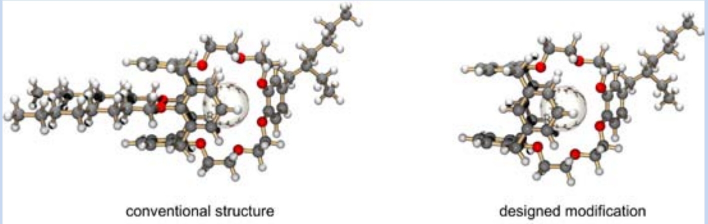
[31] Sava, D.F., M.A. Rodriguez, K.W. Chapman, P.J. Chupas, J.A. Greathouse, P.S. Crozier, T.M. Nenoff. "Capture of volatile iodine, a gaseous FP, by zeolitic imidazolate framework-8," *J. Amer. Chem. Soc.*, 2011, *133* (32), 12398–12401.

Molecular Modeling Improves Design of Selective Sequestering Agents

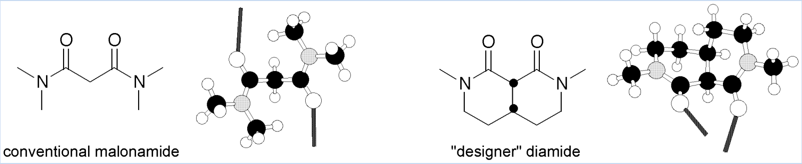
The earliest study (1994–1996; EM-50 funding) using molecular modeling methods for design of sequestering agents focused on optimizing the performance of the SREX reagent. The reagent, di-t-butyl-dicyclohexano-18-crown-6, exists as two regioisomers, and each form has six chiral centers. All 40 possible isomers were evaluated for Sr^{2+} binding affinity and Sr^{2+}/Ca^{2+} selectivity to identify the most effective Sr^{2+} getters. Purification of individual isomers and testing in solvent extraction systems has confirmed these rankings.



Another design goal was to modify the CSEX reagent to achieve enhanced Cs+/K+ selectivity. The effort (1997; EMSP) led to the discovery of a new class of calix[4]crown ethers, derived from 1,3-dideoxygenated calix[4]arene. Experimental surveys demonstrated that the new calix[4]arene architectures display Cs/Na selectivities exceeding 10^6 and Cs/K selectivities exceeding 10^3, tenfold improvements over previously studied calix[4]arene crown ethers. Modification of the CSEX reagent architecture by removal of two alkoxy groups yields a cavity predicted to have enhanced Cs+/K+ selectivity. This prediction was confirmed by experimental measurement.



A final example is provided by diamide extractants for trivalent f-block cations. Structural evaluation of conventional malonamide extractants developed for use in the DIAMEX process revealed the O-donor atoms in these architectures to be poorly organized for complexation. Using structural design criteria obtained from theoretical and experimental data regarding the conformations of amides and metal-amide complexes, an alternative bicyclic architecture was designed and tested. Liquid-liquid extraction measurements with hydrophobic analogs revealed the designed extractant gave a spectacular performance enhancement, exhibiting Eu(III) and Am(III) distribution coefficients *10 million times* larger than obtained using the best engineered malonamide extractant under identical experimental conditions. Aqueous formation constant measurements confirm that the performance enhancement is due to an increase in metal-binding affinity.



As with drug design, current scoring algorithms rely on structure-function relationships, taking advantage of the fact that certain easily computed or measurable candidate properties correlate with the property of interest that may be impossible to calculate with experimental accuracy. Examples include speciation, reaction mechanism, equilibrium constants, separation factors, interphase transport and equilibria, precipitation from solution, micellization, third-phase formation, hydrolysis, radiolysis, and oxidation states. Long-term research toward solving these problems will ultimately entail the development of novel methods and the software to implement them.

2.3 Technical Gaps

Following is a description of the technical gaps and other challenges identified for current separation methods, interfacial systems, and new molecules and materials, including actinide-lanthanide separation, interfacial phenomena, inorganic ion-exchange materials, inorganic membrane materials, polymer-supported complexants, neoteric media, and decorporation agents.

2.3.1 Actinide–Lanthanide Separation

Statement of the problem**:** Minimization of the long-term radiotoxicity of radioactive byproducts of uranium-based nuclear fission depends most significantly on strategies to recycle and transmute transuranic isotopes, most importantly plutonium, neptunium, and americium. Though it is always possible to improve the performance envelope of separation systems, several options are suitable for industrial application to facilitate the management of plutonium and neptunium. Americium isotopes ($^{241/243}$Am) represent a more difficult separation challenge. The chemical similarity between americium, curium, and FP lanthanides is the problem. Though americium offers an intriguing redox opportunity, the upper oxidation states are each strongly oxidizing, hence suffer stability limitations. As a result, group separations (americium/curium from lanthanides) rely mainly on the presence of ligand donor atoms softer than oxygen (nitrogen, sulfur, Cl^-) for preferential bonding with actinides. Both SX and IX methods have been developed, but the continuing global research effort dedicated to this separation attests to the absence of a fully acceptable solution to the problem. In essence, the fundamental feature needed to accomplish this separation is known. A strategy for implementing this chemistry at the production scale remains elusive (though there are some well-developed candidate separations, e.g., SANEX, TALSPEAK, that have potential).

Why this approach is difficult: Several factors contribute to the challenge of accomplishing this separation using soft donor complexants/extractants:

- Because the bonding in most coordination compounds of f-elements is predominantly ionic, soft donor atoms interact weakly with these cations under most conditions, though more strongly with actinides than lanthanides.

- Because the interactions are weak and differences between lanthanides and actinides are subtle, complexants/complexes must incorporate multiple soft donor atoms for adequate separations to be attained.
- Incorporating multiple soft donors results in complex structures that can be expensive and difficult to synthesize.
- The cations are relatively large and so demand a larger binding cavity than most d-transition elements.
- Because the valence orbitals are core-like in their spatial extension, cation-directed valence effects are practically nonexistent—the coordination geometry in complexes is defined mainly by steric effects and coulombic attraction (thus the metal ion cannot assist in defining coordination geometry).
- Both classes of metal ions are strongly hydrated, moderately susceptible to hydrolysis (and so to precipitation of metal hydroxides); thus either aqueous complexants must be used and/or acidic conditions must be maintained.
- Radiation fields can be high, thus consideration of the potential for reagent degradation is essential.
- For SX applications, ligand design must balance sometimes conflicting requirements: phase compatibility, the need for interfacial activity, maintaining rapid phase transfer kinetics, the need for reversibility.

Successful separations have been developed around soft donors in aqueous and organic media—there are potential advantages to either approach. To date, none has been put into practice, though some have been tested at the pilot scale.

Why pursue such a difficult challenge?

- Partitioning and transmutation of the transplutonium actinides reduces the long-term radiotoxicity of the waste from advanced fuel cycles.
- Reduced radiotoxicity increases design safety margins for repositories.
- The alternative redox approach to separating americium from curium and lanthanides is equally challenging scientifically.
- The pyrometallurgical approach has unresolved waste management challenges and is best suited to a fuel cycle based on fast reactors.

What is the science-based approach to development of such reagents?: The science-based approach is to combine lab-scale efforts in organic synthesis with lab-scale studies of separations/coordination chemistry involving trivalent lanthanide and actinide metal ions. Studies with surrogate metal ions can provide valuable information, but the metal ion partitioning studies must be done with representative species. Computational chemistry tools should be employed for the design of appropriate ligand architectures to promote rapid progress toward viable candidate ligands. Characterization studies are based on monophasic and biphasic solution thermodynamics and kinetics investigations complemented by structural studies to establish design criteria for computer modeling of molecular interactions through multi-molecule system performance. As basic studies progress and the properties of new reagents are improved, feedback from process designers should be integrated and reagents/conditions adjusted to develop reagents and processes most suitable for scale-up to application levels. This approach parallels that taken in the extensive European program that has developed the malonamide, BTP, and BTBP extractants and potential SX processes using these extractants. This program still continues to search for improved alternatives to the current best systems.

This approach could be used to examine, prepare, and evaluate a range of complexing agents suggested by past experimental work and augmented by molecular-mechanics-based computational design. The complexing agents could be soluble in aqueous solution, used as phase modifiers, phase transfer catalysts, organic extractants, or specialized reagents suitable for application in neoteric solvents. The basic design criteria can also be employed in the development of cation receptors for polymer-based resin materials. Besides developing extraction ability and selectivity in reagent design, adjusting phase compatibility/solubility control and methods for improving radiation stability should also be considered. Appropriate ligand architectures can also find application in analysis for process control or nuclear materials accountability applications.

2.3.2 Interfacial Phenomena

The transfer of mass to or across phase boundaries is ubiquitous in separations science, controlling kinetics, and often selectivity. In addition, a host of so-called interfacial problems lie at the heart of fouling phenomena that, despite the best attempts at design, can deter or halt progress in scaling-up chemistry in process equipment. Important phase interfaces are listed in Table 1 (Section 1.2 of this appendix). Their atomic/nanoscale reactivity, structures, and transport properties are in general poorly understood, and the lack of fundamental molecular-level understanding of interfacial phenomena has often led to Edisonian approaches to resolving technological challenges related to chemical separations.

The unique properties of fluid–solid interface systems emerge from a complex interplay of short- and long-range forces and reactions among the molecular fluid components, solutes, and substrates. Potential gradients (chemical, electrical, etc.) can be highly nonlinear at the Ångstrom-nanometer scale, leading to unexpected behavior. The finite size, shape, directional bonding, charge distribution, and polarizability of solvent and solute fluid components are convoluted with their ability to reorient, “unmix,” and react with one another and the substrate. The truncated solid surface exposes under-coordinated atoms that drive dynamic interactions with the adjacent fluid by local bond relaxation, charge redistribution, dissolution, precipitation, sorption, and porosity development/destruction.

Following are processes of potential interest that would benefit from a more in-depth probe of fundamental fluid–solid properties in separation science:

- Crystallization of pure mineral phases from supersaturated solutions—a non-energy-intensive separations technology, where solution composition, temperature, pressure, and other environmental parameters can be manipulated to control nucleation and growth rates (e.g., radium sequestration through incorporation as an impurity in a nucleated solid phase).[32]
- Selective sorption of ions onto solid surfaces via control of substrate pore size, surface potential, ion solvation and complexation in solution (e.g., molecular modeling and electrochemical studies indicate that inorganic cations and anions in aqueous solutions show a wide range of diffusion rates in carbon nanopores, and one could conceive of a tailored series of electrochemical capacitor anode/cathode couples that could separate product streams enriched in specific salts)
- Selective transport of ionic and molecular species through nanopores by control of pore size, pore shape, surface functionalization, and manipulation of solvophobic/solvophilic properties of the solvent and substrate (e.g., mesoporous carbon and ceramic films tailored for selective transport of gaseous and/or dissolved species in a wide range of solvents)
- Mobilization and separation of selected species via controlled formation of large molecular clusters, polyatomic ions and colloidal particles, or crystalline nanoparticles, wherein the stability of the macroatomic entities, their morphologies, densities, magnetic and electronic properties, and their transport properties in porous solid substrates can be manipulated by controlling the environmental conditions and/or the substrate/solvent/cluster interactions (e.g., the well-known Al_{13} "Keggin" ion is a more efficient coagulant for water filtration than the more commonly used ferric chloride or aluminum sulfate by up to three orders of magnitude[33]

To better address these challenges, a paradigm shift is needed in the conventional understanding of the fluid–solid interface, away from continuum-solvent descriptions and hypothetical interfacial structures, toward a *quantitative, fully dynamic, and chemically realistic description of the interactions of electrons, atoms, and molecules that give rise to macroscopic fluid/solid interfacial properties.* New experimental (e.g., high-intensity neutron scattering[34]) and

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[32] Curti, E., K. Fujiwara, K. Iijima, J. Tits, C. Cuesta, A. Kitamura, M.A. Glaus, W. Müller. "Radium uptake during barite recrystallization at 23 ± 2 °C as a function of solution composition: An experimental 133Ba and 226Ra tracer study." Geochim. Cosmochim. Acta, 74, 2010: 3553-3570.

[33] Stewart, T. A., D.E. Trudell, T.M. Alam, C.A. Ohlin, C. Lawler, W.H. Casey, S. Jett, M. Nyman. "Enhance water purification: A single atom makes a difference." Environ. Sci. Technol., 43, 2009: 5416-5422.

[34] Kumar, N, P.R.C. Kent, A.V. Bandura, J.D. Kubicki, D.J. Wesolowski, D.R. Cole, J.O. Sofo. "Faster proton transfer dynamics of water on SnO_2 compared to TiO_2." *J. Chem. Phys.*, 134, 044706.

computational (e.g., metadynamics[35]) techniques of fluid–solid interfaces put this paradigm shift within sight.

However, there is a critical need to address the fundamental gaps in our current understanding of interfacial systems and answer these questions of high importance to future energy technologies:

- How does the interfacial region differ in structure, dynamics, and reactivity from the bulk properties of the fluid and solid phases?
- How do these altered properties couple with complex interfacial textures to influence chemical reactions, ionic and molecular transport, and charge transfer within and across the interface?
- How can we control and manipulate interfacial phenomena by informed selection of fluid- and solid-phase components, interfacial geometries, field gradients, temperature, pressure, and other environmental parameters?

These questions, some of which also pertain to liquid–liquid interfaces, permeate the fundamental science needed to solve our nation's long-term energy production, storage, and utilization needs, as described in nearly all of the DOE/BES Basic Research Needs and Grand Challenge reports.

2.3.3 Inorganic Ion-Exchange Materials

Inorganic crystalline oxide materials (e.g., zeolites, molecular sieves, clays, etc.) have chemical, mechanical, and thermal stability that is essential for a number of nuclear-related separation applications. In general terms, separation selectivity is determined by a combination of ion or molecule sorption to pore, chemical bonding inside of pore, and surface interactions between ion/molecule and solvent (e.g., water). Undertaking structure-property relationship studies on nanoporous materials that are selective for ions or molecules provides information as to why their bulk selectivity works. This information is then utilized to tune or design novel, optimized, and improved separations materials that have *high selectivity with high capacity*. Additional challenges arise in tailoring materials for stability and functionality in aggressive media, such as at the extremes of acidity or alkalinity. Moreover, pore structure holds the key to design of materials with adequate kinetics, down to nanometer dimensions.

This is a technical area that can scientifically support fundamental to applied research and the commercialization of products to be used in environmental cleanup, commercial fuel reprocessing, and detection/sensing systems for NNSA applications. Target ions and molecules of interest for EM, NE, and NNSA are very similar, such as cesium, strontium, volatile FPs ($^{129}I_2$, ^{85}Kr, $^{14}C[CO_2]$, ^{3}H), and lesser actinides.

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[35] Stack, A. G., P. Raiteri, J.D. Gale. "Accurate rates of the complex mechanisms for growth and dissolution of mineral using a combination of rare-event theories." *J. Am. Chem. Soc.*, Published on Web, July 1, 2011.

The ability to design a separation material for high selectivity, but also for easy processing, into a durable waste form is highly valuable for NE and EM applications. Targeting waste forms as natural mineral analogs allows for predictive extrapolation of waste form durability. Therefore, advanced planning from the separations stage helps plan for waste form and possible repository needs. Examples of successes in this area are seen in CST for Cs^+ conversion to pollucite,[36] and Sandia octahedral molecular sieves (SOMS) for Sr^{2+} to perovskite[37] and iodate/iodide (aq) to Bi-O-I minerals.[38]

2.3.4 Inorganic Membrane Materials

The synthesis and testing of inorganic zeolite membranes have been intensely studied because of their potential applications in the domains of gas separation, pervaporation, and reverse osmosis, as well as in the development of chemical sensors and catalytic membranes.[39,40,41,42,43] Specifically, researchers are developing new technologies, such as zeolite membranes, for ion separations in aqueous solutions. A successful membrane for the separation of radiological ions from ion mixtures must have both high flux and high selectivity. Inorganic membranes, which have good thermal stability and chemical inertness, are highly attractive. Distinctively, zeolite membranes combine pore size and shape tunability with the inherent mechanical, thermal, and chemical stability necessary for long-term separations. The effective pore size distribution, and hence the separation performance, of a defect-free zeolite membrane is intrinsically governed by the choice of the zeolitic phase.[44,45,46,47]

Membrane development for EM, NE and even NNSA needs might include 1) development of microporous zeolite and clay membranes for efficient ion selectivity in water with a wide range of salt concentrations, 2) understanding of the mechanisms of ion transport in the membranes and the effects of microstructure and material properties on separation performance for guiding membrane improvement and process optimization, 3) evaluation of the membranes for treating

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[36] Balmer, M.L.; Bunker, B. C. “Waste Forms Based on Cs-Loaded Silicotitanates”, Pacific Northwest Laboratory, PNL-SA-26071, 1995.

[37] Nyman, M., A. Tripathi, J.B. Parise, R.S. Maxwell, T.M. Nenoff. “Sandia Octahedral Molecular Sieves (SOMS): Structural Effects of Charge-Balancing the Heteroatomic-Substituted Framework.” *J. Amer. Chem. Soc.*, 124(3), 2002: 1704-1713.

[38] Krumhansl, J.L. and T.M. Nenoff. “Hydrotalcite-like Layered Bismuth-Iodine-Oxides as Waste Forms.” *Applied Geochemistry*, *26(1)*, 2011: 57-64.

[39] Armor, J. N. *J. Membr. Sci.* 1998: 147, 217.

[40] Caro, J., M. Noack, P. Kolsch, R. Schafer. *Microp. Mesop. Mat.* 2000: 38, 3.

[41] Nenoff, T. M., C.M. Aberg, R.J. Spontak. *MRS Bulletin: Membranes for* H_2 *Purification*, 31(10), 2006: 735-741.

[42] Ockwig, N.W. and T.M. Nenoff. *Chem. Rev.*, *107*, 2007: 4078-4110.

[43] Snyder, M. A. and M. Tsapatsis. *Angew. Chem. Int. Ed*. 46, 2007: 7560-7573.

[44] Vroon, Z.A.E.P., K. Keizer, M.J. Gilde, H. Verweij, A.J.J. Burggraaf. *Membr. Sci.*, 113, 1996: 293.

[45] Geus, E.R., M.J. DenExter, H.J. van Bekkum. *Chem. Soc. Faraday Trans*. 88, 1992: 3101.

[46] Bakker, W. J. W., F. Kapteijn, J. Poppe, J.A. Moulijn. *J. Membr. Sci.* 117, 1996: 57.

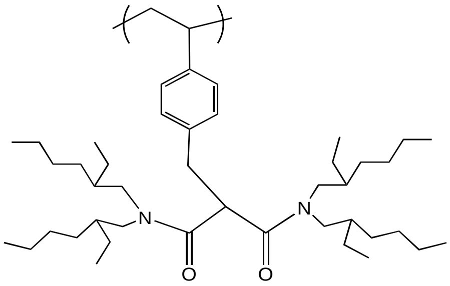
[47] Bai, C., M.D. Jia, J.L. Falconer, R.D. Noble. *J. Membr. Sci.* 105, 1995: 79.7.

radioactive water ion mixtures, and 4) ability to grow selective membranes on sensor platforms (fiber optics, surface acoustic wave [SAW] devices, etc.) for selective, ultra-sensitive and highly accurate responses.

2.3.5 Polymer-Supported Complexants

Structural nature: The application of IX resins to metal ion separations is well known. However, the polymers now being developed for metal ion separations operate with mechanisms that are not solely IX; therefore, the more general term "polymer-supported complexants" is recommended. The polymers are often crosslinked and so may be used in continuous operations within columns; they may also be uncrosslinked in order to be water-soluble, and separations are then achieved when their use is coupled to ultra-filtration membranes. The chemistry of the functional group, and hence the separations achieved, is identical in both methodologies. This discussion will focus on issues involving crosslinked polymers, since they offer a simple mode of operation.

The organic materials that form the basis of polymer-supported reagents are, most often, polystyrene or poly(glycidyl methacrylate), with the former being more versatile than the latter. Phenol-formaldehyde polymers can be used but under more limited conditions. Polypropylene has been underutilized but offers a distinct advantage in achieving rapid rates of loading. A principal reason for the importance of polystyrene is that it can be prepared in the form of beads of a size appropriate for loading into a column for large-scale separations. Its formation from styrene via suspension polymerization is a well-known industrial process. The polymers are crosslinked with divinylbenzene in order to maintain insolubility in the functionalization reactions and the final application. The functionalization reactions covalently bond the ion-selective ligand onto the polymer support. The choice of the ligand is central to achieving the targeted separation. Once loaded with metal ions, the polymer beads can be stripped with an aqueous-based eluent, thus making the polymer-supported complexant regenerable, re-usable, and environmentally compatible. Additionally, polystyrene is not limited to being utilized as beads: the immobilization chemistry remains the same when polystyrene is grafted onto another polymer, such as polypropylene, that can be fabricated as a membrane.



Polymer-supported complexants: A wide array of ligands has been immobilized onto polymer supports and their metal ion affinities quantified through their distribution coefficients. The examples that follow illustrate only a few of the functional groups being studied for actinide and lanthanide separations.[48] Bulky tetraalkylmalonamides have a greater affinity for U(VI) than

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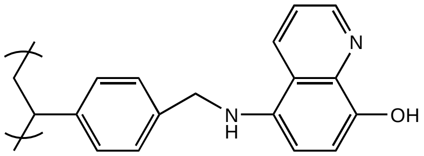
[48] The examples presented are from a review: Yang, Y. and S.D. Alexandratos. "Affinity of Polymer-Supported Reagents for Lanthanides as a Function of Donor Atom Polarizability." *Ind. Eng. Chem. Res, 48,* 2009: 6173–6187. All references may be found therein.

Th(IV) due to hindrance from the alkyl chains towards complexation of Th$(NO_3)_4$. Organophosphorus acids play a central role in SX chemistry, and they have important properties once immobilized onto polystyrene. In one example, high affinity for U(VI) was obtained at low acidities due to a dual cation exchange/chelating mechanism: phosphoryl and carbonyl moieties chelate the uranyl ion, while the phosphinic acid stabilizes the complex through IX. Carbamoylmethylphosphonates and carbamoylmethylphosphine oxides, coordinating complexants known to extract transuranic elements in the TRUEX process, have been immobilized and shown to have affinity for Ce(III), Eu(III), and Yb(III). Polyamino/ polycarboxylic acids such as diethylenetriamine-pentaacetic acid, hydroxamic acids, and hydroxyquinolines form stable chelates with trivalent lanthanides and actinides and are examples of ligands with oxygen and nitrogen donor atoms. Quinoline-8-ol, in which the pyridyl nitrogen and phenolic –OH groups chelate metal ions, has been bound to polystyrene and found to have a high affinity for U(VI) over Th(IV) and La(III).



Uranium from seawater: The problem of recovering uranium from seawater is an important targeted application that encapsulates all of the issues relevant to metal ion separations. The solution is highly dilute; there is a large excess of competing ions; and the uranyl ion is present in the form of a complex with a high stability constant, all of which limit the choice of functional groups to one that is highly selective for UO_2^{2+}. Additionally, its removal from a huge body of water makes the final form in which the ion-selective polymer will be applied particularly challenging, as does the fact that the process must be completely compatible with the environment. Attention has been focused on the amidoxime ligand, which is easily prepared from polyacrylonitrile. However, despite decades of research and impressive progress, a process has not yet been developed that is ready for routine operation. Research is needed into additional ligands and new platforms to deploy the final polymer. The most promising avenues to be explored include diphosphonic acids as the ion-selective ligand and novel methods of functionalizing polypropylene since it can be utilized as a mesh that will operate passively within the ocean currents. Additionally, what is learned here will be applicable to a wide range of separations, including those in environmental remediation.

Issues to be addressed in designing ion-selective polymers for DOE-relevant separations: Through an analysis of metal ion distribution coefficients from research with both soluble and immobilized complexants, four factors have been identified that affect ion–ligand affinities most significantly: 1) the basicity or polarizability of the ligand as compared to the acidity or polarizability of the ion, 2) the solution pH and its effect on protonation of the ligand, 3) association of the metal ion with counterions in solution, and 4) the affinity of the ion for its waters of hydration.

In designing a program with organic materials that will meet DOE needs for targeted separations involving actinides (and the rare earths as well as environmental remediation), the general issue that must be addressed is the need for ligands that are relatively easy to prepare on polymers that achieve rapid rates of loading.

The data suggest that polystyrene-based organophosphorus acids offer the greatest potential for the design of ion-selective resins because of the following characteristics:

- They are readily immobilized on polystyrene.
- They can be prepared proximate to a variety of auxiliary groups that influence polarizability and hence tune their affinity toward the targeted separation.
- The diphosphonates are excellent chelants with high affinities for hexavalent ions over a wide range of solution pH values.
- They can be prepared proximate to a sulfonic acid ligand that enhances the polymer's hydrophilicity and leads to rapid rates of metal ion complexation since the ion does not need to lose its waters of hydration in order to enter the polymer microenvironment.

Moreover, expanding the program to include optimization of grafting reactions onto polypropylene broadens the applications to membranes that can be prepared with high surface areas and thus rapid rates of loading.

2.3.6 Neoteric Media

Despite the demonstrated effectiveness of SX processes employing conventional organic diluents in nuclear fuel reprocessing and nuclear waste treatment,[49,50] there has been a growing interest in the possibilities afforded by less conventional alternatives. In large measure, this interest has been driven by the increasing appeal of processes exhibiting both high efficiency and selectivity *and* minimal environmental impact, a combination of characteristics not readily obtained with traditional extraction systems, which are frequently characterized by the use of toxic, volatile, or flammable diluents. Nash[51] and others[52] have noted that any of several "unconventional" systems, in particular aqueous biphases,[53] solid sorbents incorporating supported extractants,[54]

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[49] Horwitz, E.P., W.W. Schulz. "Solvent extraction in the treatment of acidic high-level liquid waste: Where do we stand?" *Metal Ion Separation and Preconcentration: Progress and Opportunities*. A.H. Bond, M.L. Dietz, and R.D. Rogers, Eds. American Chemical Society, Washington, DC, 1999: 20-50.

[50] Dietz, M.L. and E.P. Horwitz. "Combining solvent extraction processes for actinide and fission product separations." *Science and Technology for Disposal of Radioactive Tank Waste*. W.W. Schulz and N.J. Lombardo, Eds. Plenum Press, New York, 1998: 231-243.

[51] Nash, K.L., G.J. Lumetta, S.B. Clark, J. Friese. "Significance of the nuclear fuel cycle in the 21st century." *Separations for the Nuclear Fuel Cycle in the 21st Century*. G. J. Lumetta, K. L. Nash., S. B. Clark, and J. I. Friese, Eds. American Chemical Society, Washington, DC, 2006: 3-20.

[52] Wai, C.M., A.S. Gopalan, H.K. Jacobs. "An introduction to separations and processes using supercritical carbon dioxide." *Supercritical Carbon Dioxide: Separations and Processes*. A. S. Gopalan, C. M. Wai, and H. K. Jacobs, Eds. American Chemical Society, Washington, DC, 2003: 2-8.

[53] Huddleston, J.G., S.T. Griffin, J. Zhang, H.D. Willauer, R.D. Rogers. "Metal ion separations in aqueous biphasic systems and using aqueous biphasic extraction chromatography." *Metal Ion Separation and Preconcentration: Progress and Opportunities*. A.H. Bond, M.L. Dietz, and R.D. Rogers, Eds. American Chemical Society, Washington, DC, 1999: 79-100.

supercritical fluids (particularly supercritical carbon dioxide, SC-CO_2),[55] or ionic liquids (ILs),[56] may ultimately provide a viable alternative to traditional, aqueous-based actinide and FP separations. At present, however, the need for high salt concentrations to generate a biphase, while acceptable in analytical applications, argues against the utility of aqueous two-phase systems for many large-scale separations.[57] Similarly, despite attempts to improve the physical stability of solid-supported extractants,[58,59] their suitability for process-scale applications remains questionable. In contrast, both SC-CO_2 and ILs, certain drawbacks notwithstanding, appear to offer promise as the basis for new separation schemes for actinides and FPs.

Of these two classes of so-called "neoteric"[60] solvents, supercritical fluids by far constitute the more thoroughly explored "non-traditional" approach to actinide and FP separations, both in terms of the development of workable technology and an examination of the underlying chemistry. It has been known for nearly two decades, in fact, that under appropriate conditions, complexes of various metal ions, including those of interest in nuclear applications, can be extracted into SC-CO_2.[61] In spite of this, a number of important fundamental and applied questions regarding their use remain unanswered, among which are the following:

- Does fluorination represent the most effective strategy for ensuring adequate solubility of extractants and extracted metal complexes in SC-CO_2?
- Does the introduction of silicon-based functional groups into an extractant, which has been demonstrated as a means of improving the SC-CO_2 solubility of one class of extractants (i.e., alkylenediphosphonic acids),[62] represent a "generic" alternative?
- Might increased attention to the design and use of phase modifiers obviate the need for extractant functionalization?

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[54] Dietz, M. L. "Recent progress in the development of extraction chromatographic methods for radionuclide separation and preconcentration." *Radioanalytical Methods at the Frontier of Interdisciplinary Science*. C. Laue and K. Nash, Eds. American Chemical Society, Washington, DC, 2004: 161-176.

[55] Wai, C. M., B. Waller. *Ind. Eng. Chem. Res.* 39, 2000 : 4837.

[56] Dietz, M. L. *Sep. Sci. Technol*. 41, 2006 : 2047.

[57] Nash, K.L. "Twenty-first century approaches to actinide partitioning." *Separations for the Nuclear Fuel Cycle in the 21st Century*. G. J. Lumetta, K. L. Nash, S. B. Clark, and J. I. Friese, Eds. American Chemical Society, Washington, DC, 2006: 21-40.

[58] Alexandratos, S.D. and K.P. Ripperger. *Ind. Eng. Chem. Res.* 37, 2998: 4756.

[59] Dietz, M.L., E.P. Horwitz, A.H. Bond. "Extraction chromatography: Progress and opportunities." *Metal Ion Separation and Preconcentration: Progress and Opportunities*. A.H. Bond, M.L. Dietz, and R.D. Rogers, Eds. American Chemical Society, Washington, DC, 1999: 234-250.

[60] Seddon, K. R. *Kinetics and Catalysis* 37, 1996: 693.

[61] Laintz, K.E., C.M. Wai, C.R. Yonker, R.D. Smith. *J. Supercrit. Fluids*, 4, 1991: 194.

[62] Dietz, M.L., D.R. McAlister, D. Stepinski, P.R. Zalupski, J.A. Dzielawa, R.E. Barrans, Jr., J.N. Hess, A.V. Rubas, R. Chiarizia, C. Lubbers, A.M. Scurto, J.F. Brennecke, A.W. Herlinger. :Recent Progress in the Development of Supercritical Carbon Dioxide-Soluble Metal Ion Extractants: Solubility Enhancement through Silicon Functionalization." *Nuclear Waste Management: Accomplishments of the Environmental Management Sciences Program*, T. Zachry, Ed. American Chemical Society, Washington, DC, 2006: 250-267.

- Given that the stated purpose of employing SC-CO_2 as a substitute for a conventional organic solvent is to devise nuclear separation processes that are more environmentally benign, can the ancillary processes associated with its use (e.g., extractant recycle) also be rendered "greener"?
- Is any process for nuclear separations requiring that high pressures (e.g., 72.9 atm. in the case of SC-CO_2) be maintained *really* viable?

Fundamental questions remain unanswered to an even greater extent for ILs, a relatively new and, in many respects, remarkable class of solvents that have attracted enormous recent interest in a variety of applications, among them nuclear separations.[8] Consideration of the unique physicochemical properties of these solvents, which typically include a near-absence of vapor pressure, the ability to dissolve a wide variety of solutes, and an extraordinary degree of thermal stability, make their appeal in this application readily apparent. Adding to their attractiveness as prospective extraction solvents is the observation that under certain conditions, they can provide extraction efficiencies far exceeding those seen with conventional organic solvents.[63] A number of recent investigations, however, have shown that this increased efficiency frequently comes at the cost of added system complexity. When a neutral extractant is employed with a conventional organic diluent, for example, the extent of extraction of the metal ion of interest is readily controlled simply by changing the aqueous phase anion concentration, as partitioning of a neutral metal complex represents *the* pathway by which extraction occurs. This is frequently not the case for the same extractants in ILs, however, which have been found to function as liquid cation-[64] or anion-exchangers[65] in addition to process solvents, thereby complicating the recovery of extracted metal ions. Adding to the difficulties in applying ILs as extraction solvents is the recognition that complexes not observed in conventional systems may predominate in ILs, further complicating the development of extraction processes based upon them.

Such observations raise a number of significant questions that must be addressed if ILs are ever to provide a basis for viable large-scale separations, among which are the following:

- What processes are involved in the transfer of a metal ion from an aqueous phase into an IL in the presence of various types of extractants, and how can the balance among these processes be controlled?
- To what extent can the behavior of ILs as separations media be understood on the basis of the behavior of conventional separation systems?
- How are the various structural features of ILs related to their performance and utility as media for separations?

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[63] Dai, S., Y.H. Ju, C.E. Barnes. *J. Chem. Soc., Dalton Trans*. 1999: 1201.

[64] Dietz, M. L. and J.A. Dzielawa. *Chem. Commun*. 2001: 2124.

[65] Jensen, M. P., J. Neuefeind, J.V. Beitz, S. Skanthakumar, L. Soderholm. *J. Am. Chem. Soc*. 125, 2003: 15466.

- Is it possible to develop guiding principles for the rational design of IL-based separation systems?

All of these questions, as well as those posed for supercritical fluids, touch upon a number of broader issues, which constitute “grand challenges.” Most notable among these are the following:

- Can molecules and materials (here, solvents) be designed to have predictable properties?
- What is the nature of the interactions of the matrix components with the species of interest in a separation?
- Can the structure of complexes and the thermodynamics of complexation processes involving small donor molecules be predicted in these new media?

Only by answering such questions will the full potential of novel media such as supercritical fluids and ionic liquids in nuclear separations be realized.

2.3.7 Decorporation Agents

Accidental or inadvertent intake of radionuclides from occupational exposure or environmental exposure is a primary DOE concern. The recent Fukushima Daiichi nuclear disaster, the largest nuclear accident since Chernobyl, resulted in the release of large amounts of radioactive materials into the environment. It highlighted the pressing need for the interventional therapies to mitigate the health effects of the internal contamination potentially with multiple radioisotopes. In addition, acknowledged threats involving the potential deliberate release of radionuclides into local environments by terrorists now prompt new concerns and the need for improved methods of removing internally deposited radionuclides; these include chelation therapy, blocking uptake, and accelerating the clearance of ingested or inhaled radionuclides from the body. Effective chelation therapy after internal contamination has been shown to reduce the radiation dose, radiation effect consequences, and in some cases the chemical toxicity associated with internally deposited radionuclides. To date, only a few standard treatments are available for certain radionuclide intakes. Intelligent design of the new decorporation agents will address the DOE/Department of Homeland Security/Department of Defense/Department of Health and Human Services need for effective, selective, orally active, non-toxic, and cost-efficient sequestering agents.

The radionuclides likely associated with nuclear accident and terrorist activities exhibit drastically different chemical and biological properties, depending on their nature, and can be categorized as follows:

- Group 1. Alkali metal ions: ^{137}Cs
- Group 2. Alkaline earth metal ions: ^{90}Sr and ^{226}Ra
- Group 3. Transition metals: ^{60}Co, ^{90}Y, and ^{192}Ir

- Group 4. Actinide metals: ^{241}Am, $^{238/239}$Pu, and $^{238/235/234}$U
- Group 5. Metalloids and mon-metals: ^{210}Po, ^{32}P, and $^{129/131}$I

Radioactive elements of military concern include enriched and depleted uranium, plutonium, tritium, and radium. In addition, misuse or overdose of the nuclear medicine diagnostic agents, such as ^{99m}Tc, ^{99}Mo, ^{111}In, and $^{125/131}$I, is of concern.

Effective chelation therapy using diethylenetriaminepentaacetic acid (DTPA) has been shown to reduce the consequences of radiation effects associated with internally deposited transuranic radionuclides. Properties of the DTPA sequestering agents are summarized in Table 4. Even though CaDTPA has demonstrated high efficacy when administered intravenously within a few hours of actinide intake, it cannot be used for prolonged treatments because it depletes essential biological metal ions from the patients. ZnDTPA has lower toxicity and can be administered over long periods of time at small doses, but is less effective as an immediate post-contamination treatment. DTPA agents have short residence time in the human body and are quickly excreted, exhibit limited biokinetics, and do not access intracellular and bone deposits of actinides. Similarly, hydroxypyridinonate (HOPO) ligands have been shown to be potent chelators for plutonium decorporation.[66] To this end, a number of HOPO ligands have been tested *in vivo*, and selected candidates are currently in pre-clinical studies. Only a few other standard treatments are available, such as potassium iodide for ^{131}I and Prussian Blue (ferric hexacyanoferrate (II)) for ^{137}Cs. Details of these drug therapies for radiation emergencies can be found at http://www.fda.gov/Drugs/EmergencyPreparedness/BioterrorismandDrugPreparedness/ucm063807.htm.

To date, no effective therapies are known for other radionuclides, although it is apparent that different groups of radionuclides will require different synthetic receptors possessing specific functional groups. Often chelators with demonstrated strong *in vitro* affinity to the specific metal ions are unsuitable for the *in vivo* applications due to the high toxicity, fast metabolism, inability to effectively remove a radionuclide from the target organ, or other reason. To this end, availability of decorporation agent design methodology targeting the *in vivo* chelators that not only exhibit high decorporation efficacy but also possess properties compatible with the living organism is of paramount importance to accelerate development of intervention therapies for internal contamination.

Regardless of the route of radionuclide uptake (inhalation, ingestion, or wound), the radionuclide is systemically absorbed at a rate that depends upon the physicochemical form of radionuclide and its solubility in biological fluids, and transported by blood to the target organs (e.g., bone, kidney, liver, etc.). The behavior of a radionuclide in a living organism is controlled by the kinetics and thermodynamics of equilibrium processes, such as the interaction of the

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[66] Gorden, A.E.V., J. Xu, K.N. Raymond, and P. Durbin. “Rational Design of Sequestering Agents for Plutonium and Other Actinides.” *Chem. Rev*., 103, 2003: 4207-4282.

Table 4. Overview of DTPA decorporation properties

Property	DTPA
Mode of action	Chelation
Chemical functionality	Polyaminocarboxylic acid
Biological properties	N/A
Toxicity	Toxic, toxicity reduces in order DTPA > CaDTPA > ZnDTPA, DTPA being acutely toxic.[b]
Target radionuclides	Soluble species of tri- and tetravalent actinides and lanthanides, Co, Mn, Zr, Ru. Cannot be used for uranium contamination.[a] Does not bind Np(V).[c] Not strong enough to solubilize and bind hydrolyzed transuranic elements and subsequently formed colloids and polymers.
Efficacy	Overall high for isotopes of Pu, Am, Cf, Cm. Very efficient when administered within minutes of radionuclide intake. Efficacy rapidly drops within few days after the event of internal contamination.
Length of treatment	CaDTPA can be used only in early treatment up to few days because of its toxicity. ZnDTPA can be systemically used for several years.
Biokinetics	Does not penetrate intestinal epithelium. Being highly hydrophilic, DTPA agents distribute only in extracellular water and cannot interact with intracellular actinide deposits.[e] Unable to remove radionuclides from the bone.[c]
Administration	Intravenous injection, infusion, or inhalation. Local infiltration in wounds. Oral administration is inefficient and is considered only for long-term ZnDTPA treatment.[d]
Contraindications	Kidney, liver, intestinal, haemopoietic disorders. Pregnancy. Not recommended for children.
Availability	Commercially available. Distributed through the national stockpile. Not generally available, particularly in large quantities.

a. Gerber, G.B. and RG Thomas. "Guidebook for the Treatment of Accidental Internal Radionuclide Contamination of Workers." Chapter 6, Methods of Treatment. Radiat Prot Dosimetry, 41, 1992: 27-36.

b. Gorden, A.E.V., J. Xu, K.N. Raymond, and P. Durbin. "Rational Design of Sequestering Agents for Plutonium and Other Actinides." *Chem. Rev*., 103, 2003: 4207-4282.

c. Guilmette, RA, A. Hakimi, P.W. Durbin, J. Xu, and K.N. Raymond. "Competitive binding of Pu and Am with bone mineral and novel chelating agents." *Radiat. Prot. Dosimetry*, 105, 2003: 527-534.

d. Ramounet B., S. Matton, G. Grillon, J.L. Poncy, and P. Fritsch. "Efficacy of Localised DTPA Treatment for Decorporation of Np Injected Intramuscularly as Np(IV) or Np(V)." *Radiat. Prot. Dosimetry*, 79, 1998: 463-465.

e. Taylor, D. M., G. N. Stradling and F. Menetrier. "Biokinetics of radionuclides and treatment of accidental intakes." *Radiat. Prot. Dosimetry*, 105(1-4), 2003: 637-640.

radionuclide with the biological ligands. Understanding the speciation and solution chemistry of the radionuclide *in vivo* is the critical pre-requisite to predict toxicity and to design a successful decorporation agent. For computing binding affinities and dominant speciation of the radionuclide, *in vivo* thermodynamic constants are needed for its complexation with inorganic ligands (e.g., hydroxide, carbonate, phosphate), small organic chelators (e.g., lactate, citrate, etc.), and large biological molecules such as amino acids, proteins, carbohydrates, peptides, and other. In addition, the design of the decorporation agents should incorporate consideration of toxicity and overall safety. Briefly, requirements for an effective emergency decorporation agent include the following:[67]

- High affinity and selectivity toward target multiple radionuclides
- Low toxicity
- High oral activity
- Ability to permeate cell membranes to achieve effective concentration at the site of radionuclide deposition in the target organ
- Ability of metabolites of the chelation agent to retain binding capacity for the radionuclides
- Availability for safe, convenient, and rapid distribution in large quantities to the general public
- Application for both medical mitigation and prophylactic purposes in the event of a nuclear emergency: no additional harm induced

3. OPPORTUNITIES FOR CROSSCUTTING RESEARCH AND PROGRAM PARTNERSHIPS

3.1 Summary of Opportunities for Program Partnerships and Role of Science

Program partnerships: Drawing from the discussion of technology needs (Section 1.4 of this breakout session report), this section identifies key overlaps among EM, NE, and NNSA programs to find potential opportunities for program partnerships. Due to the challenges in developing new technologies, success will depend on a partnership between fundamental science conducted by the DOE Office of Science (SC) and applied science conducted within EM, NE, NNSA, and other agencies both internal and external to DOE.

DOE has recently adopted a model for technology maturation from discovery science through a series of “gates” to higher technology readiness levels.[68] Although this model has proven to be a valuable tool

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[67] Taylor, D. M., G. N. Stradling and F. Menetrier. “Biokinetics of radionuclides and treatment of accidental intakes.” *Radiat. Prot. Dosimetry*, 105(1-4), 2003: 637-640.

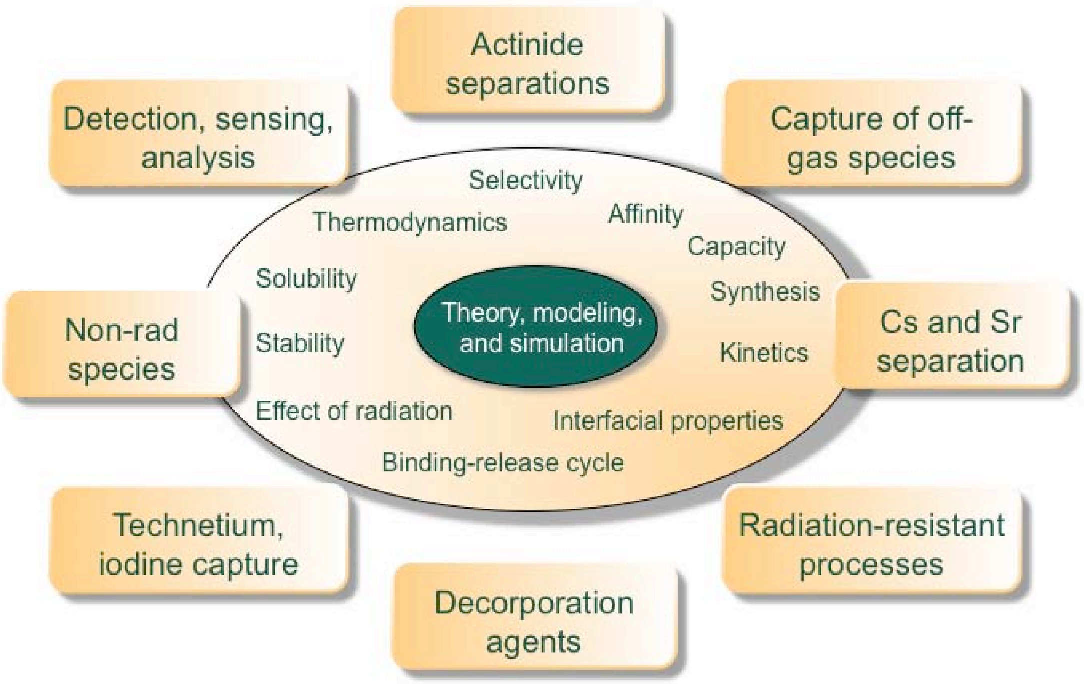
[68] DOE. “Technology Readiness Assessment Guide,” DOE G 413.3-4, 2009.

in evaluating actual technology readiness for deployment or for advancing to the next stage of development, its linearity is not a useful construct for the purpose of visualizing and managing the essential interplay between fundamental science and technology development. Rather, in addressing the myriad diverse technical hurdles summarized in Table 2, applied technology development must continually employ fundamental understanding and often create new fundamental understanding. As the system complexity increases during scale-up, system integration, and demonstration with real process solutions, the chance for discovery and corresponding role for science actually increases. Therefore, the formula for success is a strong and continuing presence of science throughout the technology-maturation process.

In view of the real role of science in technology development, the graphic below summarizes eight areas for potential program partnerships drawing from a core of fundamental science. At the core is theory, modeling, and simulation, entailing both use of and development of directed computational design tools, which is a major opportunity for program partnership in itself. These tools are then used in a design method that must satisfy a series of process needs for optimal molecular or material properties, such as selectivity, rapid kinetics, and stability (see Table 2).

In the rest of Section 3, the elements of the identified opportunities for program partnerships in the figure below are discussed in greater detail.

Opportunities for program partnerships incorporating a central role for science in the design of molecules and materials for the development of new separation processes



3.2 Overlaps in Programmatic Needs Related to Design of Molecules and Materials

Overlaps in programmatic needs can be identified by examining common matrices that must be treated in the separation process or by examining the common species that are targeted for separation. Table 5 lists the various media of interest in separations or in analysis. The media range from the human body to used nuclear fuel (UNF) to specific types of wastes, off-gas, process media, ore, and soils. For each matrix, the programs are listed that have significant stake in technology development. Some matrices, such as tank waste or soils, are primarily of interest to EM, while others, such as gas streams, reprocessing streams (e.g., HLW), and UNF, have broad overlapping interest. Similarly, Table 6 (next page) identifies program overlaps in species targeted for separation, as gleaned from Section 4 of the main body of this report. It is presumed that SC has underlying fundamental impact on, and interest in, all of the matrices and targeted species identified in the two tables.

Table 5. Table of matrices of interest in nuclear separations

Area of Interest	Program				
	EM	NE	NNSA	DoD	DHS
Human body	X		X	X	X
Soil and groundwater	X				
Building materials	X		X		X
Gas streams	X	X	X		
Tank waste	X				
HLW/aqueous	X	X	X		
Low-level solid waste	X	X			
UNF	X	X	X		
Molten salts	X	X	X		
Ore	X	X			
Seawater		X	X		

3.3 Crosscutting Computational Tools for Design of Molecules and Materials

To advance modeling and simulation capabilities to the point where they can provide maximum benefit toward development of highly selective separations processes, sustained and coordinated efforts are needed that couple molecule generation on the computer, scoring algorithms, code development, and experimental data. Existing computational tools and methods should be evaluated for their applicability in deriving structure–function relationships that will allow for rapid screening to identify candidates with desired properties. The focus should be on enabling the selection for experimental development and testing of candidate agents with characteristics that can be applied to separations and detection schemes of interest to EM, NE, and NNSA.

Table 6. Table of target species for separations

Area of Interest	Program					
	EM	NE	NNSA	DoD	DHS	SC
Actinides: U, Np, Pu, Am, Cm	X	X	X			
Volatiles: I, Tc, Cs, Xe, Kr, C, ^{3}H	X	X	X			
Human body contaminants: U, Pu, Ra, ^{90}Sr, ^{129,131}I, ^{137}Cs, ^{60}Co			X	X	X	X
Pyroprocessing/molten salt: U, TRUs, FPs	X	X	X			
^{99}Tc and ^{129}I as ubiquitous contaminants/risk drivers	X	X	X			
Mercury in groundwater, soil, building materials	X		X			X
Cr(VI) in groundwater	X					
^{137}Cs, ^{90}Sr in tanks, soil, groundwater, building materials, off-gas	X	X	X			
Non-rads Al, Na, S, Cr, HNO_3, Be, Zr, Pd	X	X				
^{60}Co in groundwater, equipment, RDD cleanup	X	X	X			

Program partnerships could include the following relevant contributions:

Office of Science:

- Basic Energy Sciences
    - Relationship between molecular structure and physicochemical property
    - Fundamental studies of interfacial phenomena, including transport
    - Fundamental studies of radiation stability
    - Self-assembly as an approach to molecular recognition
- Advanced Scientific Computing Research
    - Translation of new approaches and algorithms for modeling and simulation of complex systems of interest (e.g., scaling, incorporation of quantum calculations)

Office of Nuclear Energy/Office of Environmental Management:

- Agent design improved by computational quantum chemistry and computational thermochemistry
- Applicability of MD simulations for preferential gas sorption, ion exchange predictions, molecular interfacial transport, speciation, and complexation thermodynamics
- Scaling of molecular models for macroscopic predictions of separation kinetics
- Studies of relevant mechanisms in processes

3.4 Opportunities for Crosscutting Research

3.4.1 Design of Process Materials for Technetium and Iodine Capture

As highly mobile, long-lived FPs either as anions or gaseous species, ^{99}Tc and ^{129}I often occur together and contribute to long-term risk in similar ways. Therefore, they represent a dual problem for separation and analysis in many contexts. An opportunity exists to treat the two radionuclides in a program partnership, especially as they might be separated or analyzed together. It is envisioned that the partnership would seek first in a fundamental sense to understand the speciation of the radionuclides, as they can take on different oxidation states, and then to delineate appropriate principles for separations from common types of media (e.g., aqueous, gas, and surfaces). From these considerations, existing separation or analytical agents could be improved upon, or design methodology could create entirely new candidate materials.

3.4.2 Separation Agents for Fission Products ^{90}Sr and ^{137}Cs

Like the dual problem of ^{99}Tc and ^{129}I, separations and analysis of the FPs ^{90}Sr and ^{137}Cs occur together in many contexts and thereby represent another opportunity for a program partnership. Unlike technetium and iodine, however, strontium and cesium exist as well-defined species in most cases (with notable exceptions, such as colloids). Thus, the approaches to separation and analysis may more often be similar; therefore, corresponding design methods for molecules and materials more straightforward. As an example of using a common binding agent, separation from HLW aqueous streams can be accomplished by crown ethers or calix-crowns as molecular binding agents in SX, whereas solid ion-exchange materials can be designed with the same crown ethers or calix-crowns as pendant functionalities. Although efficient separation methods exist for ^{90}Sr and ^{137}Cs in many types of media, the continued emergence of new problems (e.g., soil contamination in Japan) and the need for more efficient methods will drive research and development worldwide for decades to come. Both radionuclides are thought to be tempting for use in RDDs, making their detection and removal from building materials an important problem for future research. In general for NNSA applications, the opportunity reflects the simple need for detection ability with approaching 100% reliability. Finally, another driver lies in the expected efficiency gain in combined separations, either to separate just these two radionuclides or remove them with other radionuclides.

3.4.3 Design of Decorporation Agents

A clear area of emphasis relevant to EM, NE, and NNSA is developing new reagents and materials for decorporation of radionuclides from personnel. The requirements for such reagents are high selectivity for the species of interest, high stability under biological conditions (which include media of approximately 0.5 M ionic strength, 37ºC, and potentially pH ranging from 2 to 10, though most of the important chemistry occurs near pH 7). The target species of concern include all of the most important radionuclides identified above plus selected nonradioactive materials (e.g., mercury). Due to the complexity of molecules that typically survive in biological systems and the systems in which they operate, the molecular design challenge is amplified by the incomplete understanding of mechanisms of metal ion transport phenomena in biological systems. At the same time, there are clear linkages between the sorts of phase transfer phenomena that govern metal transport in biological systems, environmental media, and SX transport systems. Thus, any and all research will be crosscutting.

3.4.4 Design of Binding/Transduction Agents for Detector/Sensing/Analysis

Development of improved materials for analysis, detection, or sensing applications is a major need common to the missions of EM, NE, and NNSA. A selective agent can be deployed to pre-concentrate a solute to increase the sensitivity of an analytical method, or the selective agent can be coupled with a transduction method to directly provide a measure of the concentration of the solute. The applications range from “traditional” analytical chemistry methods, to on-line process monitoring for process control or safeguards, to rapid measurements in the field for environmental or personnel contamination and forensic determinations.

Computational design of more selective separation agents is generally relevant in this crosscutting area, wherein molecular design must couple binding with a transduction function to directly signal the presence of target species. In some cases, this can be rather straightforward, as in the use of colorimetric agents to bind metal ions; and computational methodology can assist, for example, by predicting spectra of metal ions bound to a receptor site. In other cases, the attempt to develop a signal from a host-target system can be problematic. For example, chemically attaching a selective agent to a solid to allow a more convenient and robust platform for analysis can significantly alter the binding of a target species to the agent.

3.4.5 Design of Separations Materials for Capture of Gaseous Species

Gaseous/volatile FPs (principally xenon, krypton, bromine, iodine, tritium, radiocarbon, and under some conditions technetium, cesium) represent a unique hazard in processing of UNF, as these species may be difficult to contain (due to low/no reactivity and the natural dilution associated with the solid-liquid-gas phase transfer process). Separation materials for gaseous species focus principally on sorbents that can selectively capture the targets from a multi-component vapor phase. The potential environmental mobility of such species makes the identification of a stable waste form for long-term disposal a high priority. For some of these species, a combination of oxidation state manipulation, chemical reactivity, and size selectivity offers some promise for sequestration. The low chemical reactivity of the noble gases represents a more difficult challenge. Some of these species are similarly challenging waste management problems in pyrometallurgical processing of used fuel.

3.4.6 Effects of Radiation and Design of Materials for High-Dose Conditions

Radiation damage is an unavoidable feature of any manipulation of radioactive materials. Molecular/materials design can contribute to the creation of more radiation-stable molecular arrangements, but because the energy deposited is typically adequate to break many bonds, it is not possible to design materials that are immune to radiation damage. Research on fundamental effects of ionizing radiation on the properties of complexing agents and separation materials has been done to support the development of new separation processes as a feature of process optimization activities. Identified needs include systematic efforts that include data mining from existing resources, new experimental studies dedicated to process development and to increased fundamental understanding, and computational modeling to provide a robust understanding of mechanistic features. Improvement in this capabilities base will substantially aid reagent/material effectiveness and process applicability. Developing materials that have the potential to be self-healing (or to "spontaneously" reverse the effects of free radical induced degradation) are interesting areas for investigation. Since radiation damage is a universal feature, these issues crosscut the interests of all DOE offices responsible for monitoring or handling radioactive materials.

3.4.7 Separation Agents for Non-Radioactive Species

The suite of nonradioactive species relevant to DOE interests (aluminum, sodium, chromium, mercury, sulfur, phosphorus) must be considered to focus primarily on species of primary concern to EM. The unique chemistries associated with the separation of these species present a variety of uniquely challenging problems, as has been noted in the technology needs discussion of this document (Section 1.4.2, EM, Removal of non-radioactive species from high-level waste). As the interests of NNSA must address issues of misuse of radioactive materials in general, these species may be of some concern to this organization as well. In imagined application of chemical separations in advanced nuclear fuels cycles (of interest to NE), the species in this list of the greatest potential concern would be phosphate, which can exist in process effluents, though typically at much lower concentrations than are seen in EM tank wastes. Actinide-bearing waste forms based on phosphate have been suggested as potential waste forms for managing some wastes from advanced reprocessing schemes.

3.5 DOE Center of Knowledge

Although separation science and technology (SS&T) remains the foundation for energy technology development in the DOE complex, it is perhaps surprising that there is no current mechanism for DOE programs to coordinate and gain synergy from their similar but separate SS&T research activities. Supposing that common problems specifically associated with designing molecules and materials for selective separations could be addressed by pooling resources and expertise, it is expected that an overall more productive and efficient research enterprise would result. At present, any coordination that exists is happenstance, depending primarily on individual investigators seeking impact across programmatic lines on their own initiative. Further, no particular system for evaluating SS&T needs in a sustained manner exists within any DOE program. A litany of "research needs" documents produced in an ad hoc manner for at least two decades points to real programmatic needs and shows that there is a recurring, though fragmented, desire to evaluate these needs within individual programs. The next step that is needed is to coordinate this evaluation process, provide for a mechanism for sustaining it, and seek synergy in research efforts for the strongest possible impact through a DOE center of knowledge in "Molecular Design for Radioactive Material Separations."

In some respects, such a center of knowledge represents a “Back to the Future” movement, as there was once just such a virtual center of knowledge (arguably a center of genius, considering what was accomplished) in nuclear science and technology at the DOE national laboratories in this country. For a revitalization to occur, a virtual center of excellence that recognizes and expands upon the capabilities and talents within the DOE laboratory complex represents a rational approach. The computational resources that have been developed in recent years have advanced considerably, and although plant-scale molecular modeling is not yet possible, important capabilities are in place. Given the limited numbers of Ph.D. graduates being produced in this field in the United States, it is probably also important that the center of knowledge include a clear connection to, and involvement by, the academic community.

For a successful re-invigoration of this field to occur, it is critically important that facilities for the handling of radioactive materials be maintained, improved/upgraded, and expanded. Molecular/material design can only proceed productively with closely coupled computational and experimental programs operating, sometimes in lock step, sometimes at cross-purposes (modeling activities should always be guided to some degree by the skeptics). Without experimental data, computational modeling can follow unproductive, unrealistic, or incorrect pathways that are not consistent with physical science/engineering technology. Molecular/material design may be validated in some cases, at least initially utilizing nonradioactive analog systems (e.g., rhenium for technetium, lanthanides for trivalent actinides), but the ultimate validation requires experimental work with “the real stuff.” In this case, the real stuff is radioactive and so by definition demanding of special facilities like those existing at the national laboratories and a few select universities. This includes not just large-instrument “user facilities” but also laboratories wherein it is possible to work with radioactive materials at a wide range of concentrations, up to and including hot-cell facilities.

The primary vision for a DOE center of knowledge in molecular design is almost certainly a virtual center, located across the laboratory complex and including participants from academia and, as appropriate, from industry. A central “node” in this virtual center could possibly house centralized facilities and coordinating expertise to integrate activities across the complex. However, the strength of the virtual center is to enable the vast resources with the DOE complex and its affiliated research institutes to be brought to bear on the diverse needs for new molecules and materials for separations. This virtual center will thus include facilities and equipment dedicated to work with the radioactive materials, including but not limited to DOE user facilities and computational resources, but will focus most importantly on the scientific and technological interests of experts in the science and technology that supports the objectives of molecular design. The recovery of information “mined” from the open literature and non-classified government research reports maintained in an accessible database would minimize the loss of productive effort repeating quality work—and would represent a valuable resource. Many (but not all) of the large-scale resources (user facilities) are operated by the Office of Science; therefore, this Office’s participation in the center is a rational connection to be made. To the extent practical, it may be advisable for the center to be in communication with international organizations similarly engaged, e.g., Europe's Integrated Infrastructure Initiative for Actinide Science (Actinet), the Japan Atomic Energy Agency, and the International Atomic Energy Agency (IAEA).

Building tomorrow's workforce must also be a high priority, through the support of both academic institutions contributing to development of "isotope experts" and retraining Ph.D. scientists with explicit training in complementary fields but no direct experience with radioactive materials. Funding for sustained research projects commensurate with the typical duration of a Ph.D. thesis is needed to solve the current difficulty in involving academic research participation with short-term project funding. Access to the facilities of the center must be readily accessible. Establishment of an appropriate communication structure should also be a part of the plan. One opportunity for profitable linkages between the DOE laboratory centers and academic/industrial partners will arise in the area of organic/inorganic synthesis, neither of which is represented in depth within the existing DOE complex. Such activities do not necessarily demand direct access to radioactive materials handling facilities; they thus offer an opportunity for synthesis activities to be pursued without the considerable overhead represented by federal laboratory facilities.

In summary, a center of knowledge is envisioned to provide a vehicle for solving real DOE separation problems in the most efficient manner possible, drawing upon the common interests and resources of diverse DOE programs. In terms of design of molecules and materials, the vision shown in the figure in Section 3.1 seeks to bring the tools of science to bear upon definite opportunities for program partnerships. The strength of the center concept lies in its instituted ability to coordinate, direct, and integrate materials design research and development into these opportunity areas.

Appendix C. Breakout Session Report: Scale-up of Separation Processes from Bench-Top to Plant

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1.0 Introduction

This working group focused on the scale-up issues facing the U.S. Department of Energy (DOE) Office of Nuclear Energy (NE), the DOE Office of Environmental Management (EM), and the National Nuclear Security Administration (NNSA) as they advance separations technology from the laboratory to plant scale to achieve their mission goals. This group attempted to identify areas of common need in terms of processes and time frames. In doing so, the group attempted to draw from past successes and lessons from across the DOE complex and from international nuclear industrial experience. The working group addressed certain key questions, including the following:

- “What are the appropriate demonstration levels that must be considered?”
- “What is learned at each step of the scale-up process?”
- “What are the roles of modeling and simulation, and how and when can simulants be used?”

Numerous areas of commonality were identified and potential opportunities for leveraging were noted, along with a need for the preservation of significant bodies of knowledge, expertise, and capabilities from across the DOE complex.

2.0 Needs

2.1 NE Scale-up Needs

It is anticipated that a great deal of scale-up testing will be required to support NE fuel cycle separations in the future. The current focus of the Fuel Cycle Research and Development (FCR&D) Program is science-based, engineering-driven research to better understand potential separation processes as well as identify transformational technologies that could potentially reduce the cost and complexity of advanced processing facilities. As such, there is currently little effort focused on equipment scale-up to support NE.

It is likely that one option for future used fuel separations facilities that process light water reactor (LWR) fuel will incorporate solvent extraction processes to some degree. Much of the equipment associated with solvent extraction processes in the nuclear industry is well understood with regards to scale-up as a result of the decades of experience operating the plutonium–uranium extraction (PUREX) process in the United States and internationally. As advanced separation technologies are developed, however, the scale-up of these specific processes in solvent extraction equipment will be required. This is true regardless of whether pulsed columns, mixer-settlers, or centrifugal contactors are chosen. Data relative to throughput, efficiency, and hydrodynamic behavior of the solutions will be required and must be acquired using engineering-scale equipment, at a minimum.

Processes that have not been implemented industrially, such as voloxidation and electrochemical systems, will require development of specific prototypic equipment and scale-up testing. This could involve engineering-scale testing with simulants and/or material derived from actual used fuel as well as mockup testing of full-scale equipment. The approach taken should build on past experience here in the United States, and international experience and approaches to scale-up of equipment and processes have been demonstrated to be relatively successful; the approach taken should build upon this experience, both positive and negative. If transformational technologies significantly different than current processing technologies are implemented, it is expected that a more rigorous effort to evaluate and understand scale-up issues will be required.

With regards to common areas of interest within NE, EM, and NNSA, there are challenges related to differences in the time frame planned for implementation of process equipment. EM is focused on short-term implementation to support cleanup, whereas NE FCR&D is focused on a long-term solution to the build-up of used nuclear fuel (UNF), perhaps a decade or two in the future. Nonetheless, there are several areas of potentially common interest, including centrifugal contactor design and operation, feed clarification, melter design and operation, and evaporator development. Modeling and simulation is also a common area of interest. For example, computational fluid dynamics (CFD) modeling of centrifugal contactors is supporting centrifugal contactor design for NE and EM. Process modeling tools are also being used by NE, EM, and NNSA to support flowsheet development and material accountability studies.

2.2 NNSA Scale-up Needs

Stated broadly, the mission of NNSA has four primary components (prior to transfer of the EM–to-NNSA oversight):

1. Management of the nation’s nuclear weapons stockpile
2. Operation of the naval reactor program
3. Nuclear nonproliferation and safeguards
4. Oversight and coordination of the safe transport of weapons components

Issues related to separations differ greatly between these focus areas. The fourth area (safe transport of weapons components) does not have the same kind of scaling issues as the other areas, inasmuch as it does not involve chemical processing.

Rather than facing scale-up issues, the stockpile mission of NNSA may be more impacted by scale-down issues affecting component refurbishment and dispositioning tasks. This reflects decreases in required throughput due to the shift in mission from production in support of large (and sometimes expanding) inventories to treaty-mandated stockpile reduction (e.g., downblending and/or preparation for safe, monitored storage). Scale-down in these applications is reflected not only in the downsizing of existing equipment and facilities, but also in the conversion of continuous processes to batch operation, and in the need to address potential changes in performance (particularly separations) that may result. The problem is essentially the same as that of scale-up, only solved in reverse. The need is still the ability to determine or predict the transferability of performance data between facilities of two specific scales.

The avoidance of nuclear criticality and the protection of fissile material are very important considerations in safeguarding any process development activities, at engineering scale or above, that involve fissile material such as plutonium or highly enriched uranium. Consequently, it is essential to incorporate and test sensing equipment and computer data acquisition and interpretation in scaled operations to establish their adequacy. Further, it is necessary to maintain fissile material accountancy both for process control and for detection of unauthorized diversion of fissile material.

Although aspects of this type of material accountability are well established, when new and perhaps radically different processes are brought online, it will be necessary to reevaluate existing sensor materials by using related equipment. Computer modeling of the systems, both with respect to individual process steps and integrated systems, is an essential and well-established approach to maintaining accountancy.

Nuclear nonproliferation and safeguards missions raise distinctly different issues. Key components of nonproliferation include detection of clandestine fissile material processing facilities, evaluation of unconventional (nonindustrial) technologies and processing pathways, and characterization of materials generated by these alternative technologies. These tasks include detection of activities directed toward pursuit of a long-term weapons capability in International Atomic Energy Agency (IAEA) declared or undeclared facilities operated by nation or state actors, and detection of materials processing in very small (bench- or pilot-scale) installations intended for short-term, small-production use. The most cost-effective means for establishing signatures and demonstrating detection capabilities is testing that utilizes full-scale, fully operating facilities. In reality, the number of processes of potential interest to proliferators is too large, and access to operating facilities may be too limited to permit this approach. Consequently, the evaluation of processes at some reduced scale is generally required.

The chief consideration to be applied in this context is the same as that for any chemical process; the reduced-scale process must produce results that are representative of the facility of concern. Nonproliferation interests include speciation of products, formation of by-products, interaction of reagents and products with process and environmental contaminants, and transient behavior. Therefore, issues to be considered in scaling include fidelity of materials transfer operations (e.g., hydraulics), chemical reaction kinetics (including mass transfer operations involving speciation), and use of materials (reagents, materials of construction, and likely contaminant sources) identical to those present in the facility of concern. Due to the wide variety of chemistries involved and the range of equipment types that could be used, determination of scale is a function of both the specific unit operation and type of data that is desired. For example, if the desire is to determine equilibrium speciation of nuclear materials free of chemical contaminants, any experiment conducted at the appropriate stoichiometry, temperature, pressure, and atmosphere will suffice. If transient behavior including speciation effects from chemical contaminants is of interest, great care must be exercised to perform testing under conditions identical to those at the scale of concern.

2.3 EM Scale-up Needs

The EM program has many engineering process scale-up needs. Scaling up the processes will be constrained by timing and budgetary considerations. Notwithstanding these considerations, there are a large number of processes and equipment pieces that require testing and scale-up, some at several levels of scale-up. EM is dealing largely with first-of-a-kind plants, limiting availability of lessons learned from previous plants. Each tends to be somewhat unique, with different waste streams based on the site history. The scale-up needs are confounded by the wide variety of tank waste materials and uncertainty in their physical and chemical properties. Designing processes and scaling them up is complex because of the wide variability in the streams to be processed and the potential need to test many compositional variations of feeds in the laboratory to accurately simulate what is going to happen in-process. Consequently, a very ambitious program would be required to meet the scale-up needs. For the present workshop, no attempt will be made to address the very large programmatic commitments, time constraints involved, and budget requirements for meeting the scale-up needs.

The following is a discussion of examples of important scale-up requirements for some of the processes under consideration for use. In particular, site scale-up requirements for the Hanford site are addressed.

Storage Tanks

The waste storage tanks contain a mixture of soluble salt solids, insoluble sludge solids, and aqueous solutions. The solids depth ranges from inches to several feet, and the solids include particles and agglomerates with a wide range of sizes and densities. When wastes from different tanks are blended before transfer to the vitrification plant, new solids may precipitate, some immediately, some over a period of time. Historically, such processes as dissolution with hot water or acid, mixing with in-tank horizontal jets, and sluicing have been used, although this is not an exhaustive list. Avoiding selective sedimentation of heavy solids is important because local accumulations of plutonium oxide could pose a criticality problem. In addition, radiolysis and chemical reactions produce hydrogen and other gases, so flammable gas risks may be present both before and during waste transfer and mixing.

The primary need is to assess the adequacy of mixing and mobilization; secondarily, there is a need to evaluate the potential for additional solids being contributed by precipitation in blended wastes and for flammable gas release during mobilization. Important physical phenomena and properties include particle settling under mixed and unmixed conditions, particle agglomeration rates, multiphase flow under transient conditions (rotating jets, active sluicing), and rate of mobilization of solids beds under those same conditions. Laboratory-scale tests can provide information on (for example) particle settling under simple, easily defined conditions, the solubility of species in blended wastes, the kinetics of precipitation, and the shear stress required to mobilize solids. Translating these properties into predictions of full-scale mixing and mobilization is likely to require tests at more than one scale. Computer simulations that account for the phenomena could reduce the number of different scales that require testing. Because it is difficult to design simulants to simultaneously represent all waste properties, tests that use actual tank waste in small-scale processes could produce significantly more meaningful results (particularly for settling) than would simulants.

Vitrification Plant

After wastes are transferred to the vitrification plant, the solids of greatest concern are typically sludges. The key process steps are keeping the slurry mixed, taking representative samples to support processing decisions and assess possible criticality issues, transferring sludge slurries within the plant, and being able to re-mobilize cohesive and non-cohesive sludge layers in tanks after postulated off-normal mixer shutdowns. Pulse-jet mixing has been chosen as the primary mixing and mobilization process, with air sparging also being planned for mixing in tanks that are expected to contain the more non-Newtonian sludges. As in the Hanford waste tanks, it is important to avoid conditions that allow selective sedimentation of heavy solids, retention of flammable gas, and plugging of lines and equipment. Conditions that produce corrosion of vessels, equipment, and lines and shorten plant lifetime must also be avoided.

Scale-up testing and/or simulation are needed to evaluate the potential for flammable gas retention and rapid release in sludge wastes, assess the adequacy of mixing and mobilization, confirm representativeness of sampling, and define the measurements needed for process control. Important physical phenomena and properties may include corrosion chemistry and kinetics, particle settling under both mixed and unmixed conditions, multiphase flow under transient conditions (pulse-jet mixing), non-Newtonian rheological properties of slurries, mobilization of solids beds using jets (possibly of non-Newtonian fluids), and solids cohesive properties that contribute to plug formation. As for the waste storage tanks, a combination of multi-scale testing, simulations, and small-scale testing with actual waste would be the most effective approach.

K-Basin Storage

In the K-Basin, uranium-containing sludges are stored in containers. Hydrogen is produced in the stored sludge, with potential accumulation in vessel-spanning bubbles that could rapidly release hydrogen and produce flammable concentrations in the vessels. Fins on the vessel walls have been proposed as a way to direct gas to the surface as it is generated, preventing accumulation. Scale-up testing and/or simulation are needed to evaluate the potential for flammable gas retention and rapid release in the sludge in the vessels. Important physical phenomena and properties include movement of gas in pores and gas percolation through channels and waste mechanical behavior as gas accumulates in pockets or layers.

Next-Generation Melters

As the first-generation waste melters reach the end of their useful lives, they will be replaced by new melters. These new melters may not be the same type or size as the melters they replace. New melter types and sizes will require scale-up testing and/or simulation.

Solids Filtration

Filtration of a very wide variety of solid suspensions will be required. Cross-flow filtration is proposed for this operation because of its resistance to plugging and fouling. This type of filtration will need to be tested on several scales on solids representative of the solids to be filtered. At Hanford, a pretreatment engineering platform (at 1/4.5 scale) was constructed that employed cross-flow filters to pilot the operation of the Waste Treatment Plant (WTP) using a single simulant. Over the course of the mission, the plant will process waste tanks with a wide spectrum of solids composition and rheological behaviors. These tanks contain multiple layers of various wastes, and some have not been sampled. Therefore the need to anticipate issues, at scale, before they are encountered by the WTP will persist throughout the WTP mission.

Pretreatment Plant Processes

Several different separations processes will be carried out in pretreatment facilities. Testing at several scales of the individual process steps and of the processes integrated to study process interactions will be required. Examples of processes include the removal of aluminum, removal of chromium, and separations of actinides.

Transfer Line Plugging

Slurries of mobilized solids will need to be transferred from waste tanks to process feed tanks and from there to process equipment. The possibility exists that the solids may settle out in transfer lines, causing line plugging and requiring extensive, expensive, and time-consuming line clean-out. Certain solids can produce gels that contribute to line plugging. Appropriate simulants will need to be developed and tested for transfer characteristics and adequacy in representative pumping and piping equipment. Methods of unplugging transfer lines will need to be tested in prototypic systems at several scales to be employed in the various transfer lines.

Common Scale-up Needs

Common to all of these mission needs is the requirement to move technology from the laboratory to plant scale. The specifics of the separations technology being developed to meet the mission needs will be described in other sections of this report. These technologies may be evolutionary or revolutionary in nature. Table 1 provides an overview of the types of technology needs that exist and are being developed to support the mission needs of EM, NE and NNSA.

Table 1. Overview of Separations Technology Scale-Up Needs

Technology	NE	NNSA	EM
Mixing	X		X
Melter	X		X
Solid/Liquid Separations	X	X	X
Off-Gas Separations	X	X	X
Extraction Processes	X	X	X
Liquid/Solid Transfer	X		X
Testing Sensors on Scaled System	X	X	X
Instrumentation, Analytical	X		X
Electrochemical Systems	X	X	

Conceptually, scale-up is relatively simple. Engineering principles are applied to a chemical or physical process to increase its throughput to achieve a desired plant capacity. However, we are dealing with very complex chemical matrices and with phenomena that are not yet fully understood in all cases. For example, the design of the Defense Waste Processing Facility

(DWPF) began with small-scale melters and went on to the one-third-scale Integrated Defense Melter System (IDMS) to test phenomena that would not be manifest in smaller-scale testing. In particular, noble metal particles would accumulate at the bottom of the melter and short out the melter at larger scale but not at small scale. Phenomena such as these are best identified when there is a clear mission need and a well-defined flow sheet.

In general, the practical process problems are affected by multiple physical phenomena that scale differently and that must be understood individually before their combination can be understood. In any given test, only one or two phenomena at a time can be considered. This was the case, for example, in the Hanford pretreatment engineering platform testing. As a further practical point, the use of simulants is generally necessary, but the scaling of their properties is difficult, as is finding and combining constituents to produce the desired properties.

Finally, in many cases, new technologies are being coupled with existing technologies and may result in some unexpected behaviors. As a result of all these factors, the scale-up process is very complex and must be tailored to a specific situation; no single standard approach fits every application.

2.4 What are the Appropriate Scale-up and Demonstration Levels?

Discussion: It is very important to first determine what the scale-up goals are. For example, it may be important to have a pilot plant or demonstration plant that is large enough to provide material that may be needed for other parts of fuel cycle development. For example, if it is desired to obtain enough actinide elements to produce targets useful for determining nuclear physics data needed for actinide burn-up calculations, then a different scale of operation may be needed than that required for demonstrating new separations processes or product purity. One should establish scale-up goals that will meet as many aspects as practicable of the entire fuel cycle’s needs so as to avoid unnecessarily duplicative activity. This activity may be greatly enhanced by appropriate modeling (see discussion below).

Scale-up is not a series of well-defined steps. Rather, it is a continuum with overlaps between one scale and the next. Demonstration of some processes and equipment at a small scale may be adequate for the design and construction of the largest plant. With this in mind, scale-up should be performed at the smallest scale in which the needed data can be obtained.

The scales needed are quite specific to the particular set of processes that are being developed. Voloxidation is a good example. In terms of overall process performance and fission gas release, only limited data can be obtained from non-radioactive testing; tests must be run with irradiated fuel. Full scale is not required to develop a gas-release thermal profile, so an intermediate scale can be used for process development. But there are other areas that require full-scale testing with inactive materials, such as the temperature profile across the unit at full gas flow. Generally full-scale tests are not done with fully active materials because flexibility is drastically reduced. Physical changes are difficult to make because of contamination or safety controls, criticality can become a factor because of the presence of fissile materials, and significant quantities of radioactive waste are typically generated. While there are exceptions, generally a larger-scale active test should not be conducted until the process has been fully defined.

2.5 Sequencing of Scale-up

Discussion: The scale-up strategy must be consistent with the type of data that is desired. The data is situational; it depends heavily on the flowsheet and the plans for operation (the safety basis). Therefore, providing any general guidance is very difficult. Generally speaking, scale-up proceeds from laboratory (or bench) scale, to pilot (or engineering) scale, to demonstration (or prototypic) scale, to full scale (when a final large-scale plant is envisioned). Other possible ways to define scale are relative to final throughput of the facility. Laboratory scale may be regarded as 1/100,000 to 1/10,000 scale; pilot scale may be 1/1,000 to 1/100 scale; and demonstration may be 1/100 to 1/1 scale. This is a prudent sequence of scale-up when a very large plant is envisioned that helps guard against unpleasant surprises and expensive retrofitting.

But there really is no one-size-fits-all approach to scale-up. If applicable scale-up information is available from elsewhere, then it may be possible to skip or simplify one or more scale-up steps. It is best to carefully determine the number of scale-up steps needed to ensure successful scale-up based on already available scale-up information and on process complexity and novelty. The number of scale-up steps depends strongly on the goals established for each level of scale-up. The more goals addressed at each scale-up, the fewer scale-up steps are likely to be needed. What data are needed for the scale-up of each specific unit operation is going to vary. Based on chemical engineering experience, it is known that some things scale better than others. There are many factors that come into play; for example, kinetics becomes very important in some of the more novel separations, particularly for liquid–liquid extraction in a centrifugal contactor rather than a mixer-settler.

2.6 How Many Steps of Scale-up Are Needed?

Discussion: As already noted, several scale-up steps may be required, depending to a significant extent on the anticipated size of the large-scale plant relative to the size of the pilot plant or the demonstration plant, as well as the complexity and novelty of the processes. If the processes use separations reagents (e.g., extractants that have never been used in large plants on a continuous operating basis), then several stages of scale-up may be needed to unearth subtle but important factors such as reagent consumption or radiation damage leading to adverse chemical reactions in the process, problems in recycle, or excessive waste volume. Smaller-scale plants should be operated for a sufficient time period (as determined by the process) for subtle adverse effects to become apparent.

2.7 Process Considerations/Issues

Discussion: There are issues that arise with full-scale plants that do not necessarily show up during the operation of pilot plants or demonstration plants because of the smaller amounts of material being handled in these plants. This is due to a variety of factors, such as shorter operating times and differences in materials used (for example, use of simulants). Issues such as crud formation, process upsets, solvent and reagent recycle, and inappropriate inter-stage surge capacity have all been observed to cause problems in large plants in the past. These potential issues arising from scale make the selection of an appropriate scale-up factor very important. Large plant operating experience should be used as a guide in selection of the proper scale-up factor for the smaller plants so that the problems noted above will be apparent and solutions for them can be built into plant operation.

The duration of pilot plant testing also depends somewhat on the history of the process being developed. If it is an evolutionary process, a modification to an operational industrial plant, then the need for long-term testing is less. If it is a revolutionary (transformational) process, then the need for long-term testing is much greater. Even in the case of well-established and understood processes such as PUREX, issues still arise with process changes, and operational knowledge is still being gained. For most new processes, aside from generally applicable plant design experience, there is no industrial process basis.

There is a distinct advantage to active testing at a smaller scale: off-normal events can deliberately and safely be induced to examine potential excursion in concentration, pressure, or temperature—something that would not be allowed at a larger scale.

The duration of tests is a key factor in the scale-up process. Large-scale operations facilities face both acute and chronic problems. Chronic problems include third-phase build up, cruds, wear, erosion, fatigue, and corrosion. Often, scale-up is focused on acute problems. But it is the chronic problems that usually impact plant operations. Extended tests are required to learn what long-term issues come up from routine operations and how the system responds to changes, upsets, and multiple cycles. In an extraction or ion exchange process, for example, solvent or ion exchange resin degradation in a radiation field can significantly impact separation efficiency; similarly, conditions under which formation of precipitates in pipes and tanks occurs can be determined best through term operations. The entire process, with all recycle lines, must be operated on a continuous basis long enough to see these effects because they may determine long-term performance.

Large-scale operations facilities face both acute and chronic problems

Improvement to long-term scale-up testing capabilities would be of benefit. While there are accepted methods for certain types of accelerated testing (e.g., accelerated corrosion tests and accelerated radiation stability tests), not all degradation processes can be effectively accelerated with current methods. This is particularly true for combined effect.

2.8 Use of Simulants

Discussion: Simulants in laboratory studies, in engineering-scale tests, in pilot plants, and in cold testing of large plants can be useful when the process or operation being simulated is not critically dependent on specific chemical or physical properties of the simulants vis-à-vis those properties of the real material. On the other hand, there are many separations processes and operations in which simulants may give poor or misleading results. Scale is important in this regard, as is test duration. Factors such as radiation damage to solvents or hydrolysis may be very important. While radiation damage and hydrolysis on uranium or most fission product extraction, or on hydrodynamics, can be simulated fairly well with a gamma irradiation loop (such as the MARCEL loop in France or the irradiation loop at INL), the impacts of degradation products on some specific elements (e.g., neptunium and technetium) are difficult to simulate because they produce effects that are not seen when using cold stimulants. There is no good way to simulate the behavior of neptunium in the PUREX process; lanthanide separation from actinides similarly cannot be simulated; and rhenium is a poor simulant for technetium in some valence states; the chemistry of ruthenium is very complex in the spent fuel.

There are also a number of potential issues that can be readily evaluated with cold simulants: hydraulics, heat transfer, weight, stress, mechanical, altering of solids. For certain key process behaviors, a simulant will be sufficient. In plants at all scales, it is possible to use un-irradiated uranium as a simulant for used or spent fuel when studying hydraulic and equipment behavior.

No matter how good the simulants are, there are always unknown issues that arise. Often, there are unexpected interactions simply because there are components in feed that were not put into the simulant either because their presence was not known or they were considered relatively unimportant. They are later shown to be important. The use of simulants is valuable and cost-effective, but the limit and underlying assumptions used in the simulants must be understood when extrapolating the results.

An example where issues arose is the in-tank precipitation process (ITP) at Savannah River Site. Scale-up was done on very small scales with simulants that did not adequately represent the real materials. The filtration process was “successfully” developed and demonstrated at a small scale, but when it was run in a cold-type test at a larger scale, there was a reaction that created tar that fouled filters nearly beyond recovery. Other issues arose from the separate development of the cesium precipitation process using sodium tetraphenylborate, separate development of the monosodium titanate sorbent for strontium, and the coupling with the filtration process. Ultimately the ITP process was abandoned in 1998 because of the production of a larger volume of flammable benzene than was expected.[1] Running these coupled tests is best, as the interfaces between unit operations can pose chemical or hydraulic problems, etc.

2.9 Modeling and Simulation

Discussion: With the introduction of very sophisticated modeling and simulation computer models, it is possible to calculate mass and energy balances, to simulate time-dependent phenomena, and to provide visual representations of separations processes. These very powerful tools can help to

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[1] *Alternatives for High-Level Waste Salt Processing at the Savannah River Site*. Washington, DC: National Academies Press, 2000. <http://www.nap.edu/catalog/9959.html>

design and optimize separations processes and equipment; elucidate scale-up issues; and provide information on product and waste stream volumes, radioactivity content, and nuclear criticality potential. On a more fundamental level, modeling can guide separations reagent design and efficacy. Continued development of new and better computer models and simulation codes is needed. A comprehensive and vigorous experimental program should be established to provide the necessary data for computer model code development, validation, and implementation. The importance of strengthening these capabilities has been shown in France; in well-understood situations, these capabilities have allowed a step in scale-up to be skipped. The Advisory Committee on Nuclear Waste and Materials of the Nuclear Regulatory Commission[2] identified the following research needs relevant to modeling and simulation of reprocessing systems:

- Knowledge of the split of each chemical species in each process step in the plant (the separation factors), especially concerning tritium, iodine, technetium, neptunium, and radioactive material associated with the cladding.
- Developing a model that simulates the interconnected equipment in a facility flowsheet using the separation factors to determine the radionuclide concentrations and inventory. Such models need to accommodate complexation, colloids, internal recycle streams, and important conditions in bulk fluids (e.g., temperature, acidity, radiolysis).
- Understanding stability of organic extractants, solvents, and ion exchange materials and the safety implications of degradation product.

A 2006 workshop co-sponsored by NE and the Office of Science's Advanced Scientific Computing Research[3] program focused on modeling and simulation related to advanced nuclear energy systems. The workshop identified the following challenges:

- Plant-scale simulation
  - Integrated tool set to enable full-scale simulation of a plant—chemistry, mass transport, energy input, and physical layout
  - Dynamic plant models
- Computational fluid dynamics
  - Multiple fluid phases, fully developed turbulence, non-Newtonian flows, interfacial phenomena, and radical chemical processes due to the presence of ionizing radiation
- Predictive methods for thermodynamics and kinetics data as input to process simulators
  - Extend currently limited thermodynamics data reliably into broader parameter ranges
  - Incorporate limited experimental data and use computational chemistry

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[2] Offices of Nuclear Energy, Office of Advanced Scientific Computing Research, and U.S. Department of Energy, *Workshop on Simulation and Modeling for Advanced Nuclear Energy Systems.* Washington, DC: U.S. Department of Energy, 2006. <http://www-fp.mcs.anl.gov/anes/SMANES/gnep06-final.pdf>

[3] Croff, A. G., R. G. Wymer, L. L. Tavlarides, J. H. Flack, and H. G. Larson. *Background, Status, and Issues Related to the Regulation of Advanced Spent Nuclear Fuel Recycle Facilities—Advisory Committee on Nuclear Waste and Materials White Paper*, NUREG-1909. Washington, DC: U.S. Nuclear Regulatory Commission, 2008. <http://www.nrc.gov/reading-rm/doc-collections/nuregs/staff/sr1909/index.html>

- Rational design of the separations system from first-principles physics and chemistry
  - Predict what molecules will have the desired properties and can be synthesized
  - Reliably predict the properties of liquids, solvation, and kinetics in solution
- Connecting/crossing time and length scales, with uncertainty quantification
  - Access longer times without dramatic changes in theoretical and algorithmic approaches
  - Span spatial regimes; critical regime is the mesoscale (1 nanometer [nm]–1 micrometer [µm])
- Data management and visualization
  - Capture, manage, integrate, and mine data from a wide range of sources to enable the optimal design and operation of separation processes

Simulants and simulation both allow the selection of certain phenomena and the drawing of insights to guide design and experiment. Comparison of model/simulant results with data from actual materials may indicate good agreement, but often these do not agree completely. When this happens, it is critical to understand what was causing the different behavior. This can lead to improved models and simulants and a better understanding of the process itself. A recent MIT report[4] pointed out that "ultimately there is no substitute for testing to validate or disprove the conclusions of simulations. The testing time frames are long and thus the need for long-term research programs with appropriate irradiation facilities."

> **"All models are wrong, but some are useful."**
>
> *George Box*

In addition to process modeling of the plant chemistry models, systems models can aid in understanding interplay of the specific facility with the rest of the complex in which it functions. Often local changes to a process or facility to optimize performance or a specific output can have a detrimental effect on the operation of other processes or facilities in the overall system. For example, introduction of a sulfur-bearing reagent to aid extraction can reduce the durability of a waste form produced from the effluent. Models can be used to evaluate these interactions, for very complicated systems where impacts are not direct or obvious.

2.10 Scale-up and Risk Reduction

The purpose of scale-up testing is to provide additional technical information to reduce project risk and mature a technology to a point where design information can be provided or the technology can be transferred to a commercial entity for implementation. "Technical readiness levels" is a methodology adapted by DOE from a National Aeronautics and Aviation Administration (NASA) methodology to assess the relative technical maturity of a technology. In very general terms, technology readiness levels (TRLs) of 1–3 reflect the development of technical concepts (or research phase), TRLs of 4–6 reflect proof-of-principle testing (or development phase), and TRLs of 7–9 reflect proof of process performance (or demonstration

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[4] Massachusetts Institute of Technology, *The Future of the Nuclear Fuel Cycle*. Boston: Massachusetts Institute of Technology, 2011. <http://web.mit.edu/mitei/research/studies/nuclear-fuel-cycle.shtml>

phase). A TRL of 9 implies full-scale demonstration/implementation of a technology using actual feed materials. A TRL of about 7 is required to have sufficient detail on a technology to enable design activities as well as reduce technical risk to a level where commercialization by industry would be appropriate. As stated previously, there is no one-size-fits-all approach to scale-up, and technical risk can differ for technologies based on past experience. For example, scale-up of a new solvent extraction process, which takes into account over 60 years of industrial-scale equipment development and operational experience, would be much different than scale-up of a novel transformational technology that has no historical experience base. In the case of the latter, more testing would be required at prototypic or pilot scale, for longer periods of time and with actual feed materials, than for the former.

Table 2 gives some general principles of TRLs for separation processes, up to where the technology would be ready to support design activities or commercialization (i.e., TRL 7). Scale-up attributes include research transition from simple simulants to actual materials, from laboratory testing (glassware) to full-scale equipment testing, from testing single-unit operations to integrated testing, and from testing of short duration to testing (of at least some aspects of the technology) for extended time periods. It should be noted that the TRL levels are not well-defined, discrete steps, but rather a continuum of levels with some overlap. They are intended to represent general development stages and are somewhat subjective.

2.11 Mechanical Aspects of Scale-up

In the later stages of equipment scale-up, the integration of remote maintenance aspects must be considered. There is a considerable amount of this specialized knowledge to draw upon within the DOE complex that has been developed first in the defense processing facilities and later applied to DOE, NASA, and other DOE facilities, such as the Spallation Neutron Source (SNS), and fusion facilities. Remote maintenance capabilities facilities and systems should include:

- Improved remote viewing (cameras in hot cell)
- Computer-controlled remote handling systems (cranes and manipulators)
- Standardized equipment module design to facilitate replacement, repair, and reconfiguration of process equipment
- Dedicated support areas for remote maintenance of both process and handling systems
- Dedicated mock-up area for new equipment testing (both operational and maintenance)

3-D virtual design aides should be considered for the interface of the facility and process equipment. Studies can be conducted with these models to better understand both operational and maintenance attributes. NE should draw on the experience of EM staff for the backend cleanup of reprocessing facilities (and similar plants) and the wastes generated as well as waste disposal requirements (configuration, storage, etc). NNSA experience on proliferation issues, systems, and resistance configuration requirements should also be integrated into remote design concepts.

Table 2. Relationships of Scaling and Technology Readiness Levels (TRLs)

TRL	Descriptive Terms from TRA Standard[a]	Scale[b] of Testing or Demonstration Implied by TRA Standard	Level of Integration of Components	Simulants vs. Real Radioactive Materials	Type of Data Expected	Length of Testing and or Process "Run"[c]
1	"basic technology" and "process principles"	Paper and laboratory scale (i.e., test tube)	None	Simulants[d]	Chemical performance	Short tests in laboratory
2	"equipment and process concept"	Laboratory scale (batch testing)	None	Simulants with tracers	Chemical performance	Short tests in laboratory
3	"equipment and process analysis," "proof of concept in a simulated environment"	Laboratory scale (batch and limited continuous)	Single-unit operations	Simulants with tracers	Chemical performance, laboratory-scale equipment and process	Short tests in equipment
4	"lab-scale testing of similar equipment," "in a relevant environment"	Laboratory scale (continuous)	Single-unit operations	Simulants to limited testing with actual materials (laboratory)	Equipment performance and process refinement	Equipment tests of short to medium duration
5	"bench scale equipment" "process testing," "demonstration in a relevant environment"	Laboratory scale to engineering scale (continuous)	Single-unit operations to coupled (integrated) unit operations	Simulants at engineering scale plus actual feed materials at bench scale	Equipment and process integration and operational	Equipment tests of medium duration with targeted testing on long-term effects
6	"prototypical engineering scale equipment," "process testing in a relevant environment"	Engineering (pilot scale) to prototypical scale (continuous)	Coupled-unit operations	Simulants at engineering scale plus actual feed materials at bench scale	Process performance and operational	Equipment tests of longer duration to begin to define operational parameters
7	"full-scale, prototypical system," "in a relevant environment"	Full scale continuous	Coupled-unit operations	Simulants at full scale plus actual feed materials at bench to engineering-scale	Operational performance and procedures, safety basis	Equipment tests of sufficient length to fully define operational parameters

a. Scaling and testing terms taken from the description of the TRL, in DOE Guide 413.3-4.

b. There was significant discussion of how to determine scale, when the final size of a facility may well be unknown; thus, some parameter other than equipment size may need to be used, such as throughput or batch size.

c. Length of time at various stages may be dependent, in part, on the level of "novelness" of the process being developed and the variability of feed expected, along with whether flexible outputs are anticipated. It can also depend on the time period you have to develop your answer.

d. Simulants refers to both chemical and physical property simulation. Simulants depend on the thermodynamic, kinetic, and hydrodynamic data needed; early stages may use a number in different tests, while process-based tests may require more complex simulants covering a broader spectrum of attributes. Also, if feed material for a process is variable, more simulants may be required.

3.0 International Aqueous Separation Scale-up Experience

There is a great deal of international experience relative to the scale-up of solvent extraction-based separations processes. This includes scale-up of the PUREX process to support the Thermal Oxide Reprocessing Plant (THORP) separations facility in the United Kingdom and the approach utilized by the French Alternative Energies and Atomic Energy Commission (CEA) for the scale-up of PUREX and other novel solvent extraction processes being developed in France. These approaches have been demonstrated to be successful and serve as guide for scale-up testing requirements for advanced separation facilities designed and constructed in the United States. A description of the processes utilized in the United Kingdom and France are provided below.

3.1 CEA, France

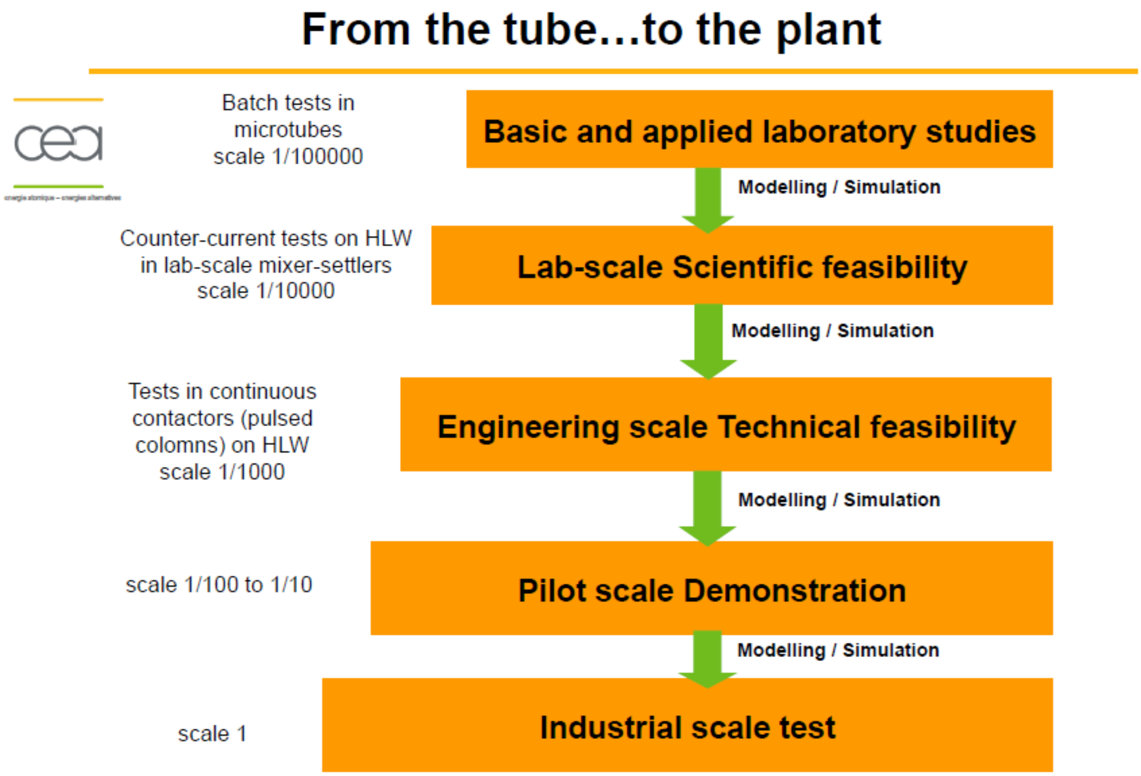
The CEA Marcoule design approach relative to scale-up is based on back-and-forth iterations between modeling and basic laboratory studies, integration active tests in hot cell facilities, inactive tests, and characterization of industrial equipment in order to build simulation codes that allow a correct scale-up of the process from the test tube to the plant. As shown in Figure 1 from CEA, the development of a new process should undergo the following steps (and the corresponding approximate scales):

- Basic and applied laboratory studies (scale 1/100,000)
- Laboratory-scale scientific feasibility (scale 1/10,000)
- Engineering-scale technical feasibility (scale 1/1,000)
- Pilot-scale demonstration (scale 1/100 to 1/10)
- Industrial-scale test (scale 1)

After selecting the appropriate extracting system, accurate and parametric experimental data (thermodynamics, kinetics, physical properties, and solvent degradation) must be acquired at laboratory scale (batch test tube) to develop a first model which is used to design process flowsheets. Counter-current tests are then performed on surrogate and genuine solutions, in laboratory-scale mixer-settlers, in order to demonstrate the validity of this model and the feasibility of the concept (in terms of recovery and purification performances). Then, continuous contactors (pulsed columns) are used to check the compatibility of the extracting system with the continuous equipment in terms of hydrodynamic and transfer kinetics. At Marcoule (Atlanante-CBP facility), 15-mm pulsed columns can be used to perform the test on a high-level waste (HLW) solution and demonstrate the technical feasibility at the engineering scale.

The scale-up of the contactor (from the Φ15 mm to the Φ900 mm industrial size, in the case of pulsed column) is an important step and needs a full characterization of the equipment and of the

Figure 1. Typical scale-up sequence



emulsion in this equipment (drop size, phase transfer efficiency, dispersion coefficient, and so on) in order to correctly model the scale-up. Moreover, intermediate tests can be carried out on a section of the industrial column on an inactive or uranium surrogate solution to validate the hydrodynamic behaviour at scale 1. However, depending on the confidence level of the simulation and the knowledge, expertise and industrial feedback on this equipment, this intermediate step could be skipped. The scale-up of the centrifugal contactors used in the plutonium purification cycle at UP2-800/R4 (La Hague plant) is a good example to illustrate the method. Several tests were performed in the Atalante facility on laboratory-scale centrifugal contactors; thanks to a good modeling of the phase transfer efficiency and the physical characteristics of the phases in the laboratory-scale contactors, these tests enable reaching a scale factor of 100 from Atalante to La Hague plant. Figures 2 and 3, provided by CEA, show the types of data collected at various levels of scale-up.

In dealing with nuclear materials, the impact of the radiolysis on the solvent must also be carefully studied, understood and scaled up. Assessment of the long-term solvent behaviour in an irradiation loop (MARCEL loop) is very useful to check the resistance of the solvent under a continuous run of hydrolysis and radiolysis and to evaluate the performance of the solvent cleanup and the potential impact of the degradation products on the hydrodynamic and recovery performances. The degradation products and their behaviour in the plant must be identified and quantified. The impact of the water-soluble degradation products on the fission products' concentration must be carefully studied at a representative scale with regard to the safety of the process. The impact of new complexing agents (added at the stripping steps in particular) on the actinide conversion, or the possibility of destroying them prior to vitrification, should also be taken into account in the demonstration of the overall process.

Finally, the synthesis of a large quantity of extracting (or complexing) reagents and the adaptation of online analysis for new processes (pH, for example, for actinide/lanthanide [An/Ln] separation processes) are other key points to consider in the industrialization process. The recent experience in France with the development and installation of the cold crucible induction melter at La Hague showed the benefit of using a team with a combination of scientists, technologists, operators, and maintainers all involved from the beginning. Technology was developed with operators engaged; when they did the scale up, the team running the program ended up installing and running the technology in the La Hague plant.

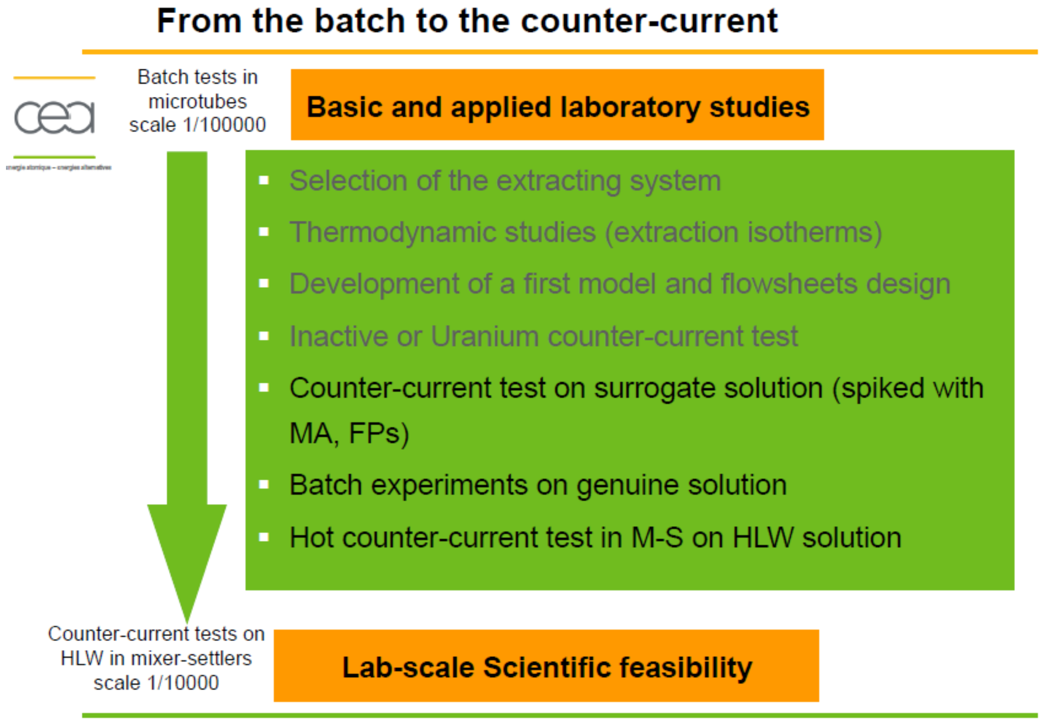
3.2 THORP Separations Facility, United Kingdom

In conducting research, development, and demonstration work for the United Kingdom THORP project, British Nuclear Fuels Limited performed a large scientific and engineering development program against defined plant requirements across very wide subject areas in a progressive manner to optimize project and operational costs and minimize risks. Scientific data, trials, and results of mechanistic and process modeling were required to support design, confirm operability, and underpin safety cases.

Most THORP development work was “warm” (chemical separations) or “cold” (mechanical). The principal “hot” rig was the “highly active miniature pilot plant,” with a processing capability of 1 kg heavy metal (HM)/day of irradiated LWR or advanced gas-cooled reactor fuel. This bench-scale facility (10-mm diameter pulse columns, 2-m height, plus small mixer-settlers) had a throughput scaled down by 1/6,250 compared to THORP. It confirmed the complete chemical flowsheets for several fuel types but did not demonstrate process integration and control. It possessed a relatively low TRL. There was a similar “warm” rig that did not use active fission products.

For the chemical separations flowsheet, the majority of research and development experimental work was performed using miniature and engineering-scale pulse column equipment with “warm” (e.g. U, HNO_3, TBP/OK and/or selected components of neptunium, plutonium, technetium, nonradioactive fission product simulants at various concentrations with low penetrating dose) feeds. This was carried out iteratively in conjunction with modeling studies and supported by existing know-how and engineering assessments. This commenced early in the development cycle and extended over most of the cycle because of technical “surprises.” It was combined with very limited “hot” (i.e., high active using spent nuclear fuel) miniature flowsheet confirmation tests. Some testing was “cold” (i.e., using nonradioactive process simulants).

Figure 2. Scale-up from engineering technical feasibility scale to pilot or industrial scale



From the batch to the counter-current

Batch tests in microtubes scale 1/100000

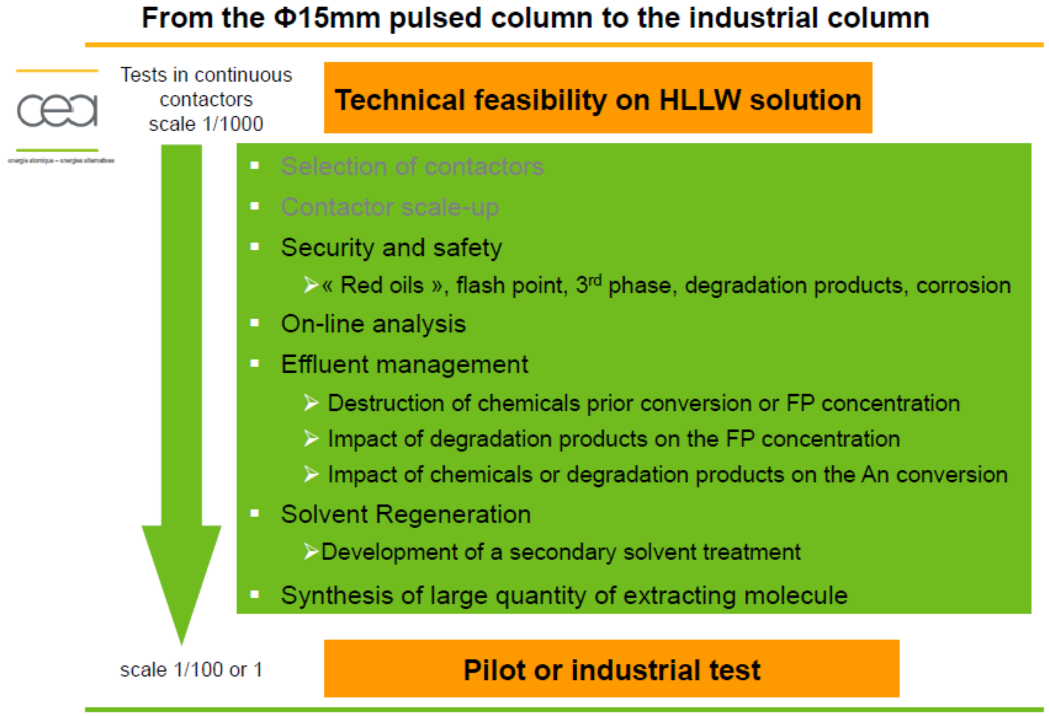
Basic and applied laboratory studies

- Selection of the extracting system
- Thermodynamic studies (extraction isotherms)
- Development of a first model and flowsheets design
- Inactive or Uranium counter-current test
- Counter-current test on surrogate solution (spiked with MA, FPs)
- Batch experiments on genuine solution
- Hot counter-current test in M-S on HLW solution

Counter-current tests on HLW in mixer-settlers scale 1/10000

Lab-scale Scientific feasibility

Figure 3. Scale-up from fundamental laboratory to feasibility studies



From the Φ15mm pulsed column to the industrial column

Tests in continuous contactors scale 1/1000

Technical feasibility on HLLW solution

- Selection of contactors
- Contactor scale-up
- Security and safety
  - « Red oils », flash point, 3^{rd} phase, degradation products, corrosion
- On-line analysis
- Effluent management
  - Destruction of chemicals prior conversion or FP concentration
  - Impact of degradation products on the FP concentration
  - Impact of chemicals or degradation products on the An conversion
- Solvent Regeneration
  - Development of a secondary solvent treatment
- Synthesis of large quantity of extracting molecule

scale 1/100 or 1

Pilot or industrial test

Chemical separations process equipment and control was developed and tested using uranium active pulse column engineering-scale systems. Effects of deviation from flowsheet conditions and recovery were investigated to support preparation of safety case and operating documentation. The strategy sought to separate engineering, hydrodynamics, and mass transfer effects of major “warm” species from the chemical interactions of minor fission product “hot” species with each other and process reagents such as reductants. Mechanical equipment units in THORP, generally, were “cold” tested (i.e., using nonradioactive simulants), developed, and finalized using full-scale items. The onus is then on development of realistic simulants using post-irradiation examination, modeling, sample irradiations, and laboratory-scale radioactive tests. However, this full-scale work was plant-specific and performed in the later part of the plant development cycle. No full-plant integrated mock-up engineering facilities were used prior to the construction of the full production plant, although many key equipment areas were tested at full scale or engineering scale.

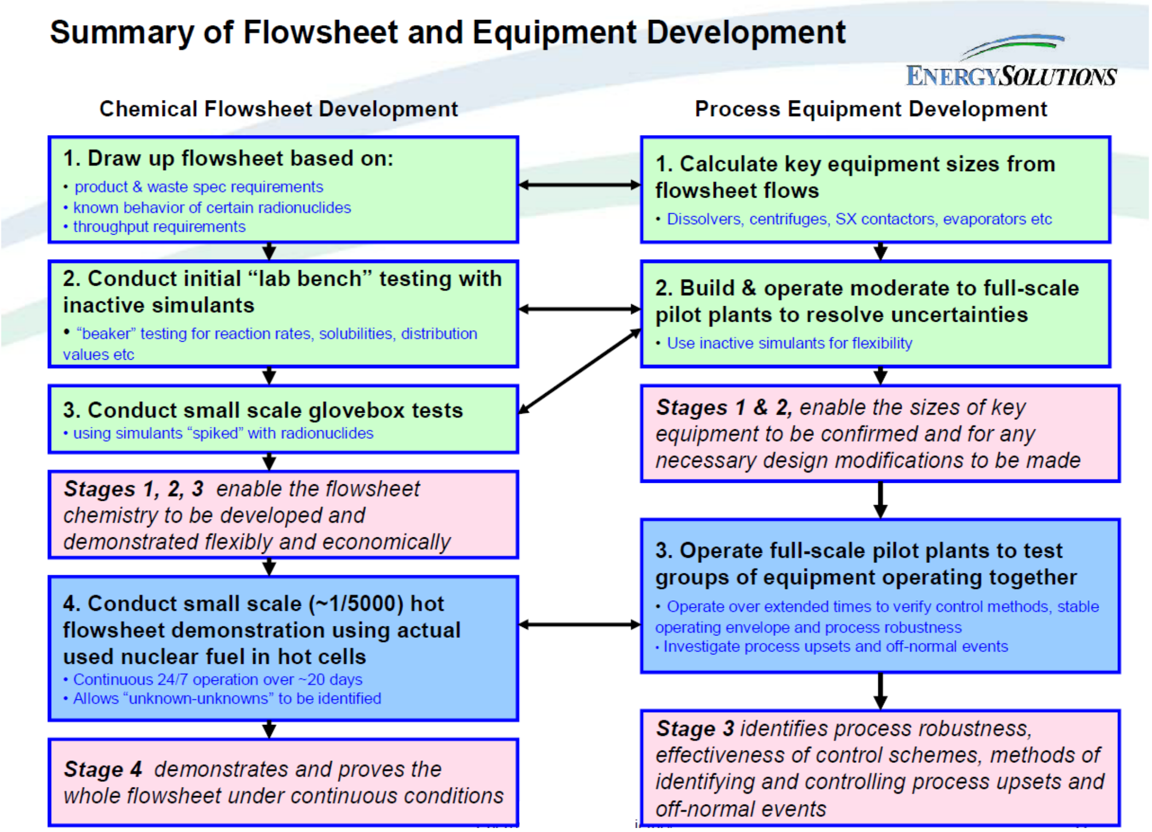
In a 15-year program for THORP development, the use of “hot” (high active using spent nuclear fuel) testing of full-scale or engineering-scale equipment was avoided on engineering, economic, and regulatory grounds. (The exception was active trials of the monitoring of intact spent nuclear fuel assemblies within pond.) However, the selected process flowsheet chemistry was an advancement of existing PUREX and operational know-how, and applicable experience was available from ongoing commercial reprocessing plants in the United Kingdom and France. Development activities were not undertaken within a production plant, although operational data and experience were analyzed and used.

For THORP, extensive cold testing of full-scale industrial units against clear and optimized commercially based reliability requirements was essential. The lack of reprocessing plant standardization, long chains of operations, complexity of individual operations, and zero-maintenance design for high active solvent extraction created the imperative for high equipment dependability. High-integrity engineering design for nuclear and nonnuclear systems is fundamental to reaching the target reprocessing throughputs, given the likely extreme outages for equipment rectification or replacement and the integral effects of failures in tightly coupled nonnuclear support systems.

A 1/6,250-scale fully active “hot” pilot plant was built and operated, supported by a separate “warm” 1/250-scale facility that scaled up the process chemistry from the hot plant and carried out unit operations. Most scale-up was associated with unit operations and full-scale work with uranium. The extensive background that already existed with the PUREX process was very useful in helping determine what scale-up was required. A similar background does not exist for the new processes being considered by EM.

Figure 4 presents a summary of the general approach to flowsheet and equipment development and scale-up as provided by Energy Solutions.

Figure 4. Approach to scale-up at THORP separation facility in the United Kingdom



Summary of Flowsheet and Equipment Development

ENERGYSOLUTIONS

Chemical Flowsheet Development

1. Draw up flowsheet based on:
- product & waste spec requirements
- known behavior of certain radionuclides
- throughput requirements

2. Conduct initial "lab bench" testing with inactive simulants
- "beaker" testing for reaction rates, solubilities, distribution values etc

3. Conduct small scale glovebox tests
- using simulants "spiked" with radionuclides

Stages 1, 2, 3 *enable the flowsheet chemistry to be developed and demonstrated flexibly and economically*

4. Conduct small scale (~1/5000) hot flowsheet demonstration using actual used nuclear fuel in hot cells
- Continuous 24/7 operation over ~20 days
- Allows "unknown-unknowns" to be identified

Stage 4 *demonstrates and proves the whole flowsheet under continuous conditions*

Process Equipment Development

1. Calculate key equipment sizes from flowsheet flows
- Dissolvers, centrifuges, SX contactors, evaporators etc

2. Build & operate moderate to full-scale pilot plants to resolve uncertainties
- Use inactive simulants for flexibility

Stages 1 & 2, *enable the sizes of key equipment to be confirmed and for any necessary design modifications to be made*

3. Operate full-scale pilot plants to test groups of equipment operating together
- Operate over extended times to verify control methods, stable operating envelope and process robustness
- Investigate process upsets and off-normal events

Stage 3 *identifies process robustness, effectiveness of control schemes, methods of identifying and controlling process upsets and off-normal events*

The necessity for fully active demonstration was influenced by a number of factors:

- The plant was supported by a wealth of technical experience gained from the operation of historical commercial reprocessing facilities on the site.
- The PUREX process upon which the plant was based was already understood.
- Most scale-up issues were associated with the engineering performance of the unit operations that could be replaced by full-scale inactive or uranium-active rigs.

The challenge faced in the United States to provide a 21st century recycle facility is compounded by the absence of the first two of the above factors. There is very limited commercial-scale civil recycle heritage in the United States, and any nonproliferating, partitioning flowsheet is both more complex and less proven than the standard PUREX technology. These issues are likely to result in an enhanced need for fully active demonstrations for a U.S. deployment—possibly at significant scale, depending on the technology adopted. Throughputs and decontamination factors will have to be confirmed and experience gained through the operation of such representative pilot facilities before full-scale deployment is attempted.

Beware of making adjustments to what are thought to be well-known processes

Based on its experience in scale-up, France would not change its methodology. The PUREX process is working quite well. If France built another plant with the same technology once equipment is proven at the engineering scale it could move directly to the industrial scale. On the process side, they might do technetium scrubbing differently. In the current plants, France had not seen that there was an extraction of technetium with zirconium in the scrubbing section. This was observed later during pilot plant testing. But by the time it was understood, it was too late into plant construction, so they implemented an alternate solution using another process to provide improved scrubbing for technetium. This was implemented at both La Hague and Rokkasho.

The United Kingdom would potentially have conducted more scale-up trials. Their facilities contain a high inventory of material, and with advances in online monitoring and spectrometry, there ought to be wiggle room to reduce the inventory size at the plant (and hence the costs), but these must be demonstrated. The United Kingdom also expressed caution about the need to beware of making adjustments to what are thought to be well-known processes. The United Kingdom experienced trouble in areas in which slight adjustments to well-known processes were made, but no additional R&D was performed on the modified process. More often than not, the adjustments had deleterious unintended consequences that far outweighed the intended improvements.

4.0 Recent U.S. Scale-up Experiences

The caustic side solvent extraction (CSSX) process is currently being implemented by EM for separation of cesium from salt waste at the Savannah River Site. Development of the CSSX process started with basic laboratory-scale testing using simulants. This led to batch contact testing using actual solutions in the proposed salt flowsheet under extraction, scrub, and stripping conditions. Radiolysis testing was then performed using a five-centimeter (cm) centrifugal contactor with a cesium-spiked solution. Complete flowsheet testing with actual waste was then performed using laboratory-scale 2-cm centrifugal contactors. Performing the tests with laboratory-scale contactors was necessary in order to minimize the amount of feed solutions needed and the amount of waste generated, both of which would have provided serious handling issues. These tests resulted in construction and operation of a pilot-scale separation process for operation of the CSSX process with actual tank waste solution. It should be noted that the goal of this pilot-scale testing included the operational goal of processing solution from several tanks to generate needed space. This was the primary driver in building a “hot” pilot-scale process prior to construction of the full-scale facility.

The importance of performing pilot-scale work using a combination of simulants and “real” materials has been illustrated several times within EM. The DWPF at the Savannah River Site was a first-of-a-kind facility that began radioactive operations in 1996. This operation was preceded by about five years of start-up testing of structures, systems, and components. The start-up testing was preceded by a decade of testing at the Savannah River National Laboratory on systems of various size and complexity, including operation of a 1/3-scale nonradioactive melter system known as the IDMS. The IDMS ran for a period in excess of five years during construction of the DWPF and provided an important platform for testing and design concept verification. Examples of some of the data collected include system qualification data in support of the following:

- Tank mixing and sampling
- Glass flow and mixing in the melter
- Canister welding and decontamination
- Overall process flowsheet development and demonstration

The operation of the IDMS led to several important discoveries that were factored into the design process for the DWPF and were essential to the successful start-up testing program and operation of the DWPF. These included the following:

- Determination that hydrogen modifications were needed in the facility prior to radioactive start-up that would have been significantly more costly after start-up and/or led to operational safety issues
- Data related to melter off-gas flammability calculations that was collected during melter pilot testing and serves as the technical basis for the facility documented safety analysis

The large integrated pilot capability provided by the IDMS was dismantled after start-up and has been replaced by a number of smaller unit operations that are less costly than integrated pilot capabilities but still offer the benefits of larger-scale systems when integrated with bench-scale and real-waste testing.

A second key example that clearly points to the need for extensive scale-up testing and proper simulants involves the WTP at Hanford and the use of pulse jet mixers (PJM). *"Issues were identified related to mixing system designs that will result in insufficient mixing and/or extended mixing times. These issues include a design basis that discounts the effects of large particles and of rapidly settling Newtonian slurries. There is also insufficient testing of the selected designs."* [5]

A recent review by the Consortium for Risk Evaluation with Stakeholder Participation (CRESP) points out that *"uncertainty will remain about PJM performance until extensive experience has been gained through testing of full-scale or near full-scale prototypic PJM vessels and actual operation of the WTP. The current absence of full-scale or near full-scale testing presents a*

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[5] Massachusetts Institute of Technology, *Comprehensive Review of the Hanford Waste Treatment Plant Flowsheet and Throughput*, CCN 132846, v. <http://www.em.doe.gov/pdfs/final_ert_review_of_eac.pdf>

large risk for the WTP program. A second large source of uncertainty that will impact WTP performance are the characteristics of the actual waste feed to WTP.” [6]

4.1 Center of Separations Knowledge

There currently exists a significant body of knowledge and expertise within the DOE complex that must be preserved in order to support the long-term mission needs of the Department. This includes not only the information and data captured in formal reports but a wealth of knowledge, experience, and lessons learned during the development of isotope recovery processes and nuclear operations that reside in the collective knowledge of current and retired staff. The latter has proven to be particularly difficult to capture and is best developed through actual hands-on experience and learning. In addition to the data and experience that exists, a number of critical demonstration capabilities should also be preserved because of their value as test beds for future scale-up operations and for training new personnel.

Any center created is more likely to be virtual than a brick-and-mortar type institution. The distributed model makes sense because of the different capabilities and expertise that exist at various institutions within the Department, within industry, within academia, and internationally. The appropriate functions of the center need to be defined in detail, but issues to consider include:

- Facilities and capabilities that need to be preserved for scale-up activities in the future (dependent on the technologies to be scaled)
- Facilities integral to ongoing operations of the Department (where possible, these ongoing operations should be leveraged against data needs and requirements to generate data and experience that will advance future Department missions)
- Institutionalization of systems and processes that help “pass on” the experiential knowledge in the nuclear processing community
- A very strong connection to the university programs to preserve the needed disciplines of radiochemistry, process engineering, and “radiochemical engineering” that are currently struggling in today’s university environment
- A mentoring program to get people into the field

The Nuclear Stockpile Stewardship program is a possible model for the center. What helped make the Nuclear Stockpile Stewardship program work was that all interested stakeholders were involved in scoping the solution and a model was developed that “forced” organizations into a collaborative mode.

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[6] The Consortium for Risk Evaluation with Stakeholder Participation III, *CRESP Review Team Letter Report 7 – PJM Vessels.* Nashville, TN: CRESP, July1, 2010. <http://www.cresp.org/CRESPIII_reports/CRESP_Review_Letter_Report_7_Final%20_%207-1-2010.pdf>

5.0 Findings and Recommendations

1) There are a number of specific common areas between NE, EM, and NNSA to explore in the near term. These include the following: improving solid–liquid separations processes, off-gas systems, evaporation systems, de-nitration systems, and melter/immobilization/stabilization systems.
2) Scale-up, whether of unit operations, integrated processes, engineering demonstrations, pilot plants, or full-scale demonstrations must be very carefully considered with respect to scale-up goals. Goals may be of the following types:
    - Demonstrate unit operations on the appropriate scale, which can be a fraction of full scale or, when necessary, full scale.
    - Demonstrate that integration of the component parts of a separation process can be functional and seamlessly integrated.
    - Demonstrate that a scaled version of an engineering process is of an adequate size to meet not only the immediate process objective but also the goals of other programs that may rely on output from the process demonstration.
    - Establish the utility of simulant or surrogates to reproduce the desired characteristics of feeds to the process being investigated.
    - Demonstrate the appropriateness and efficacy of process monitoring and control instrumentation.
    - Demonstrate the validity of fissile materials accountancy instrumentation or other equipment related to recording, evaluating, and informing fissile material flow and handling irregularities.
    - Provide verification and needed improvement to computer models of the process.
3) As the scale-up cycle progresses (see Figure 5), ensure that the development team has carefully considered specific scale-up goals and that these goals are reflected in design specifications for construction of test equipment at each step of the scale-up process. Also ensure that the contractor that builds the equipment fully understands the functional requirements of the equipment and the need for adhering to design specifications.

4) Scale-up operations can provide both data and experience for larger-scale future facilities and operations while also addressing a current mission need. For example, the operation of the Modular Caustic-Side Solvent Extraction Unit at Savannah River Site is accomplishing an important mission need (i.e., generating tank space) while providing a radioactive test bed and data for the design and construction of the larger-scale Salt Waste Processing Facility.

5) Provide for flexibility in the scaled-up process. This will allow process upsets and unexpected process difficulties requiring some process changes to be accommodated.

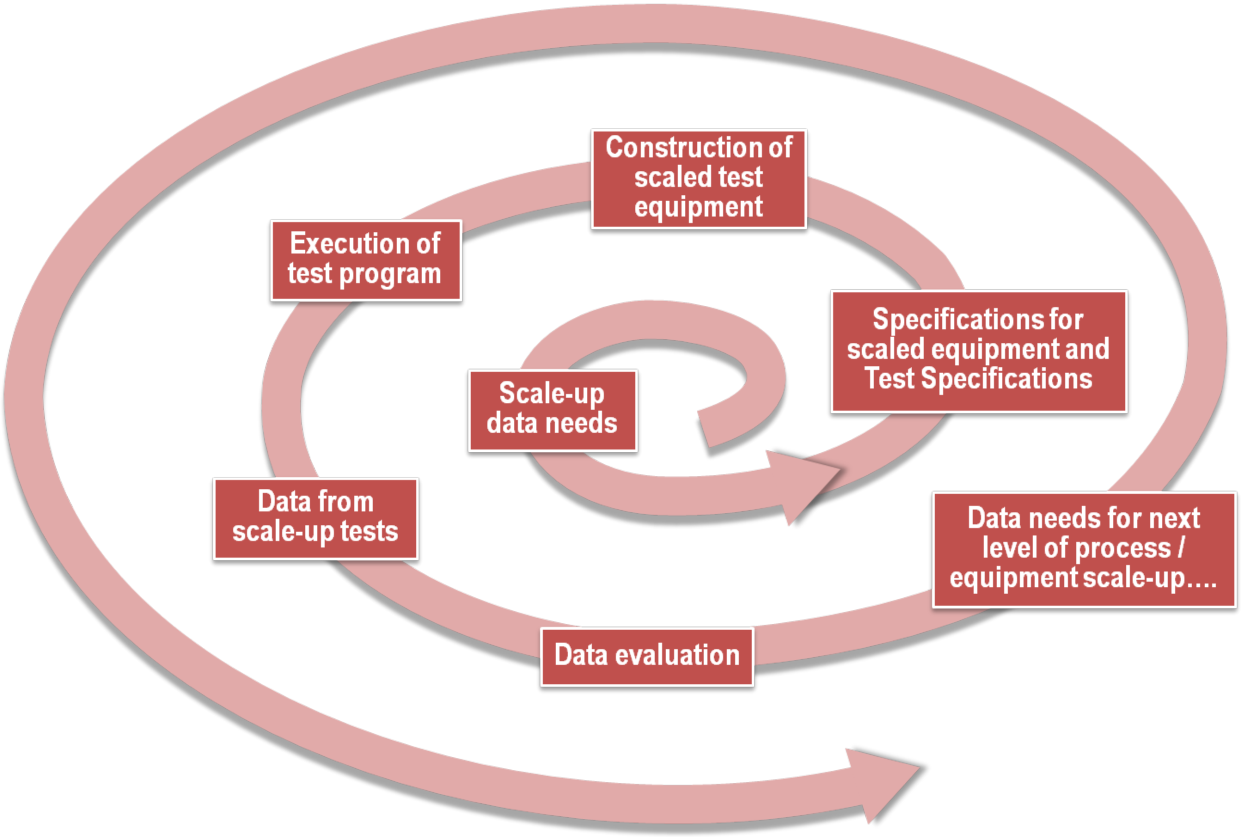
6) There currently exists a significant body of knowledge, expertise, and separations capabilities within the DOE complex that must be preserved. An effort should be undertaken to define the appropriate functions of a possible center for separations knowledge, as well as inventorying the facilities that could be used to support separations scale-up over the next five to twenty years.

7) Advancing the capability to conduct small-scale, integrated radiochemical processing with actual material will be beneficial, and this would likely involve improved process monitoring and control that could be applied in the actual plant.

8) An opportunity and technical challenge for improving the capability to do process scale-up with less experimental testing and at smaller scales is to develop improved modeling capabilities for common and essential process physics and chemistry where scale-up issues are known to be difficult.

9) Ancillary issues include the need for a broad-based, bi-partisan solid foundation to maintain and advance these issues in the United States.

Figure 5. Scale-up cycle



Appendix D. Breakout Session Report: Interface Issues between Separations and Waste Forms/Fuel Fabrication

CHAIR:	**David Kosson**, Vanderbilt University
CO-CHAIR:	**Bob Sindelar**, Savannah River National Laboratory
FEDERAL COORDINATOR:	**James Marra**, Office of Environmental Management
ORGANIZER:	**Bill Wilmarth**, Savannah River National Laboratory

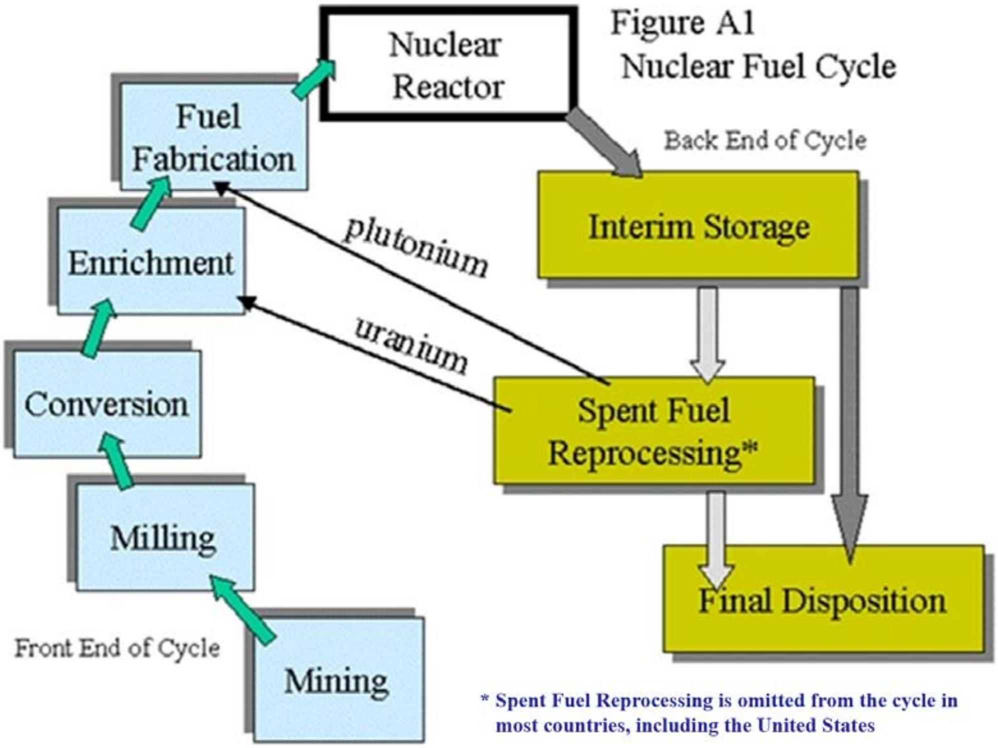
PANELISTS:
Ken Bateman, Idaho National Laboratory
Charles Forsberg, Massachusetts Institute of Technology
Werner Lutze, The Catholic University of America
Tina Nenoff, Sandia National Laboratories
Eric Shaber, Idaho National Laboratory – Battelle Energy Alliance
George Vandegrift, Argonne National Laboratory

1.0 Background Information

The interfaces of nuclear fuel separations processes to the production of waste forms and to fuel fabrication should be considered within an even broader context of the entire nuclear fuel cycle for nuclear power production. Radioactive wastes are generated from uranium mining, conversion and enrichment, fuel fabrication and conditioning, and fuel recycling. Past waste management practices have produced additional technical challenges, such as the need for pre-treatment of tank wastes prior to further processing. Wastes from post-separations streams pose challenges to any closed nuclear fuel cycles, along with the purity of recycled uranium and burnable actinides either as an integral part of the fuel or as a separate target in a reactor core. A modified open fuel fabrication cycle requires waste forms and disposal pathways for actinides and fission products removed during the minimal reprocessing (see Section 1.2 of this report for a brief discussion of the three fuel cycles under DOE-supported study).

While the fuel cycle for nuclear power is a dominant concern, disposition should also be considered, including stabilization for disposal and potential recycle of materials and wastes generated from other reactor cycles, such as the production of molybdenum-99 (Mo-99) for medical uses using low-enriched uranium (LEU) fuel. Therefore, a holistic vision must be given to any nuclear fuel cycle to ensure that the selected alternatives for each of the major parts of the nuclear fuel cycle (see Figure 1) would mesh with each other prior to their specification.

Figure 1. Nuclear fuel cycle for power reactors showing direct linkages of (proposed) spent fuel reprocessing or separations with fuel fabrication and waste forms destined for final disposition [reproduced from BRC report, figure A1]



**Note that the recycled uranium may be enriched as precursor to fuel fabrication. Also, transuranic (TRU) waste (with long-lived actinides) would likely be part of the stream for fuel fabrication to enable their burn-up in reactor.

Furthermore, the system should be designed in a flexible manner so as to enable incorporation of novel materials, methods and processes from research institutions such as national labs and universities in real-world settings post-engineering development and/or infrastructure construction completion. In this regard, an overarching systems analysis is a foundation from which the interfaces are well identified.

Fuel cycle selection for the present U.S. reactor fleet (104 operating reactors with 65,000 MTHM used nuclear fuel in storage) and for near-term additions to the fleet with advanced light water reactor (LWR) designs is sufficiently mature to facilitate identification of transformational technology opportunities in fuel design, waste form specification, repository selection, and other fuel cycle component considerations. Further development of specific fuel cycle component technologies will provide alternatives for consideration; subsequent systems analyses will enable risk-informed selection of the “best” cycle(s) with explicit cost–benefit information. Risks include safety and security considerations and programmatic risks or risks in achieving stated goals (e.g., development of a single glass waste form for sequestering multiple waste species must be evaluated against multiple sets of waste forms optimized for waste volume loading and durability, but would require additional separations processing and associated risks). “Waste

Forms Development and Technology," published by the National Academies of Science, supports this point and recommends reevaluation of the one-glass waste form, recommending a "good as glass" approach (see below).

U.S. Department of Energy and National Nuclear Security Administration Programs

The U.S. Department of Energy (DOE) Office of Nuclear Energy (NE) Fuel Cycle Technology (FCT) program investigates fuel cycle components for commercial reactors. NE identified many program needs in common with the DOE Office of Environmental Management (EM), including interim to long-term storage and the ultimate disposition of spent nuclear fuel and orphan legacy materials (e.g., U-233). Repatriation of enriched uranium and other materials to the United States by the National Nuclear Security Administration (NNSA) carries attendant storage and disposition needs. Furthermore, critical medical isotope production (e.g. Mo-99) also presents program needs.[1] All these nuclear materials are subject to monitoring and security functions. Publicly available documents detail DOE and NNSA program activities:

1. The FCT *Separations Campaign Implementation Plan*[2] provides an overview of the campaign activities plan: "Develop the next generation of fuel cycle separation technologies that enable a sustainable fuel cycle, with minimal processing, waste generation, and potential for material diversion."
2. *The Waste Forms Campaign Implementation Plan*[3] describes the affiliated campaign for development of waste forms from the waste streams that would emanate from the separations processes and would be subject to repository disposal. This campaign seeks to produce high-waste-volume-loading forms that are highly durable in, and tuned to, specific repository environments.
3. *Tank Waste Retrieval, Processing, and On-Site Disposal at DOE-EM*[4] provides an overview of the remaining technical challenges involved in, predominantly, processing and immobilizing HLW, describes the need to better understand the chemistry of HLW stored in tanks and DOE sites, and notes that there are still substantial opportunities to use science and technology to improve the processing and immobilization methods to be used by the Department.
4. *The Technology of Waste Forms*[5] picks up where the above report and several others left off.[6] This report provides a detailed description of the basic science and technology of

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[1] Medical Isotope Production Without Highly Enriched Uranium, National Research Council of the National Academies, the National Academies Press, 2009.

[2] Todd, T.A. FCRD-SEPA-2010-000042, Separations Campaign Implementation Plan, March 2010.

[3] Vienna, J.D. FCRD-WAST-2010-000043, Waste Forms Campaign Implementation Plan, March 2010.

[4] "Tank Waste Retrieval, Processing, and On-Site Disposal at Three Department of Energy Sites," National Research Council of the National Academies, the National Academy Press, 2006.

[5] "Waste Forms Technology and Performance," The National Academies Press, 2011.

HLW forms. It notes that there are substantial opportunities to use scientific and technical advances to improve processing and immobilization processes and urges a risk-informed, systems approach to decision making regarding processing and immobilization processes and, by implication, R&D.

5. *Waste Forms for an Advanced Fuel Cycle*[7] provides a brief summary of the definitions and present regulations, requirements, and standards along with performance of waste forms and engineered barrier systems in the disposal environment that drive their development. Radioactive wastes are classified, primarily based on origin, as high-level waste (HLW), low-level waste (LLW) including greater than Class C, and mixed waste. This origin-based classification system impedes efficient waste management and environmental protection, as well as limiting development of new waste forms. For example, borosilicate glass, the waste form developed by EM and used in production for defense programs' HLW for the past 15 years, is the only mature HLW form available in the United States. Future waste forms that are close to equilibrium with the disposal environment would simplify disposal facility design with respect to need for engineered barriers. Waste form design should consider geologically stable materials and use natural analogues as part of long-term durability assessment.
6. *Reactors and Fuels*[8] notes the present design and advancing future fuel designs are directly tied to reactor design, and there are typically tight purity limits on feed (e.g. from recycled uranium) materials.
7. *Fuels Campaign Report*[9] discusses fuel for actinide burners and advanced fuels of metal, oxide, and particle designs being considered in the fuels campaign of the FCT program.

Nuclear Separations Technologies Workshop Presentations

The following sections summarize the principal points of panelist presentations and the ensuing discussions from the two-day workshop (presentations are available on the NE website: http://www.ne.doe.gov/).

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[6] For example, "Advice on the Department of Energy's Cleanup Technology Roadmap: Gaps and Bridges." National Research Council of the National Academy, National Academy Press, 2009.

[7] Vienna, J.D. "Waste Forms for an Advanced Fuel Cycle," monograph from CRESP short course "Advanced Introduction to Nuclear Chemistry and Fuel Cycle Separations," to be published by Vanderbilt University Press, 2011.

[8] Croff, A.G. "Reactors and Fuels," monograph from CRESP short course "Advanced Introduction to Nuclear Chemistry and Fuel Cycle Separations," to be published by Vanderbilt University Press, 2011.

[9] Pasamehmetoglu, Kemal. Advanced Fuels Campaign Execution Plan, INL/EXT-10-18954, October 2010.

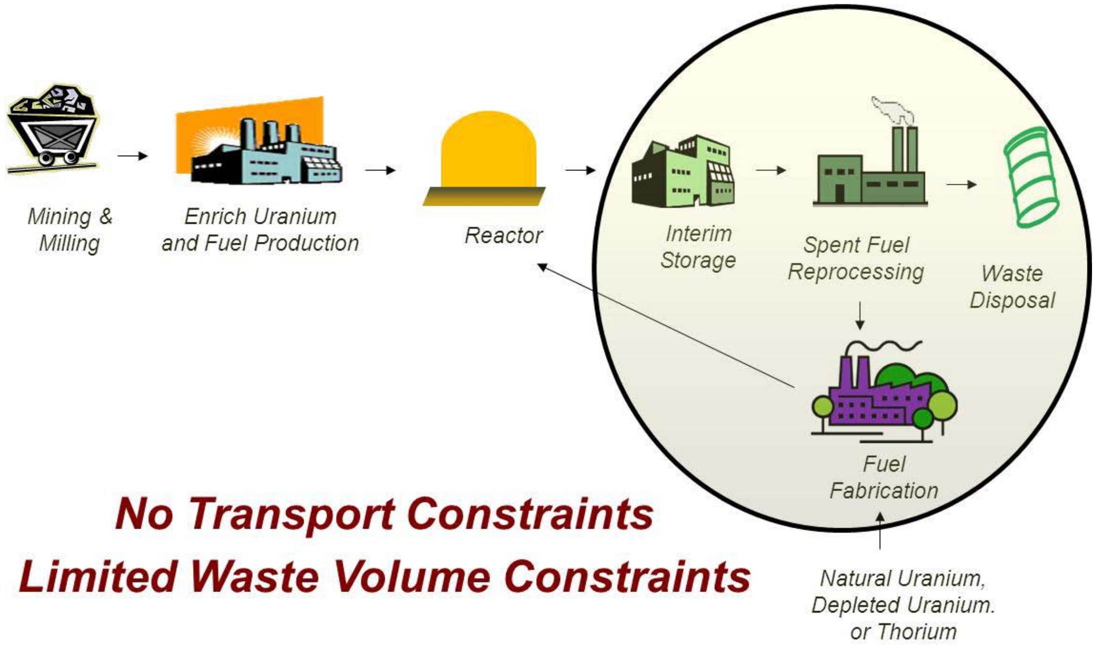
Commercial Fuel Cycle Interfaces: Fabrication and Waste Management—Interfaces Drive Separations Requirements

PRESENTER: **Charles Forsberg**

This presentation and discussion identified grand challenges for the interfaces of fuel fabrication and waste management:

- Capital separations costs are small (<10%) compared to other components in a reprocessing plant (e.g., HLW storage).
- Uranium (U)/plutonium (Pu) ratio blend and purity needs of the fuel drive cost, not the separations technology needs. Nonproliferation concerns drive towards lower concentration of Pu blend.
- Traditional reprocessing/disposal system uses separate facilities and locations. A co-located single facility for interim storage, reprocessing, fuel fabrication, and waste disposal represents a transformational paradigm (see Figure 2).
- Improve waste form and repository performance through low waste loadings. There is an option to terminate repository safeguards by lowering the fissile content of any wastes below the IAEA safeguards termination threshold. There is also an option to improve the performance of solubility-limited waste forms by adding nonradioactive isotopes of radioactive species to reduce the radionuclide release rate from the waste form (as applicable).

Figure 2. Benefits of Co-Located Nuclear Fuel Cycle Component Facilities
[ref. Forsberg]



Waste Streams from Aqueous and Advanced Separations Processes

PRESENTER: **George Vandegrift**

This presentation and discussion identified several pitfalls for the interfaces of fuel fabrication and waste management.

- Reactors and fuel cycles for NE, EM, and NNSA must consider power reactors and research reactors.
- Radiopharmaceutical production presents additional challenges, including reactor/fuel system optimization (e.g., to produce uranium–molybdenum LEU fuel for research reactors) and waste stream challenges in fuel development and isotope recovery from the targets.
- Radioactive waste generation and waste form interfaces are not limited to backend processes but should include the front-end steps of mining, enrichment, etc; look at all waste streams.
- Expediency to produce materials (e.g., weapons-grade materials) did not consider waste generation and disposition at the time.

Pyroprocessing

PRESENTER: **Ken Bateman**

This presentation and discussion focused on pyroprocessing technology, its technical maturity, and the concomitant waste streams/waste forms.

- Non-aqueous process using molten metals and molten salts with electrochemical methods to cause separation of actinides from fission products, cladding, etc.
- Not designed to recover plutonium, in contrast to plutonium–uranium extraction (PUREX)
- Successfully applied to EBR-II fuel reprocessing
- Metal waste form is a stainless steel and zirconium alloy that is highly corrosion-resistant and would be expected to be highly durable in repository settings
- Metallic sodium transformed to sodium chloride
- Vacuum distillation of salts from the claddings
- Salt is captured on zeolite and then is mixed with glass to form sodalite/glass waste form

Fuels and Interfaces with Separations and Waste Forms—Overview

PRESENTER: **Eric Shaber**

- Fuel fabrication must meet reactor fuel requirements.
- Input feed has to allow the fuel fabricator to meet reactor fuel specifications.
- Material composition/purity determines safeguards requirements.
- Transportation requirements on feed materials that must be shipped are incompatible with the feed material forms needed for fabrication; Department of Transportation transport between separations and fuel fabrication should be eliminated.
- Direct oxide reduction processing for metal fuel feed needs to be developed.
- Improvement is needed with the purity of recycled separations products at present.
- The modified open cycle is a major challenge for fuel fabrication and reactors; some approaches will result in fission product separations during fuel fabrication.

Waste Forms for the Future

PRESENTER: **Werner Lutze**

- Use natural analogs and local conditions of a proposed repository to determine the thermodynamically stable material systems.
- A good record of the waste for waste forms achieved, being developed, and still needed include the Hench Panel work,[10,11] the volume edited by Lutze and Ewing,[12] and the National Academies 2011 waste forms report.[13]
- Special waste forms may not be needed—charge to revisit the definitions of waste categories.
- Look at encapsulation as part of waste form development processes.
- Let nuclides and, if long-term durability is needed, nature guide waste form development.
- Use modern material science and modeling tools; but in the end, it is nature.
- Interfaces of separations to waste forms must address the waste form/disposal system.

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[10] DOE, “A Method for Product Performance Evaluation of Candidate Waste Forms for Immobilization of HLW,” Report DOE/TIC-11612. DOE Interface Working Group on HLW Form Selection Factors, 1982; available from NTIS, Springfield, VA.

[11] Hench, L.L., D.E. Clark, and J. Campbell. “HLW immobilization forms,” *Nucl. Chem. Waste Management*, vol. 5, 1984: 149.

[12] “Radioactive waste forms for the future,” W. Lutze and R. C. Ewing, Eds. North Holland, 1988.

[13] Waste Forms Technology and Performance: Final Report ISBN 978-0-309-18733-6, The National Academies Press, Washington, D.C. 2011.

NNSA Needs/Opportunities and Inorganic Materials

PRESENTER: **Tina Nenoff**

- Integrated synthesis, characterization, and modeling are recommended to achieve robust separations and waste forms.
- Volatiles, gases, long-lived fission products can be effectively separated and isolated onto sensors for detection methods (for NNSA) and/or separated and treated to produce robust waste forms with crystalline nanoporous materials, e.g., zeolites, metal–organic frameworks, molecular sieves (for NE).[14]
- High selectivity paired with high sorption capacity allows for numerous applications in waste forms.
- Research towards metrics and goals is mostly focused on complete separation, isolation, and storage.
- Differing metrics should be determined by needs (e.g., NNSA may have extreme sensitivity but not high sorption capacity needs, while NE has high sensitivity with high sorption capacity needs).
- Let nuclides and, if long-term durability is needed, natural analogs guide waste form development.[15]
- A life-cycle (collaborative) approach is needed in designing separations materials so as to link as seamlessly as possible with the corresponding waste forms and eventual repository needs.

The following list compiles challenges identified by the expert panel and participants in the breakout session.

1. Establish a baseline fuel cycle with well-defined meshed fuel cycle components.
2. Establish an approach to down-select fuel cycle components.
3. Prioritize technology development for an overall “weak” component of the nuclear fuel cycle (e.g., a waste form for volatile species) and for further technology development among the leading candidates (e.g., “zeolite 1” vs. “zeolite 2” for the volatile species waste form).
4. Develop technologies with low programmatic risk.
5. Develop management strategies for used fuel storage to allow for radioactive decay, etc.
6. Strengthen the nuclear workforce in the United States.

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[14] Garino, T.J., T.M. Nenoff, J.L. Krumhansl, D. Rademacher. “Low-Temperature Sintering Bi-Si-Zn Oxide Glasses For Use in Either Glass Composite Materials or Core/Shell 129I Waste Forms”, *J. Amer. Ceram. Soc.*, 94(8), 2011: 2412–2419.

[15] Weber, William J., Alexandra Navrotsky, Sergey Stefanovsky, Eric R. Vance, and Etienne Vernaz, MRS Bulletin, 34, January 2009: 46-53.

7. Devise a better definition for the waste form/repository interface.
8. Cultivate buy-in for facilities in the nuclear fuel cycle (e.g., a separations facility).
9. Strengthen nonproliferation approaches in fuel storage and separations systems.
10. Obtain Nuclear Regulatory Commission (NRC) licenses for nuclear fuel cycle component facilities.

2.0 Challenges & Proposed Solutions

The overarching conclusion with respect to interfaces between separations and fuel fabrication and used fuel management is the need for a systems approach to guide needed research and development that is cognizant of and informs essential national policy decisions regarding fuel cycle configurations to be developed (i.e., open, closed or modified), the role and time frames for storage of used fuel, the potential for additional processing steps (e.g., fuel "conditioning," pre-treatment of high-level tank waste), and the selection of repositories for disposal of final wastes. Development and implementation of a risk-informed waste classification system is central to defining radionuclide and materials segregation strategies, waste disposition pathways and waste forms. Early down selection of fuel cycle options to a limited set of plausible configurations and implementation time frames is central to maintaining efficient progress. The following list compiles the proposed solutions, under each respective challenge, in the form of recommended programs/activities identified by the expert panel and participants in the breakout session.

1. ***Establish a baseline fuel cycle with meshed fuel cycle components well defined.***

   Establish a reference set of plausible fuel cycle configurations based on the major driving criteria (e.g., economics, safety, environment) that includes high-level definitions of the time frames and primary options for each stage of each selected fuel cycle, including reactor type, fuel form, storage of used fuel, extent of recycling, waste forms, and waste disposition environments.

2. ***Establish approach to down select fuel cycle components.***

   Develop systems models for each selected fuel cycle option that include initial estimates of mass and energy balances, and consider used nuclear fuel currently in storage and to be generated. All major primary and secondary waste streams should be identified. The potential benefits and risks of co-locating major backend components of the fuel cycle (i.e., storage, recycling, fuel fabrication, disposal) should be evaluated. These systems models should serve as the basis for identifying major knowledge gaps and what research offers the greatest impact on the decision-making process.

   Developing implementation models that define options for the roles and economic drivers for private-sector participation should be part of systems evaluation. Caution must be exercised in the use of "bounding" assumptions and models to prevent today's bounding assumptions from becoming future constraints that are orders of magnitude too limiting compared to evolving science and engineering knowledge.

3. ***Prioritize technology development for an overall "weak" component of the nuclear fuel cycle (e.g., waste form for volatile species) and for further technology development among the leading candidates (e.g. "zeolite 1" vs. "zeolite 2" for the volatile species waste form).***

   Prioritize research through a transparent process and set of objectives informed by the outcomes of systems modeling. Recognition of the time frames for implementing potential fuel cycle options is important for distinguishing urgency for basic and applied research and demonstration of different components of fuel cycle options. A joint national laboratory, university, and industry advisory committee is recommended to ensure consideration of the full development pipeline from basic research through full implementation. Research planning should also leverage international partnerships and investments.

4. ***Develop technologies with low programmatic risk.***

   Technology development with low programmatic risk necessitates demonstration facilities for technology development and deployment. Test beds, including cold and hot facilities from bench to engineering demonstration scale, will be essential to the success of separations research and development. Pathways and funding for access to hot experimentation by university researchers need to be established. Identify potentially available and needed facilities (e.g., glove boxes, hot cells, flexible engineering-scale demonstration facilities). Implementation of hot testing should be timely in the research and development cycle of the waste form (i.e., if implemented too early in research/development process, negative data results may inhibit materials optimization or improvement). Early use of the facilities should consider EM, NE, and NNSA needs.

5. ***Develop management strategies for used fuel storage to allow for radioactive decay, etc.***

   Evaluate the potential role of used fuel conditioning prior to storage, including separation of major components and constituents. This is a new concept in response to the potential for longer-term storage prior to subsequent recycling or disposal, and may be needed to maintain materials stability and facilitate later (and potential unknown) management options.

6. ***Strengthen the nuclear workforce in the United States.***

   Expand the existing NE university program to include nuclear chemical engineering, nuclear environmental engineering, and material sciences. These essential components to the future of nuclear energy have almost been extinguished owing to the lack of investment, faculty engagement, and student interest. Nuclear energy is competing with other exciting, hi-tech fields for the best and brightest available minds. DOE and NRC should provide programmatic aid in establishing or re-establishing nuclear engineering departments in U.S. universities.

7. ***Devise a better definition for the waste form/repository interface.***

   Develop new and alternative waste forms that can be used to manage the full range of recycling waste streams (liquid, solid and gas) and are consistent with planned disposal environments.

8. ***Cultivate buy-in for facilities supporting the nuclear fuel cycle (e.g., a separations facility).***

   Conduct research on the social science and communications aspects of implementing future nuclear fuel cycles as a component of the emerging research and development plan. Ultimately, the public's and policymakers' understanding and engagement will be central to future decision making and the selected path forward.

9. ***Strengthen nonproliferation approaches in fuel storage and separations systems.***

   Conduct research on monitoring and instrumentation technologies needed for process control and to meet nonproliferation monitoring and remote detection needs. These should evolve in concert with process development (note: there is a similarity of needs for remote observation with respect to both nonproliferation and environmental remediation).

10. ***Obtain NRC licenses for nuclear fuel cycle component facilities.***

    Collect data to support licensing and evaluations by the NRC as part of the planning process.

11. ***Develop a flexible life-cycle system.***

    Enable the incorporation of novel materials, methods, and processes from research institutions such as national laboratories and universities to be implemented into post-engineering development plans and/or infrastructure construction completion.

An overarching paradigm for prioritization of recommended programs/activities is that LWR technologies are near-term vis-à-vis advanced burner reactors. In addition to the DOE and NNSA programs, common needs and program information-sharing with international partners is critical to enable cost-effective, technically sound selection of the components of the nuclear fuel cycle(s) for the U.S. energy needs.

The conclusion, with respect to interfaces between separations and fuel fabrication and used fuel management, is the need for a systems approach to guide research and development that is cognizant of and informs essential national policy decisions regarding fuel cycle configurations to be developed (i.e., open, closed or modified), the role and time frames for storage of used fuel, and the selection of repositories for disposal of final wastes. Development and implementation of a risk-informed waste classification system is central to defining radionuclide and materials segregation strategies, waste disposition pathways, and waste forms.

This easily can become a "which comes first: the chicken or the egg?" dilemma. Early down selection of fuel cycle options to a set of plausible configurations and implementation time frames is central to maintaining efficient progress and avoiding paralysis. NE has initiated a process to achieve recommendations on such a down selection in FY 2013.

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Additional Questions and Discussions from the Interface Breakout Session

The breakout session organizers and chairs prepared a set of questions and initial discussion "answers" to solicit needs and challenges, along with proposed resolutions, to topics in the session. This information is captured below.

1. ***What are the advantages/disadvantages of immobilizing separated versus combined streams?***

   Overall waste disposal strategies have much greater flexibility with separated streams. The advantages include producing tailored waste forms targeted to species and hazard level, enabling thermal management of high-activity species, enabling radiological management of high-activity species, and volume reduction. However, process costs (separations process development, waste form development, facilities to execute the separations and waste form production) and risks associated with these process steps are the disadvantages.

Additional discussion points:

1. It would be more advantageous to co-location, including the safeguards aspect. Convert HLW from separations into heat waste and store to reduce heat. Examine concepts for fuel conditioning.
2. Plutonium is not allowed in facilities licensed to make fuel.
3. Calcine waste at ID could not be put in YMP; it was not in the TSPA analysis.
4. Head-end cycle to separate iodine and technetium can help in waste management (also cesium and strontium).
5. Think about advantages for separations.
6. Certain things in PA need waste forms. Doing that requires clean fuel and bad actor species separated.
7. The safety basis is easier to deal with. It could be demonstrated with a cross-over point in the analysis where that need to separate occurs.

2. *What separations processes and conditions adversely affect or facilitate waste form chemistry and processing?*

The attendant radiation of the radioisotopes in the irradiated fuel is one clear example of a challenge to waste form chemistry and processing. Separations and concentration of radionuclides can lead to radiolysis effects and highly radioactive process solutions that can complicate waste form processing. Furthermore, high radiation levels can damage and reduce the performance of resins and similar ion exchange and separations media. The solution chemistries themselves—including aqueous solutions and solvents, and the chemical species introduced into the stream to facilitate separations—can dramatically impact waste form chemistry and its processing. A clear example is sulfur that becomes part of the raffinate in the TRUEX process. The relatively low solubility of sulfur in traditional waste forms creates challenges. Such chemical challenges have historically led to the need for additional processing of HLW (i.e., pre-treatment) and reinforce the need for integration between separations and immobilization R&D efforts.

3. *What new advances in waste form chemistry and processing can be applied to an advanced fuel cycle or other challenging wastes?*

Borosilicate glass is the current world-wide standard for immobilization of high-level radioactive waste resulting from reprocessing. Lower-activity wastes have been primarily immobilized in grout and similar matrices. Although there has been significant work in evaluating alternative waste forms over the years, few of these developments have gone into practice. Can a “good as glass” performance policy be implemented that allows for HLW to be stored in novel, non-borosilicate glass waste forms? Advances in chemistry including nanomaterials and functionalized materials could lead to transformational advances in waste form development. For example, ligands tailored to bind species have the potential to optimize waste species capture and sequestration.

Advanced separations processes including ionic liquids and gaseous separations using fluoride chemistry have potential for highly selective separations and non-aqueous, low-volume waste streams. The impacts (positive or negative) of these types of separations methods on waste form chemistry and fabrication is not known.

4. ***What fundamental waste stream characteristics need to be known to select and develop waste forms?***

The inventory and chemical form of species in the waste stream solids and solutions of course provide important waste stream characteristics needed to develop the waste form. Perhaps, more subtly, the matrices containing the radionuclides can have significant impacts on waste processing. For example, rheological properties of waste streams—those that are not easily mimicked using simulants—can cause significant issues with waste processing. Radionuclide types and concentrations can cause wide variations in thermal heat loads and radiation doses. All these factors are important considerations in the selection of separations and waste form production processes and the interplay between these areas. It is important to know the limitations of use of simulants in separations and waste form research and development; while it is vital to advance the knowledge base and research, it is important in the end to be able to test with real/hot radionuclides for ultimate performance evaluation.

5. ***What advances in fuel technology can facilitate reprocessing?***

To date, the development of fuel with a direct consideration to backend separations and waste form conditions is weak at best. Typically, considerations were made to optimizing fuel reactor performance and integrity in both normal operations and accident scenarios. To truly develop an integrated approach for the fuel cycle from fuel production to waste management, a systematic approach must be undertaken throughout the fuel cycle process.

Additional discussion points:

1. Different reactor designs require specific fuel. Do we need multiple separations facilities for the various metal, oxide, etc., fuel design, or can we have one feed fit all?
2. For what type of reactor are we trying to design fuel?
3. We are trying to open reactor designs up to higher enrichments. Maybe one can tolerate higher impurities.
4. The fuels program is looking at oxide, metal and particle fuel. MOX fuel with an actinide target would simplify assumptions.
5. Higher and higher burnups are desired.

6. Is there a compromise interim option entailing storing U_3O_8 that would allow offshoots down the road—; perhaps MOX is good interim fuel cycle type (other actinides and enrichments uncertain). Remote fabrication of fuel with actinides would be needed. Straight metal fuel is very simple to make in a hot cell.

6. *How does fuel design impact reprocessing strategies (open cycle, modified open cycle, closed cycle)?*

High-integrity fuel that can withstand long service and accident demands lends itself to an open fuel cycle because of resistance of the cladding to breakdown. It is obvious, however, that high-integrity fuel would make fuel reprocessing in modified open or closed fuel cycles more difficult. It is evident that fuel design optimization must also take into account specific reprocessing strategies and/or the need to incorporate flexibility into fuel designs.

7. *What are the needs and how can modeling and simulation tools be used to support fuel and waste form development and optimization?*

Advances in high-power computing can help speed scientific discovery if appropriately harnessed. The current NE Nuclear Energy Advanced Modeling and Simulation (NEAMS) and EM Advanced Simulation Capability for Environmental Management (ASCEM) programs are establishing advanced computing capabilities to support NE and EM program needs. The use of these tools for fuel and waste form development and optimization, specifically as they relate to the integrated fuel cycle, could help speed development by supplementing experimental and development activities.

8. *What are the political and economic considerations that must be accounted for in fuel/ separations/waste form interfaces?*

Nuclear processes and facilities are complex and, thus, typically expensive to design, construct and operate. Additionally, safety systems associated with nuclear facilities are expected to be robust. Public and political views on the cost and safety of nuclear facilities and processes vary significantly. The recent incident at the Fukushima Daiichi nuclear power plant in Japan has only increased the disparity of these views. These political and socio-economic factors must be considered in considering an integrated fuel cycle. Specifically, the disposition of used fuels and wastes, and safeguards associated with handling and processing nuclear materials, must be all be considered collectively and systematically in formulating informed and defensible decisions on fuel cycle options.

Additional discussion points:

1. A systems study is needed. We need to expedite R&D and deployment. Integration needs to be more along sloshing than linear, but needs focus.
2. The question needs to consider disposal too. UFD is looking at salt and clay. Risk in Belgium is from fission products, not actinides.

3. Consider a joint EM and NE and international glass corrosion program. Check against, salt, clay, tuff, granite. We need more of that kind of thinking for disposal.
4. The disposal system has to be risk-informed.
5. Glass models should not be overly conservative.
6. The near field is critical. We must know what the glass response is in each environment.
7. Do we consider the waste package when we think of waste form? Reducing environment keeps technetium and neptunium immobilized.
8. We should encourage thinking of enabling fuel cycle options. Look at the whole cycle to make sure all parts have alternatives.
9. We have not resolved what to do with our waste and should show the public we are working on it.
10. Swiss looked at overpack and waste form interactions.
11. There are risks and significant costs associated with the current approach of doing nothing while researching to find the perfect solution set.

9. ***What are the future workforce needs and challenges associated with fuel and waste form development areas?***

The present workforce with experience in fuel and waste form development is “graying,” similar to most other nuclear-related disciplines. Research work in these areas in the United States was generally limited and sporadic from the early 1990s through about 2008. Over the past few years, there has been an increase in research work in these areas with the resurging interest in nuclear energy. Throughout these periods, the experience base was definitely impacted because of retirements and reassignment of personnel. On a positive note, skill sets of recent graduates appear to be adequate with appropriate mentoring to fill personnel needs. It is expected that there will be a continued need for material scientists, chemists, physicists, nuclear engineers, chemical engineers and mechanical engineers to support fuel and waste form development activities. Experience with nuclear materials would expedite indoctrination of new employees. As noted above, modeling and simulation expertise may be extremely beneficial for future development work. Furthermore, owing to the complex nature of the nuclear fuel processes and need for integration of fuels, separations and waste processing functions, expertise in systems engineering and decision-making processes may be crucial in identification, evaluation and selection of the future fuel cycle alternatives. Related DOE agencies and NRC should help establish or re-establish new nuclear engineering undergraduate and graduate programs at universities in the United States, in a timely manner.

Additional questions:

1. Which radionuclides should be grouped together or managed separately as a result of separations processes for most effective waste management?
2. Which constituents are most likely to limit waste loading into waste forms? What separation approaches can be taken to reduce these limitations?
3. What are the disposition pathways for all used fuel components (not just radionuclides) and chemicals and components used as part of advanced fuel cycle separations? Which present the greatest challenges?
4. How can constituent immobilization be factored into design of separations processes?

Additional discussion points:

1. Joint EM and NE glass corrosion. This would give us corrosion law. Borosilicate glass is used.
2. Fundamentally, for high-level waste, phosphate glass gives us high-waste loading. Reduced volume would result.
3. EM work on advanced silicate glasses is important too.
4. Should also look at other glass systems.
5. Need to take a “systems look” at glass.
6. People are unable to move forward because decision makers are unwilling to commit to any path. Beyond-bench-scale R&D is needed. NEED DEMO FACILITY FOR BACK END FUEL CYCLE. Most efforts could be started right now, including capture.
7. Everyone likes waste loading high. But need to look at simplicity and stability of materials in proposed repository settings. For example, Swedes have package and clay that is simple and would last a long time. That is what we need to do. Native copper in Sweden is convincing as a stable barrier material.
8. Make case for simplified waste form.
9. Make case for re-classification of waste to manage waste streams.
10. Lack of places for students to work quickly with uranium, etc. Need places to do research. Need glovebox, hotcell, user facilities for universities to use.
11. ITU in Karlsruhe is a “hang out” for gloveboxes.
12. Process modeling and monitoring needs attention. Pu mass balance needs to be monitored. Am-243 and Np-239 are mother/daughter pair that should stay together. Need science-based models, need smart process controls.
13. Good, clear communication on safety basis for repository disposal of waste forms is paramount.

14. Glass waste forms in near field have a good base, but not on waste package in equilibrium with environment.
15. Waste loading and fuel. 230,000 used assemblies to date. The United States has unique gas release regulations. Need to determine what fuel could be recycled in the United States and then determine waste form.
16. Repository accommodation of heat load, etc., dictates.
17. Even with ventilation, have near-term Cs/Sr challenges with heat load.
18. Look at YMP 96°C mid-fill is T-controlled. Look at T drivers.
19. Risk-informed PA should be considered.
20. Advanced separations funding: should it be industry or government? If industry, how will use incentivize industry to separate out actinides? MOC is looking at advanced separations. In long-term ionic liquids (IL), molten salts have a lot of research interest. From engineering in short term, look at head end—gases and cladding clean up. If you have time, room-temperature solvent extraction would be good to have developed. Give needs on waste form and fuel to separations guys.
21. Need to give lessons learned and other informed needs to separations. Take out aluminum before or as part of processing, for example.
22. Question on EM for H-canyon at SRS. DNFSB says we should continue H-canyon. Need for test bed and H-canyon would serve that purpose.
23. Nuclear industry moves in small steps by adapting technology. Need near-term generic goals. Iodine capture, zirconium recovery.
24. Need for balanced university–lab–industry panel as advisors.
25. New exciting separations will occur. Supercritical liquids is exciting, but large pressurized cells are not amenable to quick demo.
26. IL are not readily handled.
27. Separations community has lack of direction. Maybe BRC will help. Need to ensure that this report will not be just another committee report thrown in trash.
28. We do want to produce a report that identifies common needs. Pace of program dependent on funding, but we want to do the right things when the time comes. We want to refer back to this document for ideas.
29. Look at adaptive strategy—interim storage and adaptive processing. Look at off-roads rather than endpoints.

Appendix E. Workshop Sponsors

Office of Nuclear Energy (NE) – NE is evaluating next-generation fuel recycling technologies that are alternatives to PUREX. Safety and security concerns surrounding civilian nuclear power must be successfully addressed in the United States and globally. By taking a leading position in helping to craft the international nuclear technology "rules-of-the-road" and providing a sound technology base for their implementation and enforcement, the Department can facilitate safe and environmentally acceptable approaches to recycling nuclear fuel while reducing greenhouse gas emissions and maintaining public confidence. NE's mission includes research and development in search of fuel-cycle technologies that improve resource utilization while reducing the risk of proliferation.

Office of Environmental Management (EM) – EM is conducting the world's largest nuclear clean up of the environmental legacy of nuclear weapons production and government-sponsored nuclear energy research, which has been vital to our Nation's security. To complete this mission, EM is developing next-generation technologies for waste treatment, groundwater and soil restoration, nuclear materials stabilization and disposition, and facility decommissioning. EM will enable nuclear futures by expertly and safely managing nuclear materials and waste, developing a skilled nuclear workforce, and supporting the creation of technologies that can be transferred, refined or retooled for energy, defense or security applications.

National Nuclear Security Administration (NNSA) – In support of national nonproliferation objectives, we are examining new approaches and technologies to dispose of surplus weapons grade materials and advance other national security missions. U.S. commitments to dispose of surplus weapon-grade plutonium to ensure it cannot be used again for nuclear weapons require a safe, secure, transparent, and effective disposal process.

Office of Science (SC) – SC enables new technologies that support the Department's energy, environment, and security missions. These basic research programs address fundamental questions. Enabling activities in support of Goal 3 include the development and exploration of a broad spectrum of new materials and chemical processes that are radiation-resistant and withstand extreme temperatures and pressures.

Appendix F. Agenda

U.S. Department of Energy

Getting from Where We Are to Where We Want to Be in
Nuclear Separations Technologies

Bethesda Marriott, 5151 Pooks Hill Road, Bethesda, MD

July 27 – 28, 2011

AGENDA

Wednesday, July 27

7:30 AM	***Registration/Continental Breakfast***
8:30 AM	**Welcome** **Andrew Griffith**, Director for Fuel Cycle Research and Development, Office of Nuclear Energy
8:40 AM	**Keynote Speaker** **Daniel Poneman**, Deputy Secretary of Energy
9:10 AM	**DOE/NNSA Office Overviews** **Peter Lyons**, Assistant Secretary for Nuclear Energy **Cynthia Anderson**, Chief Operations Officer, Office of Environmental Management **Mark Whitney,** Assistant Deputy Administrator, National Nuclear Security Agency
9:55 AM	***Break***
10:15 AM	**Program Mission Overview** **Monica Regalbuto,** Deputy Assistant Secretary for Fuel Cycle Technologies, Office of Nuclear Energy – *Nuclear Energy* **Mary Neu**, Chief Scientist, Office of Environmental Management – *Environmental Management* **Marc Humphrey**, Physical Scientist, National Nuclear Security Agency – *Nuclear Nonproliferation*
11:15 AM	**Instructions for Breakout Sessions**
12:00 PM	***Lunch with Guest Speaker*** **Darleane Hoffman**, Lawrence Berkeley National Laboratory
1:00 PM	**Breakout Sessions**: • Chemistry and Speciation of the Actinides and Key Fission Products • Design of Molecules and Materials with Selective Separation Properties • Scale-up of Separation Processes from Bench-Top to Plant • Interface Issues between Separations and Waste Forms/Fuel Fabrication

U.S. Department of Energy

Getting from Where We Are to Where We Want to Be in
Nuclear Separations Technologies

Bethesda Marriott, 5151 Pooks Hill Road, Bethesda, MD

July 27 – 28, 2011

3:00 PM	***Break***
3:15 PM	**Reconvene Breakout Sessions**
4:30 PM	**End-of-First-Day Plenary** • **Summary from Breakout Session Chairs**
5:00 PM	***Adjourn***
5:15–7:00 PM	***Reception*** *(with cash bar)*

AGENDA

Thursday, July 28

8:00 AM	***Continental Breakfast***
9:00 AM	**Reconvene Breakout Sessions**
10:15 AM	***Break***
10:30 AM	**Reconvene Breakout Sessions**
12.00 PM	***Lunch with Guest Speaker*** **Charles Forsberg**, Massachusetts Institute of Technology
1:00 PM	**Concluding Plenary** • **Breakout Session Reports**
2:30 PM	**Summation of Workshop and Path Forward**
3:00 PM	***Adjourn***

Appendix G. Participant List

U.S. Department of Energy

Getting from Where We Are to Where We Want to Be in
Nuclear Separations Technologies

Bethesda Marriott, 5151 Pooks Hill Road, Bethesda, MD

July 27 – 28, 2011

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